Comparison of calthemite and speleothem straw stalactites, and environmental conditions influencing straw diameter

Garry K. Smith

President - Newcastle and Hunter Valley Speleological Society Inc.
P.O. Box 15, Broadmeadow 2292 NSW, Australia.

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Abstract

This study investigates environmental conditions that influence the morphology of calthemite straws and draws comparisons with speleothem straws. Calthemite straws are typically deposited beneath buildings, bridges and other concrete structures from hyperalkaline solution (pH > 9), in contrast to speleothem straws that are deposited by near neutral to mildly alkaline solutions (pH 7.5 – 8.5). On average calthemite straws tend to have a smaller outside diameter range of 3.7 to 5.4mm compared to speleothem 4.5 to 6.45mm. Comparisons of straw mass per unit length revealed that on average calthemite straws were 40% the mass of speleothem straws of equivalent outside diameter. The calthemite straws had a much thinner wall thickness and were more fragile to handle. Their fast longitudinal growth (up to 2 mm/day) and thin wall thickness appears to be due to the rapid reaction of atmospheric CO_2 with Ca^{2+} in solution at the drop surface. This results in deposition of $CaCO_3$ around the straw tip, with little CO_2 diffusing up the solution canal, thereby lengthening the calthemite straw with limited $CaCO_3$ deposition in the solution canal. Solutions from slower drips have a higher saturation and deposit more $CaCO_3$ per kilogram of solution (e.g. as a stalactite and/or stalagmite), than solutions from straws with faster drip rates. As drip rates and calcium ion saturation of drip solution vary greatly beneath a structure over time and location, the analysis of drip solution is not a reliable method to determine concrete's degradation rate.

Key Words: concrete, straws, calcium hydroxide, calcium carbonate, calcium ion, calthemite, speleothem, stalactite, pH, hyperalkaline, drip solution

Introduction

Calthemites are secondary deposits, consisting primarily of calcium carbonate ($CaCO_3$), derived from concrete, mortar or lime. Typically created by deposition from hyperalkaline solution, they are found beneath man-made structures, such as buildings, bridges, tunnels and bunkers etc. Calthemites are similar in composition and typically mimic the shapes and forms of speleothems in normal pH caves, e.g. stalactites, stalagmites, straws, flowstone etc, but calthemites typically grow hundreds of times faster than their equivalent speleothem forms (Smith 2016). It has been suggested by Dixon et al. (2018) that the formation of calthemites is a natural process that did not occur prior to human modification of the Earth's surface during the Anthropocene.

Most straw speleothems form when CO_2 is degassed from near neutral pH to mildly alkaline solutions (pH 7.5 – 8.5) whereas most concrete-derived calthemite straws are created when CO_2 is sequestered into hyperalkaline solutions (Macleod et al., 1991; Hartland et al., 2010; Newton et al., 2015; Smith 2016; Field et al., 2017). Under ideal conditions, calthemite straws can grow in length hundreds of times faster than speleothem straws due to the greater calcium ion (Ca^{2+}) carrying capacity of the hyperalkaline solution and different chemical process involved. Although not common, speleothems can be formed by hyperalkaline solutions, as has occurred at Poole's Cavern, Derbyshire, UK, where leaching of overlying waste materials from historical lime production, has resulted in precipitation of speleothems (Hartland et al., 2010; Newton et al., 2015).

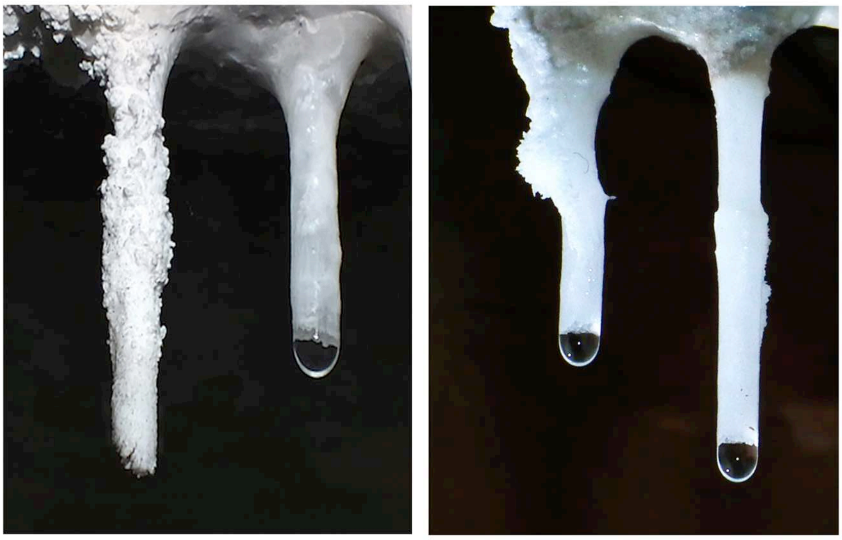

Figure 1: Calthemite straws on the left, are similar to speleothem straws on the right. Both are composed of calcium carbonate and are approximately the same diameter, but the linear masses are significantly different.

Ford and Williams (2007, p.291) state that, "*Rates of growth are usually quoted in terms of the extension of a given form rather than its accumulation of mass. Straw stalactites 'grow' fastest because they have the greatest extension per unit of areas deposited*." Growth rates of between 0.2 and 2 mm per year are quoted for straws formed by near-neutral pH to mildly alkaline solutions (Ford and Williams 2007), whereas calthemite straws can grow at rates of up to 2 mm per day (Smith, 2016).

Calthemite and speleothem straws look closely similar (Fig.1) but on closer investigation there are several physical differences. This study compares the physical attributes (mass and diameter) of calthemite and speleothem straws. Also investigated is the mass of calcium carbonate deposited by hyperalkaline solutions discharging from straws beneath a concrete structure.

Sixteen calthemite and sixteen speleothem straw samples of different diameters were measured to determine the average mass per unit length compared to outside diameter. Individual solution drops were weighed accurately to determine the relationship between calthemite straw diameter and the solution drop mass. The mass (g/kg) of $CaCO_3$ deposited from solution includes that deposited as a straw and that deposited as a stalagmite from solution that has fallen to the floor during the same time period. Mass of straw growth was calculated by using the average mass per unit length. To measure the (Ca^{2+}) leached from concrete and deposited as $CaCO_3$, dripwater was collected and evaporated to obtain the mass that would have been deposited as a stalagmite. This mass was added to the calculated $CaCO_3$ mass deposited as straw growth during the sample collection period. These data are cross-referenced to a previous study at the same location, where calthemite straw growth rates and drip rates were compared (Smith, 2016).

