

CALCITE STRAW STALACTITES GROWING from CONCRETE STRUCTURES

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In this paper, the term 'calthemite' is used to encompass the various concrete-, mortar- or lime-derived secondary deposits consisting primarily of calcium carbonate (CaCO_3) that grow from man-made alkaline structures outside the cave environment. Calthemites are very similar in composition and form to speleothems in limestone caves, but in concrete-derived straws, carbon dioxide (CO_2) is a reactant as opposed to a product. The growth rates and corresponding drip rates of four stalactite straws growing beneath a concrete building were recorded over a ten month period. The major influencing factors determining calcite deposition were the supply continuity of leachate and the drip rate. Growth rates up to two millimetres per day were recorded. Minute calcite rafts were observed and photographed on the solution drop surface. Sporadic movement of rafts around the drop surface (induced by air movement), is identified as affecting straw diameter and wall thickness. Deposition of CaCO_3 straws derived from concrete is usually associated with hyperalkaline solution ($\text{pH} > 9$) as opposed to the near neutral pH to mildly alkaline solutions ($\text{pH} 7.5 - 8.5$) that commonly deposit speleothems.

I am sure that every cave guide has been asked sometime in their career to explain the difference between cave stalactites and those hanging under concrete buildings and bridges. This sort of question probably sends shivers down your spine as you reach to the depths of your knowledge on the subject.

There is certainly the short answer - "the stalactite under a bridge is a secondary deposit of calcium carbonate (CaCO_3) derived from the cement/concrete and the cave stalactite is CaCO_3 secondary deposit derived directly from limestone".

While there are similarities in appearance and morphology, there are considerable differences in the chemistry and growth rate.



Examples of Calthemite straws in an underground carpark



Example of Calthemite flowstone on concrete water tank

So how much time and explanation does one put into a description of the differences between a "speleothem" or those "other things" which look the same but grow under concrete structures? I personally think it is nice to impart a little more knowledge on the subject to that inquisitive tourist, rather than the short answer above.

Certainly, cavers like myself have pondered over the sight of such wonders. This prompted me to take on a study of these calcium carbonate secondary deposits under manmade structures and I learnt a lot along the way. So as not to bore you too much, I have written just a little on the background to this study and then briefly detailed some key findings followed by the chemistry. This should provide a few short answers, which can be pulled out of the hat when hit with that curly question from an inquisitive tourist.

The initial focus of the study was to determine how quickly the straws grew and what factors influence their growth. Chemical reaction causing calcium carbonate (CaCO_3) deposition soon grabbed my attention and was found to be closely related to solution pH. This proved to be just the starting point, which raised many more questions and widened the project scope. The quest for answers led to a number of interesting and previously undocumented observations and the introduction of a new word.



Examples of calthemite straws in an underground carpark



Photographing and measuring calthemite straws in an underground carpark

What term to use?

Concrete secondary deposits in the shape of straws, stalactites, shawls, flowstone, stalagmites etc, mimic cave speleothems in many respects. This led me to an extensive literature search for the appropriate term to use. Descriptions in published papers circumnavigate the question of a concise term to cover calcite precipitates on man-made structures. Examples from ‘*Cave Minerals Of The World*’, Hill and Forti (1997) include: “non-cave stalactites which derive their calcium carbonate from concrete”, “formations under concrete structures” and “deposits in the outside world, while not speleothems in the strict sense, nevertheless mimic the forms taken by speleothems”.

The term ‘speleothem’ by definition can only be used to describe, stalactites, straws, stalagmites, flowstone, etc, which were created in a cave. Hence, for the purposes of my study the term ‘Calthemite’ is used to encompass the various decorations mimicking speleothems, derived from man-made structures containing cement, mortar or lime. The word ‘calthemite’ is derived from the Latin calx (genitive calcis) “lime” + Latin < Greek thēma, “deposit” meaning ‘something laid down’, (also Mediaeval Latin thema, “deposit”) and the Latin -ita < Greek -itēs – used as a suffix indicating a mineral or rock.

So in essence the simplistic analogy is that ‘calthemite’ encompasses secondary deposits derived from manmade structures outside a cave environment, where as the term ‘speleothem’ describes secondary deposits inside a cave.

Summary of Findings

1. Continuity of solution and drip rate has the most influence on a calthemite straw's growth rate.

2. Evaporation due to atmospheric temperature and humidity, had no measurable effect on a calthemite straw's growth rate.
3. No straw growth occurred if the drip rate was more frequent than 1 drip/minute.
4. A maximum growth rate of 2mm/day was recorded when there was 11 minutes between drips.
5. The pH of the hyperalkaline solution influences which chemical reaction or reactions is/are depositing calcium carbonate at a particular time and location.
6. The hyperalkaline solution creating the calthemite straws is typically pH > 9 and commonly reaches pH 13.5, which can easily burn human skin.
7. Deposition of calcium carbonate as calthemite decorations, occurs when atmospheric CO₂ diffuses into the drop solution, as opposed to normal cave speleothem chemistry where CO₂ is degassed from solution.
8. Calcite rafts may form on the surface of solution drops and can influence a calthemite straw's growth, outside diameter and create surface irregularities.
9. When there is almost no air movement, calcite rafts form a latticework over the drop surface when drip rate is slower than approximately 1 drip every 5 minutes. Air movement or a pulse of solution through the straw will break up any latticework to create small rafts, which may spin violently. Stronger air movement can shear some rafts from the drop surface and push them onto the straw's outside surface.