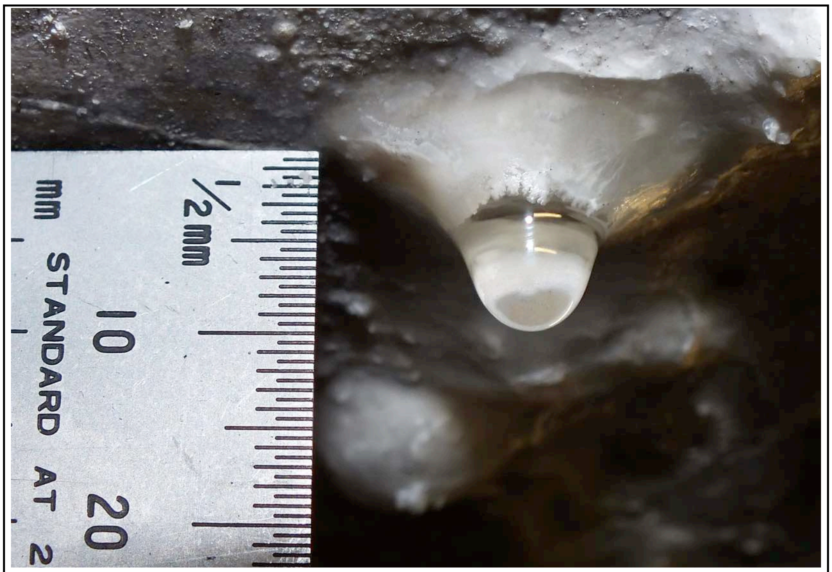

Figure 2: A calthemite cone-shaped deposit is formed as the base of the new straw transitions into a parallel-sided tube. This is also typical for the shape and size of a speleothem straw at the beginning of its formation. The diameter (typically between 15mm – 20mm) at the base of the cone is governed by the area that is wetted by solution on the underside of the concrete structure (or a cave ceiling) as the straw first begins to grow.

Straws of both types begin their development as a calcium carbonate ring typically between 15 to 20 mm diameter around the area that has been wetted by solution on the underside of the concrete structure or cave ceiling. The exact size of the $CaCO_3$ crystal ring depends on the wettability of the host surface and surface tension supporting the drop. Over time a cone-shaped $CaCO_3$ deposit forms (Fig.2), as the base of the new straw transitions into a cylindrical parallel sided tube growing downwards from the face of the host ceiling. The tube walls becomes parallel when an equilibrium is reached between the straw diameter, solution surface tension and other influencing factors

Figure 3: Typical cross-sections of calthemite straws. These have a thinner wall, are more fragile and have a less dense crystal structure than do speleothem straws. The image scale divisions are in mm.

Figure 4: Typical cross sections of speleothem straws. Compare these with Figure 3. These straws have thicker walls and a denser crystal structure, making them less fragile than calthemite straws.

as identified in this paper. To try and identify what influences a straw's diameter this study looked at the relationship between solution-drop mass and surface tension variants.

Collecting drip solution from beneath a concrete structure, and measuring the mass of $Ca(OH)_2$ leached from the concrete and deposited externally as $CaCO_3$, might prove to be a valuable aid to engineers when attempting to determine the degradation rate of concrete structures.

Study Site

The study site is a concrete building that was constructed in Belmont, NSW, Australia during 2008 and hence was 9 years old at the time of this study. The building includes a partly enclosed undercover car park with supermarket area above. Straw stalactites began growing within months of the building being completed. Poorly constructed roof guttering traps rainwater and leaks a continuous flow through a

Calthemite Straws

Straw Length mm	Weight in g	Average weight (g) / unit length (mm)	Average straw diameter in mm
17.0	0.092	0.0054	3.70
23.0	0.079	0.0034	3.90
44.0	0.213	0.0048	4.10
33.5	0.288	0.0086	4.30
19.0	0.240	0.0126	4.35
58.5	0.460	0.0079	4.45
28.5	0.124	0.0044	4.50
16.0	0.084	0.0053	4.60
14.5	0.146	0.0101	4.60
10.0	0.061	0.0061	4.60
35.0	0.239	0.0068	4.90
20.0	0.263	0.0132	5.00
21.0	0.208	0.0099	5.10
38.5	0.607	0.0158	5.20
30.0	0.386	0.0129	5.30
27.5	0.489	0.0178	5.40
Total **436.0**	**3.979**		
	Average g/mm using overall length		
		0.0091	

Table 1: Measurements of calthemite straws.

Speleothem Straws

Straw Length mm	Weight in g	Average weight (g) / unit length (mm)	Average straw diameter in mm
45.5	1.096	0.0241	4.50
44.7	1.166	0.0261	4.60
36.0	0.608	0.0169	4.90
33.8	0.769	0.0228	4.90
60.7	1.572	0.0259	5.00
54.5	1.444	0.0265	5.00
29.2	0.872	0.0299	5.00
46.8	1.201	0.0257	5.10
35.8	0.943	0.0263	5.15
50.0	1.457	0.0291	5.25
66.0	1.604	0.0243	5.30
60.5	1.429	0.0236	5.35
46.5	1.217	0.0262	5.35
47.0	1.327	0.0282	5.55
49.5	1.707	0.0345	6.00
36.5	1.435	0.0393	6.45
Total **743.0**	**19.847**		
	Average g/mm using overall length		
		0.0267	

Table 2: Measurements of speleothem straws.

small hole, onto the concrete structure. The water then finds its way into the concrete, following microscopic cracks and internal porosity, gaining solutes until it emerges from cracks in the car park ceiling, where calthemite straws are growing.

The constant supply of solution all year-round made the location ideal to study the mass of $CaCO_3$ deposited from hyperakaline solution and the solution-drip mass emerging from calthemite straws of known diameters.

Samples and Methods

Sixteen calthemite straws were removed from the underside of the concrete structure taking care to avoid skin contact with highly corrosive hyperalkaline solution (pH 13). Once removed, excess solution was drained from the straws, before they were placed in an oven at 60-70°C, to rapidly evaporate any solution still inside. The straw length was trimmed to remove any portion with significant variation in outside diameter, to facilitate comparison of sections of straws of a similar diameter. Only straws with a near-parallel external diameter were considered in this study. The final sections of selected straws reflect the bulk of the straw length, removing any short-term outliers of growth variability.

Figure 5: Gaffer tape holds the container against the underside of the concrete to collect the hyperalkaline solution dripping from a straw. The mass (in grams) of the clean container is written on its outside.