As a comparison, speleothem straw growth is also influenced by the continuity of solution and drip rate. Likewise the evaporation of solution is considered to have little influence on deposition rate. So the big difference comes down to the capacity of the solution to carry calcium ions to the site of deposition. Calcium hydroxide which leaches from the concrete is about 200 times more soluble than calcite in water and therefore facilitates the rapid growth of calthemite straws compared to normal speleothem straws in limestone caves.

The growth rates of stalactites in natural limestone caves have been well documented by repeated measurements in well-known caves. Data show that stalactites in caves rarely grow more than 2 millimetres a year and may average only a little more than a tenth of a millimetre per year. In comparison a calthemite straw can easily grow 0.5mm per day to achieve 180mm in a year. During the study one calthemite straw grew an average of 2mm per day over several days, which in theory equates to a possible growth of 730mm a year if this rate remained constant. From these figures, it is easy to see the huge difference in growth rates between calthemite and speleothem straws.

Rafts Observed on Calthemite Solution Drops

A long period between drips (≥ 5 minutes) was sufficient time for absorbed CO_2 to cause precipitation of CaCO_3 from solution and form rafts on the drop surface, which were visible to the naked eye (up to 0.5mm across). Their sporadic movement around the drop surface aided by air movement and internal solution pulses, caused some rafts to be pushed onto the straw's outer surface. These rafts influenced the thickness and irregularities of a calthemite straw's outside diameter.

A 34 second video of rafts spinning on the surface of a solution drop can be viewed on YouTube at https://www.youtube.com/watch?v=G-gm_kN5Xes



Freely moving calcite rafts whirl around solution drop due air movement

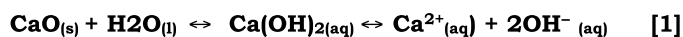
Calthemite Properties

Just like speleothems, calthemites may be coloured due to iron, copper, zinc or various minerals, deposited in conjunction with the calcium carbonate (CaCO_3). Hence the predominately white calcium carbonate will be stained orange from rusting steel reinforcing bars. Another example is copper pipes passing through or near concrete, while less susceptible to oxidation, can produce a green or blue copper oxide, which discolours calthemites.

Specialist equipment was not available to determine the morphology of the deposited CaCO_3 , however it is most likely being precipitated from solution as calcite, as opposed to the less stable polymorphs of aragonite and vaterite.

Calthemite Chemistry

When water is added to a dry concrete mix it reacts readily with the calcium oxide (CaO) in the cement to form calcium hydroxide (Ca(OH)_2), which can further dissociate to form Ca^{2+} and hydroxide (OH^-) ions. [Equation 1].



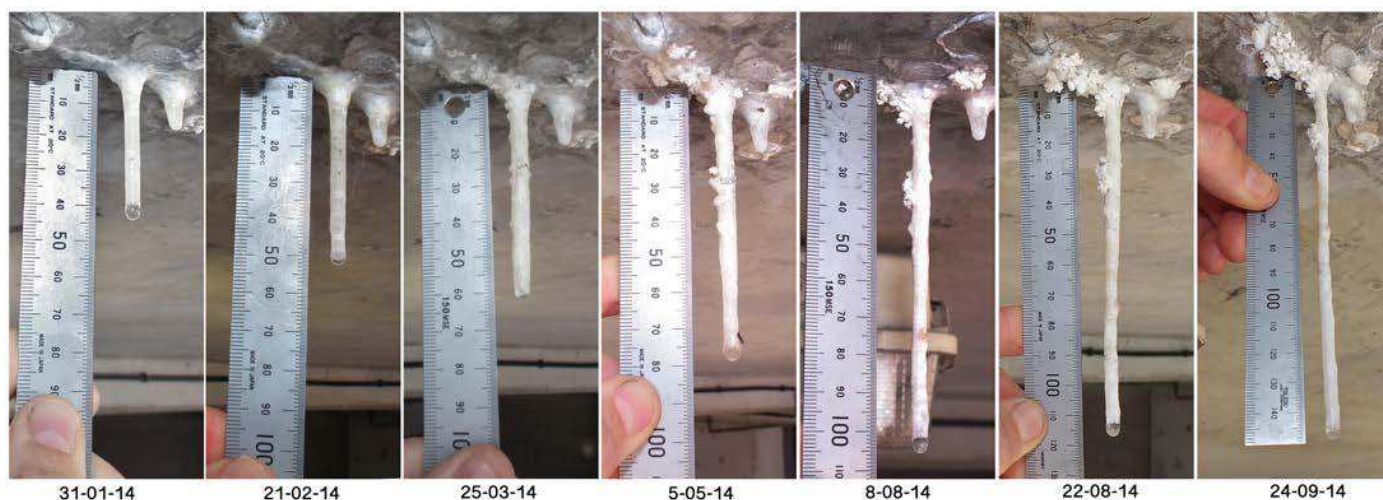
Any carbon dioxide (CO_2) trapped in the mix reacts with the Ca(OH)_2 to precipitate CaCO_3 within the concrete structure [Equation 2].