The diameters, length and mass of broken speleothem straws were measured in situ at the Timor Caves, north of Newcastle NSW, which were vandalised more than 35 years ago. In addition, permission was granted to collect and measure some broken straws from Cliefden Caves, NSW. This enabled a meaningful comparison between speleothem and calthemite straws.

Both speleothem straws and calthemite straws have small irregularities inside and outside, making neither absolutely uniform (Figures 3 and 4). As stated above, only straws with a near parallel outside diameter were considered in this study. Any straw showing signs of external diameter enlargement due to $CaCO_3$ deposited from solution film or solution trickling down the outside was rejected from the sampling. The outside diameter of all straws sampled, varied between 3.7 to 6.45mm (Tables 1 and 2). This range in diameter is relatively large, considering that Curl (1972) calculated the predicted minimum speleothem straw outside diameter should be 5.1mm at which point solution-drop diameter and mass, supported by surface tension reach an equilibrium. Curl (1972, p.129) states that a straw stalactite with a non-equilibrium diameter "*should converge, with growth, in an exponential manner to the minimum equilibrium diameter*."

Two precision jeweller scales (0-10g and 0-30g), both capable of weighing to 0.001g, were used to measure the mass of containers and their content. The straw sample pieces were measured with a precision dial vernier calliper to record their lengths and diameters to an accuracy of 0.05mm.

It was necessary to obtain some measurements of straw length and tip diameter in situ without disturbing the attached straw. This was achieved by taking digital photographs of a precision metal ruler calibrated in 0.5mm increments next to ?each? straw and enlarging the images to obtain an accurate reading. The flat underside of the concrete provided an excellent zero datum point for the ruler. Measurement error was estimated at ± 0.15mm. Specific attention was paid to angle and subject distance from camera, to minimize potential parallax errors.

To collect samples of the solution-drop mass for measurement, 70ml containers were held up hard against the underside of the concrete structure using gaffer tape, to capture a counted number of drops falling from a calthemite straw of known diameter (Fig.5). Each clean container mass was recorded before commencing the sampling. The collected solution was weighed in its collection container and the empty container mass deducted to ascertain the solution mass. The mass of a single solution-drop was obtained by dividing the solution mass by the known number of drops and recording it against the diameter of the straw from which it fell. These samples were only collected in the late evenings after the shopping centre had closed, when there was minimal air movement or vibration in the concrete structure due to vehicle movement and staff moving heavy stock pallets. This provided consistent solution-drop samples. Evaporation of solution was negligible as atmospheric air could not enter the container freely during collection of the drops (less than 30 minutes). Deposition of $CaCO_3$ at the straw tip was also negligible during this period.

To determine the deposition mass of $CaCO_3$ per mass of hyperalkaline solution, drip-water was collected from short active calthemite straws over periods ranging between 15 minutes and 3 days. Each straw's length and tip diameter was measured accurately before and after sampling, using the in situ method described previously. Solution collection was undertaken by the method described above. The collection container attachment method did not provide a perfect airtight seal, so atmospheric pressure and that within the container could equalise, without influencing the outflow of solution from the straw. This attachment method also minimised solution evaporation but it was noted that on each occasion upon removing a container, there was a thin calcite raft floating on the collected solution. This indicated that some atmospheric CO_2 was entering the containers and allowing $CaCO_3$ to precipitate at the solution surface and possibly the straw tip – depending on flow rate.

The solution was left in the container and allowed to evaporate in the sun until dry, which took up to 3 days. The dry container (with $CaCO_3$ deposited inside), was then weighed accurately and the container mass deducted to determine the $CaCO_3$ mass. The recording of straw lengths and diameter prior to and upon removal of each dripwater collection container was critical to allow calculation of the total mass of $CaCO_3$ which included the mass deposited at the straw tip plus the mass remaining in the container after evaporation of the solution. The diameter and change in each straw's length during sampling were recorded and the deposited mass of $CaCO_3$ calculated by using the average mass per linear length of straws of corresponding diameter, as described in the next section. The overall masses of $CaCO_3$ deposited from the hyperalkaline solution samples are detailed in Table 3.

Results of straw linear mass measurements.

Measurements over all straws sampled revealed speleothem straws are on average 2.9 times heavier per unit length than calthemites straws of equivalent external diameter. The disparity becomes obvious when comparing the internal solution-canal size (wall thickness) of the two straw types in figures 3 and 4. Speleothem straws averaged 26.7 mg per linear mm (Table 2), while calthemites straws averaged 9.1

Sample number	Mass (g) of calthemite solution collected	Mass (g) of CaCO3 remaining after solution evaporated	Calculated mass (g) of CaCO3 deposited as straw growth	Mass (g) CaCO3/kg of solution (including straw growth).	Calculated average Time (min) between drops	Time period to collect sample in minutes	Mass of CaCO3 deposited from solution in mg per day
1	7.304	0.018	0.0036	2.9500	9.03	1380	22.5
2	16.830	0.041	0.0071	2.8580	3.98	1400	49.5
3	6.434	0.017	0.0071	3.7460	10.70	1440	24.1
4	11.909	0.030	0.0142	3.7110	11.70	2915	21.8
5	28.740	0.101	0.0142	4.0080	7.14	4295	38.6
6	12.924	0.039	0.0142	4.1160	10.84	2930	26.1
7	13.203	0.052	0.0107	4.7450	15.64	4320	20.9
8	48.692	0.039	0.0000	0.8010	0.05	43	1306.0
9	28.964	0.020	0.0000	0.6905	0.08	45	640.0
10	2.659	0.003	0.0000	1.1282	1.10	36	120.0
11	1.748	0.001	0.0000	0.5721	0.73	15	96.0

Table 3: Calthemite leachate samples were evaporated to determine $CaCO_3$ deposited from solution. Also considered is deposition of $CaCO_3$ at the straw tip. Samples 8 – 11 had rapid drip rates with no measurable $CaCO_3$ deposition at the straw tip.

mg per linear mm (Table 1). However, this comparison is biased toward the speleothems because two significantly larger-diameter samples were collected (Fig.6). Considering just the overlapping range of straws with similar external diameters from each group, (straws between 4.9 and 5.1mm diameter), size for size the average speleothem straws are 2.47 times heavier than calthemite straws. In other words, calthemite straws are on average just 40% the mass of speleothem straws of equivalent external diameter and length. In general, speleothem straws have a denser calcite structure and a greater wall thickness, and thus a smaller solution canal down the centre than calthemite straws (Figs 3 and 4). Calthemite straws are generally rather fragile due to their thin wall-thickness.

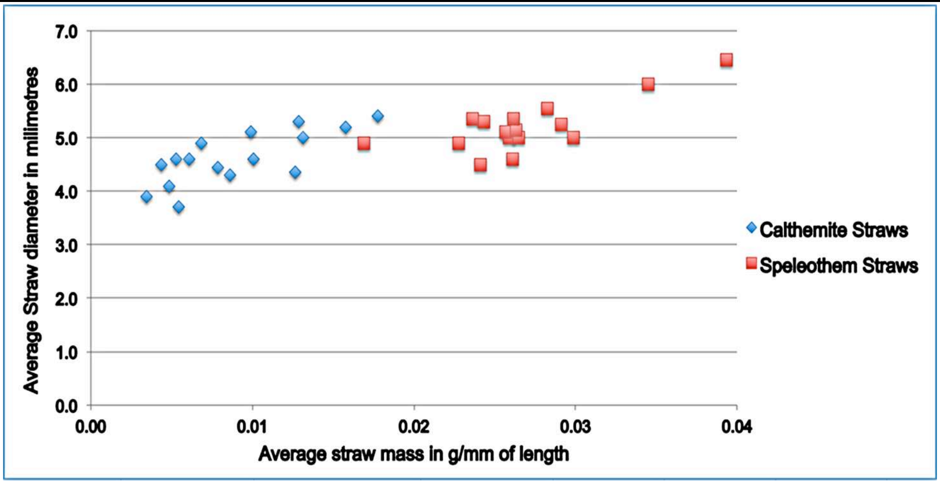

Figure 6: Straw mass (grams) per unit length (mm).

Broughton (2020, p.11 and 12) determined that calthemite soda straws consisted mostly of calcareous particles that formed "*microcrystalline aggregates of stacked rhombic crystal platelets*". The paper describes the coalesced dendritic shrub fabrics of the intra-crust walls and *"more loosely packed dendritic growths that protrude into the water flow along the central canal*", which were common in calthemite soda straws. Examples of the dendritic growths can be seen clearly on the inside of the fourth straw in Figure 3. The large disparity in straw mass per mm between calthemite and speleothem straws appears to be due to the difference in the $CaCO_3$ deposition process, as discussed by Smith (2016) and Broughton (2020). When $CaCO_3$ deposition occurs on a speleothem CO_2 diffuses out of the solution-drop; thus the diffusion of the gas from the drop occurs slowly and more evenly throughout the drop. This causes $CaCO_3$ to be deposited along the inner wall of the straw's solution canal as well as at the straw tip (Paul *et al*. 2013, Figure 7). Therefore the speleothem straw grows with a smaller canal and greater wall thickness than a calthemite straw.

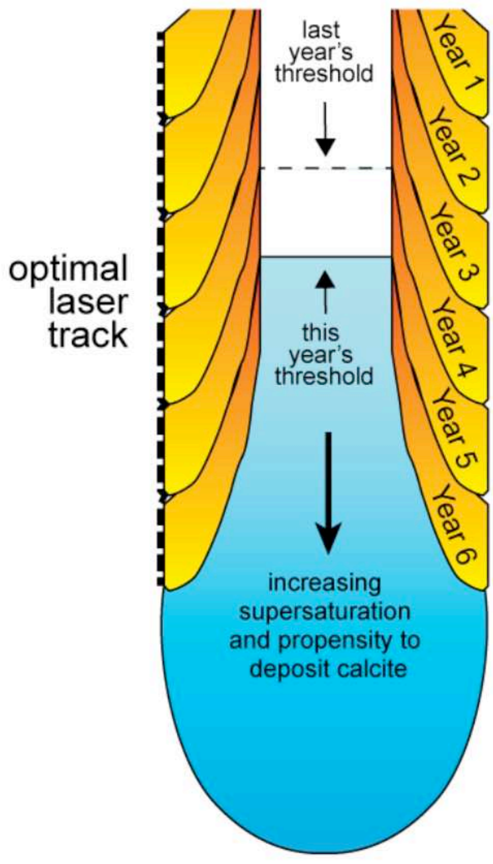

Figure 7*: Speleothem straw growth pattern. Image by Paul* et al. *2013. As the drip hangs from the tip, a combination of greater* CO_2 *degassing and lower nucleation energies occurs at the drip/straw-tip interface, producing wider layers at the edge of the straw.*

Calthemite dripwater at the study site is hyperalkaline, typically pH 13. It is well documented that, as a reflection of the different chemistry involved, the reaction rate driving $CaCO_3$ deposition from hyperalkaline solution is significantly more rapid than that causing deposition from mildly alkaline solution (Hartland 2010; Newton 2015). With the creation of calthemite straws the rapid reaction of atmospheric CO_2 with the Ca^{2+} in solution at the drop surface results in deposition of $CaCO_3$ around the tip of the straw's rim. Hardly any CO_2 has a chance to diffuse evenly through the solution-drop to cause deposition further inside the straw's solution canal. Therefore, the calthemite straw lengthens quickly, with hardly any $CaCO_3$ deposition in the solution canal.

Solution Drop Mass and Straw Diameter

As part of this study it was decided to investigate what factors influenced the mass of a solution-drop falling from a calthemite straw, in particular to identify how, or if, a straw's external diameter is governed by the solution's surface tension, which in turn might be influenced by calcium ion saturation and environmental parameters. Moore (1962) stated that the diameter of straw is equal to the diameter of a drop of water, but as Curl (1972, p.129) noted that, "*this seems rather obvious until it is pointed out that the size of a drop of water depends upon the diameter of the tube from which it hangs.*" This provided the impetus for investigating the relationship between solution-drop size and a straw's diameter.

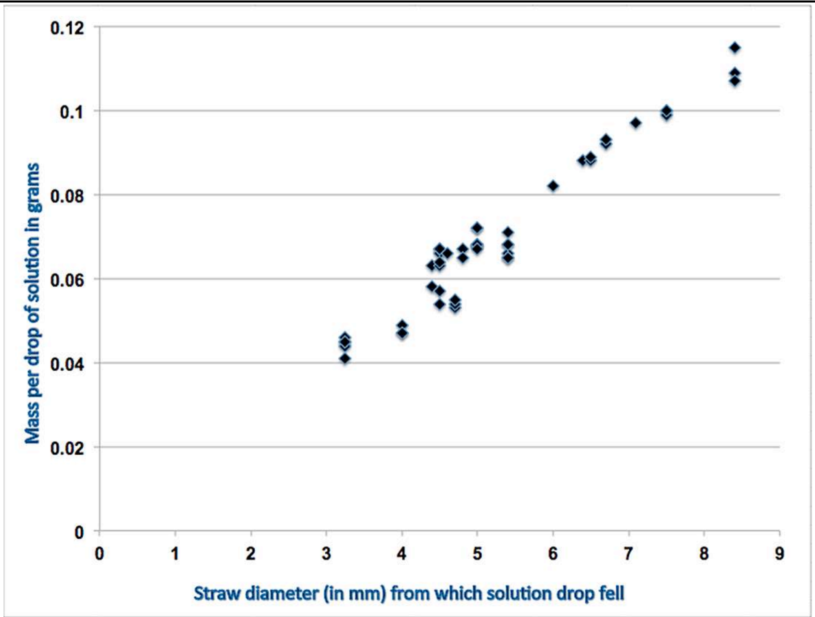

Figure 8: Graph comparing the mass of calthemite solution-drops (grams), to the outside diameter (mm) of the stalactite straws from which they fell. The solution mass included Ca^{2+} and any other dissolved minerals.