Reaction [2] occurs within the concrete matrix until all the available free CO_2 in the mixture is used up. Setting concrete



Latticework of calcite rafts on slow dripping straw during period of very little air movement



Growth of calthemite straw No.1. The sequence shows the growth of 104mm in 237 days. When there was only one drip every 11 minutes, this straw grew at 2mm per day. The date below each image relates to date of measurement recording.

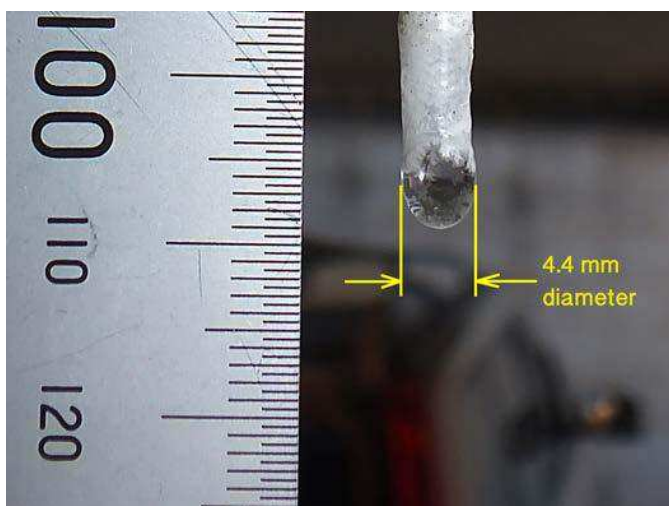
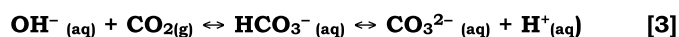


Image showing diameter of calthemite straw

exposed to the atmosphere containing more CO_2 will allow reaction [2] to continue to a shallow depth (commonly just a few millimetres) from the surface after which atmospheric CO_2 is unable to penetrate and carry on the reaction [Equation 2]. Hence, free $\text{Ca}(\text{OH})_2$ remains within the structure of set concrete.

Rain or seepage water which penetrates microscopic cracks and air voids in set concrete, will readily carry $\text{Ca}(\text{OH})_2$ in solution to the edge of the concrete where it reacts with atmospheric CO_2 to precipitate calcium carbonate [Equation 2], thus forming calthemite straws etc.

To complicate the issue, there is a period when the presence of potassium and sodium in new concrete will support a higher solution alkalinity of about pH 13.2 – 13.4. The hyperalkaline solution becomes supersaturated with Ca^{2+} compared to a mildly alkaline solution. When the hyperalkaline leachate emerges from beneath the concrete structure, CO_2 is absorbed into the solution from the atmosphere [Equation 3] resulting in the dominant ion CO_3^{2-} reacting with Ca^{2+} to precipitate CaCO_3 [Equation 4].



Over time the leachate pH will decrease to 12.5 as the majority of the more soluble potassium and sodium hydroxides are leached out and the dominant reaction reverts back to Equation [2]. As time passes, the available $\text{Ca}(\text{OH})_2$ will leach from the cement paste along the seepage path and the pH will fall even further till carbonic acid (H_2CO_3) becomes dominant and the chemical reaction will change to a similar process to that which occurs in limestone caves. The weakly alkaline leachate has a low Ca^{2+} carrying capacity (compared to hyperalkaline leachate) and CaCO_3 deposition occurs under concrete structures when CO_2 is degassed from solution [Equation 5].



The reaction Equation [5] appears to only occur under specific circumstances relating to very old concrete or mortar (possibly 10s or 100s of years old) and is essentially the same as the reaction occurring in limestone caves.

For an in-depth look at the chemistry, refer to the complete paper published in 'Cave and Karst Science', Vol.43, No.1, P. 4-10, (April 2016).

Details of full paper

This study was first presented at the ASF's 30th Biennial Conference, 21st – 26th June 2015, Exmouth, Western Australia and later published in 'Cave and Karst Science', Vol.43, No.1, P. 4-10, (April 2016), British Cave Research Association, ISSN 1356-191X.

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