For this study, a total of 48 solution samples were collected from a range of straws with different straw diameters and drip rates. In addition to the straws of parallel form up to 5.4mm diameter, (detailed in the straw mass per unit length section above), solution drops from 13 larger-diameter short straws (6.0 to 8.4mm diameter) were included. These larger-diameter straws had not grown fully to a parallel form and were included in this part of the study to determine whether their solution-drop mass correlated to the straw's relative diameter at the tip. From the counted number of drops collected in each container beneath a calthemite straw, the average drop mass was plotted against the straw diameter (Fig.8) and it was found that the observed relationship is approximately linear.

The theoretical mass m of a drop hanging from the end of a straw (Fig.9) can be found by equating the force due to gravity ($\mathbf{F_g = mg}$) with the component of the surface tension in the vertical direction ($\mathbf{F_\gamma \sin \alpha}$) giving:

$$mg = \pi d\gamma \sin \alpha$$

where α is the angle of contact with the tube, g is the acceleration due to gravity and d is the tube diameter in metres.

The limit of this formula, as α goes to 90°, gives the maximum mass of a pendant drop for a liquid with a given surface tension γ. Note that the SI units for γ are millinewtons per metre (mN/m)

$$mg = \pi d\gamma$$

This relationship is the basis of a convenient method of calculating surface tension. More sophisticated methods are available that take account of the developing shape of the pendant as the drop grows (Hansen and Rodsrun, 1991; Woodward, undated)). Curl (1972) found that surface tension is sensitive to temperature changes and impurities in the solution.

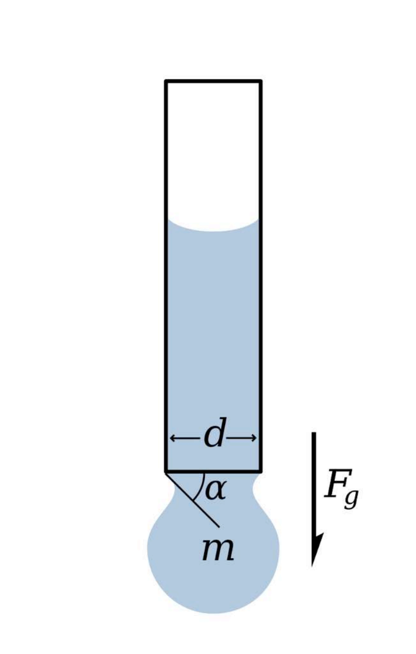

Figure 9: Solution-drop mass calculation diagram.Public domain via Wikipedia. en.wikipedia.org/wiki/Drop_(liquid)

Impurities may take the form of calcite crystals (rafts), which have been observed on the calthemite solution-drip surface (Smith, 2016), and their presence influenced by drip rate. Other minerals or other impurities present within the calthemite drip solution, might also influence the surface tension. In the cave environment speleothem drip solution impurities may include: Mg, Sr, SiO_2, SO_4, clay particles and organic matter (Borsato, 2016).

Theoretically the 'drop mass' from a stalactite straw of known diameter can be calculated as described above, but many variables can influence the solution 'surface tension' across a range of calthemite straws. Such factors can include saturation of Ca^{2+}, solution pH and impurities, serration of crystal structure around the straw tip (altering length of contact surface), solution temperature, and $CaCO_3$ rafts on drip surface (Fig.10). Also, drips may be induced to fall prematurely by solution flow rate, pulsation of solution, concrete structure vibration (movement of goods and people in supermarket) and air movement. If a drop is induced to fall prematurely, without reaching its maximum potential mass, this would translate into a false surface tension calculation. To reduce the error of a false mass measurement if a single drop fell prematurely, each reading was calculated from collecting a known number of drops from a straw and calculating the average drop mass, which was recorded against the diameter of straw from which it fell.

Figure 10: Variations in calthemite straw diameter, due to changes in solution surface tension, influenced by solution saturation of $Ca(OH)_2$ and usually associated with changes in solution supply (drip rate).

Figure 11: Slow drip rate increases calthemite straw diameter. Note the $CaCO_3$ rafts on the solution drop surface, which are a common feature at drip rates greater than approximately 12 minutes between drops.

Calculated 'surface tensions' from the collected calthemite dripwater solutions, varied between 35.9 and 43.7 mN/m over an atmospheric temperature range of 15° to 25°C. Experiments by Curl (1972) to study the relationship between speleothem straw diameter and drip mass using tap water arrived at surface tensions (expressed in equivalent units g/sec^2) ranging between 71.6 and 72.6mN/m at 21° to 22°C. However, Curl also provides a predicted speleothem solution surface tension of 74.2 mN/m at 10°C. As a comparison, the value for pure water at 20°C is 72.86 ±0.05mN/m (Pallas and Harrison, 1990).

The data collected did not definitively indicate that calthemite drip-water 'surface tension' had any appreciable influence on a straw's outside diameter. However, as determined in a previous study (Smith 2016), slow dripping calthemite straws tended to be slightly larger in diameter than fast dripping straws. This may well be due to the drop surface angle α remaining larger for a longer period as the drop forms and deposits $CaCO_3$ at the straw tip. An example of a calthemite straw with changes in diameter, is shown in both figure 10 and an example of a straw with a current growth in its diameter in figure 11. It is most likely that observations linking calthemite straw diameters to the drip rate, may also be mirrored in speleothem straw's diameters being influenced by solution drip rate. However, an extra-fast drip rate does not instantaneously create a small diameter straw or vice versa for a slow drip rate. A straw changes diameter gradually as it grows in length. Studies of growth rates (Smith 2016) have shown that it may take a matter of days or weeks for a calthemite straw to significantly change diameter as a result of a change in drip rate. A speleothem straw, due to its significantly slower growth rate, may take many months or years to change diameter provided the altered drip rate remains constant over a substantial time period to have an affect. Because of the slower growth rate of a speleothem straw, there is more chance that fluctuation in drip rate may be averaged out and the straw outside diameter remains reasonably constant.

$CaCO_3$ deposition from Hyperalkaline Solutions

This part of the study was undertaken to try and determine whether hyperalkaline drip solution could be used to measure the mass of $Ca(OH)_2$ leached from concrete and deposited externally as $CaCO_3$. A study of concrete degradation by Fagerlund (2000, p.35) determined that: "*About 15% of the lime has to be dissolved before strength is affected. This corresponds to about 10% of the cement weight, or almost all of the initially formed Ca(OH)*$_2$." Therefore it was hoped that findings during this study might be of value to aid engineers assessing degradation rates of concrete structures. Hartland *et al*. (2010) and Newton *et al*. (2015) studied hyperalkaline solutions (leached from overlying lime-waste) that form speleothems in Poole's Cavern (Derbyshire, England). This type of speleothem is found only where there has been lime burning or lime-waste tipping above a cave. Calcium hydroxide - $Ca(OH)_2$ - as found in concrete, is 200 times more water soluble than calcite (Sefton 1988), so it may be assumed that the Ca^{2+} carrying capacity of hyperalkaline solution can form calthemites faster than mildly alkaline groundwater can form speleothems. This is supported by Newton *et al.,* (2015), who found that weakly alkaline solution has a low Ca^{2+} carrying capacity (compared to hyperalkaline solution). For this study only hyperalkaline calthemite dripwater was sampled.

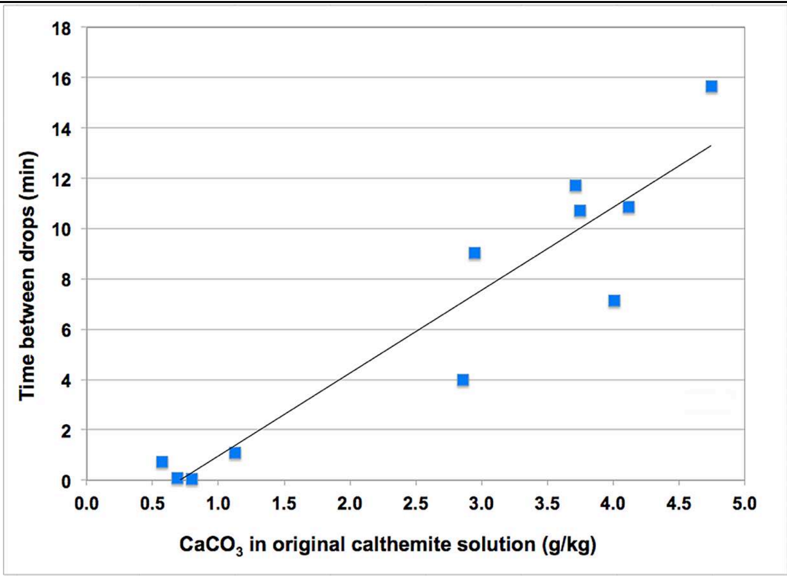

Figure 12: Drip rate in minutes between drops, versus $CaCO_3$ in the original calthemite solution (g/kg).

Samples 1 to 7 (Table 3) were collected during a relatively dry period (several weeks without rain) when drip rates were slow (between 4 and 16 minutes per drop) and it took several days to collect sufficient sample in the containers. Samples 8 to 11 were collected during a heavy rain event (50mm in 24 hours followed by several days of intermittent showers), which significantly increased the drip rate of all active straws (one drop per minute up to one drop every 3 seconds) enabling sufficient solution to be collected from each straw in less than 1 hour. The drip rate increase demonstrates a rapid response to the rain event, and therefore a short residence time within the concrete. A previous study (Smith 2016) suggests there is almost no deposition occurring at a straw's tip when the solution drip rate is >1 drop per minutes. As was expected, the mass of $CaCO_3$ deposited per kg of hyperalkaline solution was significantly less in the period with an abundance of dripwater. The greater flow rate through the concrete after the rain event suggests there was limited residence time to leach calcium hydroxide from cracks and micro pores within the concrete and transport Ca^{2+} to the under surface of the structure.

The linear relationship of "time between drips" and $CaCO_3$ deposited from solution (Fig.12), depicts the dissolution kinetic of the concrete. As the residence time of the fluid inside the concrete increases there is a steady and linear increase in the Ca^{2+} concentration in solution (deposited as $CaCO_3$). Overall the mass of $CaCO_3$ originally present in the hyperalkaline solution varied greatly from 0.572 to 4.75 g/kg of solution. The regression line on the graph (Fig.12) highlights that there is a reasonable deviation in sampled solution concentrations, which probably are influenced by other factors besides drip rate (flow-rate). It is reasonable to surmise that solution seepage path, residence time and availability of Ca^{2+} along the seepage path and possibly the original concrete constituents, play a large part in the leaching of Ca^{2+} from concrete structures. These factors indicate there is no simple way to calculate accurately how much Ca^{2+} is being leached from concrete and deposited as $CaCO_3$ by measuring solution flow rates.

As a comparison, Moore (1962) collected solution from a speleothem stalactite dripping at a 23-second interval and measured the flow rate at 30 ml/hour, in a cave atmosphere at 12.7 ºC and near 100% humidity. Because calcite rafts were forming on the surface of the pool beneath the stalactite he assumed that the drip solution was near 100% saturation. Moore calculated that the total calcite deposition from the solution was 0.014 g/day, which equates to 0.0194 g/kg of speleothem drip-water solution. This figure is in line with the far more dilute concentrations of these circumneutral pH solutions.

Conclusion

On average the calthemite straws examined had thinner wall thickness and a less-dense calcium carbonate structure than speleothem straws of equivalent diameter. It appears that the chemistry and slower deposition rate of calcium carbonate from mildly alkaline solution (low Ca^{2+} saturation) associated with limestone cave (speleothem) straws, creates a denser structure than does the hyperalkaline solution creating calthemite straws. This is well explained by the speleothem straw growth pattern image by (Paul *et.al.* 2013, Figure 7) and the structure of calthemite straws studied by Broughton *et.al.* (2020). Measurements in the present study revealed that calthemite straws are, on average, just 40% the mass per unit length of speleothem straws of equivalent external diameter.

Calthemite straws can grow in length up to 2 mm per day when the drip rate is 11 minutes between drops. As determined by (Smith 2016), when the drip rate exceeds one drop per 11 minutes the deposition rate (length gain) is reduced. The present study suggests that changes in solution residence time within concrete, expressed by the drip rate, have a great influence on both the uptake of calcium ions in solution and on the amount of $CaCO_3$ deposited subsequently at the straw tip and/or as a stalagmite. Hence, during periods of fast flow the concentration of Ca^{2+} in solution is less?? than when there is a slower solution flow rate. The time a drop remains at the tip of a calthemite straw affects the ability of solution to uptake carbon dioxide from the atmosphere and deposit $CaCO_3$, however saturation of the fluid also plays a significant role. The concentration of calcium ions carried by solution is influenced by the solution pH, flow rate, length of seepage path and time taken to travel through the concrete's micro-cracks and pores, and availability of Ca^{2+} along the seepage path.

The mass of a drop of solution falling from a calthemite straw of known diameter is directly proportional to the end diameter of the straw from which it fell. Hence, the larger the straw's diameter, the greater the drop mass. The drop mass could not be predicted accurately without knowing the solution surface tension at the precise time. However, many variables such as temperature and impurities, can influence surface tension and in turn the drop mass. Provided the possibility of a drop falling prematurely because of vibration, air movement or other factors are eliminated, a drop mass could be calculated approximately using the formula $\mathbf{mg=\pi d\gamma}$ if the straw diameter and solution surface tension γ is known. There appears to be sufficient variation in drip surface tension to have a small influence over the maximum diameter range of calthemite compared to speleothem straws. Calthemite solution drip rate appears to influence the resulting calthemite straw external diameter and the drip rate may well influence a speleothem straw's diameter. As Curl (1972) suggested, a speleothem straw's diameter at the tip is governed by the diameter and mass of solution-drop that can be supported by the surface tension. An equilibrium is reached when a straw's external diameter becomes parallel. A straw's diameter "*should converge, with growth, in an exponential manner*" to reach an equilibrium diameter. However, a straw's diameter seems to be influenced by additional factors. In the case of calthemite straws, the solution drip rate appears to exert a large influence over the external diameter of a straw and can cause the diameter to increase or decrease in an attempt to maintain equilibrium with the drip solution parameters.

Sampling and analysis of solution drip rate from straws and the Ca^{2+} ions leached from concrete (precipitated as $CaCO_3$) showed that a slower drip rate had a higher solution saturation. However, the deviation of results from a straight line indicates that other factors, such as details of the solution seepage path, the residence time within the path, and availability of Ca^{2+} along the path have an influence over the calthemite solution saturation. Hence, analysis of drip solution alone is not a reliable method of determining a concrete's degradation rate.

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References

Borsato A., Johnston V, Frisia S., Miorandi R, & Corradini F, 2016. Temperature and altitudinal influence on karst dripwater chemistry: implications for regional-scale palaeoclimate reconstructions from speleothems. *Geochimica et Cosmochimica Acta,* Vol.177, 275–297.

Broughton P.L, 2020, Morphogenesis and microstructure of concrete-derived calthemites. *Environmental Earth Science.* Vol.**79** (Article 245), 1-19. [Springer-Verlag GmbH Germany.]

Curl R, 1972, Minimum diameter stalactites. *Bulletin of the National Speleological Society*, Vol.34(4),129-136.

Dixon S J, Viles, H A, and Garrett, B L, 2018. Ozymandias in the Anthropocene: the city as an emerging landform, *Area*, Vol.50, [Published by the Royal Geographical Society, with the Institute of British Geographers.]

Fagerlund, G, 2000, Leaching of concrete: the leaching process: extrapolation of deterioration: effect on the structural stability. Report TVBM; Vol. 3091. Division of Building Materials, LTH, Lund University.

Field, L P, Milodowski, A E, Shaw, R P, Stevens, L A, Hall, M R, Kilpatrick, A, Gunn, J, Kemp, S J and Ellis, MA, 2017. Unusual morphologies and the occurrence of pseudomorphs after ikaite ($CaCO_3.6H_2O$) in fast growing, hyperalkaline speleothems. *Mineralological Magazine*, Vol.81, 565-589.

Ford, D., and Williams, P, 2007, Rates of growth of calcite speleothems. Chapter 8.3.11 in Ford, D and Williams, P, *Karst Hydrogeology and Geomorphology*, [Chichester: John Wiley & Sons Ltd]

Hansen, FK and Rodsrun, G, 1991. Surface tension by pendant drop. A fast standard instrument using computer image analysis, *Journal of Colloid and Interface Science*, Vol.141, issue 1, 1-9.

Hartland, A, Fairchild, I J, Lead, J R, Dominguez-Villar, D, Baker, A, Gunn, J, Baalousha, M and Ju-Nam, Y, 2010. The dripwaters and speleothems of Poole's Cavern: a review of recent and ongoing research. *Cave and Karst Science*, Vol.36, 37–46.

Macleod, G, Hall, A J and Fallick, A E, 1990. An applied mineralogical investigation of concrete degradation in a major concrete road bridge. *Mineralogical Magazine*, Vol.54, 637–644.

Moore, G.W. 1962. The growth of stalactites. *National Speleological Society Bulletin*, Vol.24, Part 2, 95-106

Newton, K, Fairchild, I and Gunn, J, 2015. Rates of calcite precipitation from hyperalkaline waters, Poole's Cavern, Derbyshire. *Cave and Karst Science.* Vol.42 (3), 116–124.

Pallas, N.R. and Harrison, Y, 1990, An automated drop shape apparatus and the surface tension of pure water. *Colloids and Surfaces*, Vol.43,169-194.

Paul, B., Drysdale, R., Green, H., Woodhead J., Hellstrom, J, Eberhard, R., 2013. A model for the formation of layered soda-straw stalactites, *International Journal of Speleology,* Vol.42(2), 155-160.

Sefton, M, 1988. "Manmade" speleothems. *South African Speleological Association Bulletin*, Vol.28, 5–7.

Smith, G.K, 2016, Calcite straw stalactites growing from concrete structures. *Cave and Karst Science* Vol.43(1), 4-10

Woodward, R.P, [undated] Surface Tension Measurements Using the Drop Shape Method. Available online [*accessed 02/02/2021*] from: www.jascoint.co.jp/products/contact-angle/pdf/05.pdf

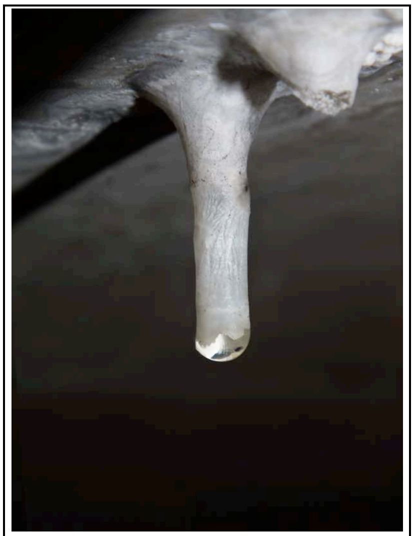


Image 1

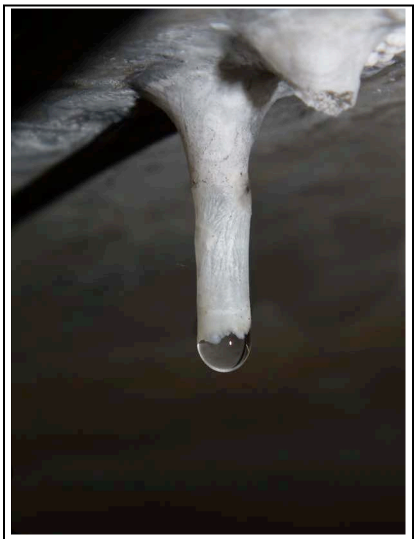


Image 2

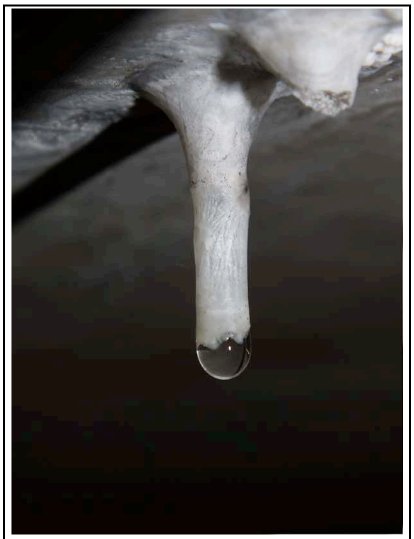
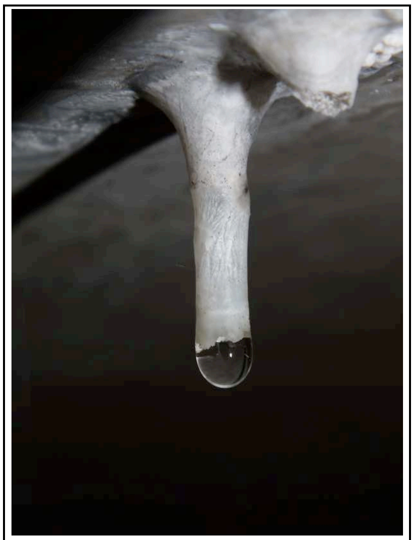


Image 3



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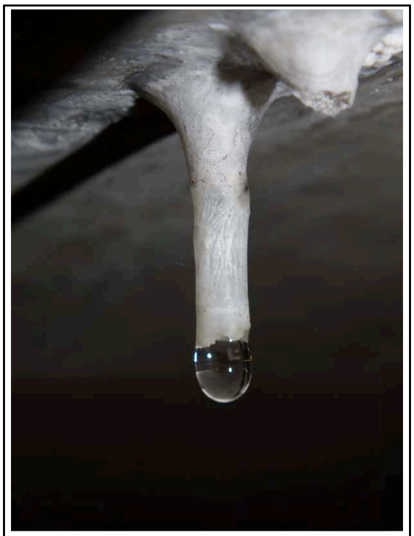

Image 5

Image 6

Image 7

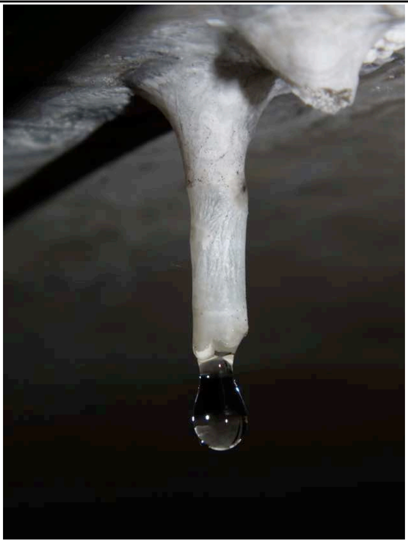

Image 8

Image 9

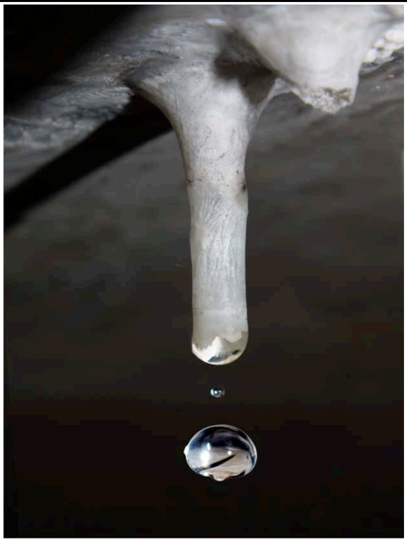

Image 10

Image 11

Unnumbered figure, comprising eleven numbered images, to illustrate the development stages of a calthemite straw solution-drop. **Images 1 – 3**: A slow-growing solution-drop forming at the base of a straw stalactite is held in place by the surface tension of the liquid. **Images 4 – 5**: The solution mass continues to accumulate and the drop shape begins to bulge out from the straw rim. **Images 6 – 7**: As the mass of solution continues to grow, the surface tension starts to loose the battle against the gravitational pull, and the drop begins to lengthen. **Images 7 – 9**. This stage of the cycle occurs very quickly as gravity overpowers the surface tension and the drop pulls away from the end of the straw. In just a few hundredths of a second the solution narrows to a teardrop shape (**Image 9**) as the drop breaks free. **Image 9 – 10**: The extreme teardrop shape in **Image 9** is what sets up a compression wave in the larger detached drop as the surface tension pulls the trailing fluid back into the drop in an attempt to regain an equilibrium shape. The narrow neck of the teardrop shape in **Image 9** is stretched out so far that it creates an additional minute drop (**Image 10**), detached from the main drop, because the surface tension is insufficient to draw that small part of the solution into the larger mass of the drop quickly enough during the instant of separation. **Image 11**: shows that a shock wave is set up as the drop breaks free, and rebounds within the fluid held together by the surface tension. Thus, as the larger drip falls, its shape oscillates between the shapes in **images 10 and 11** until the surface tension regains an equilibrium and stabilizes the drop shape. Calculations of drop mass in this Paper consider the minute drop as part of the greater drop-solution mass, which broke free at the same instant.