Calthemite Deposits, Form Stalactite Straws Beneath Concrete Structures

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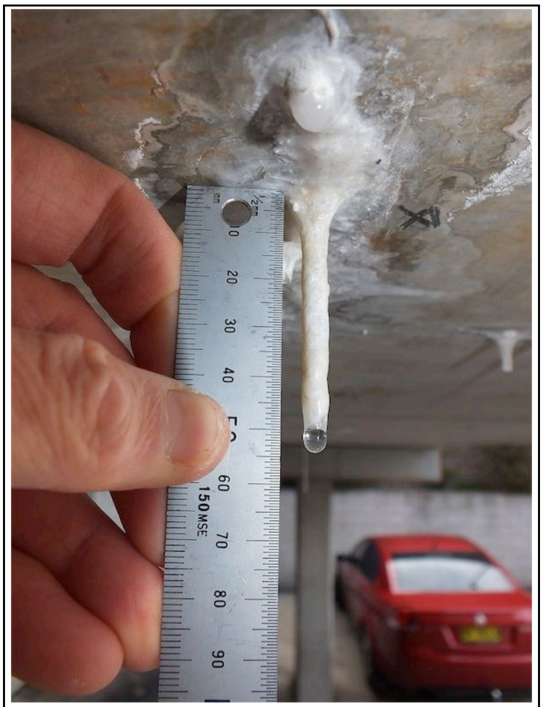
To most people the sight of straw stalactites growing beneath a concrete structure is no big deal. 'So what?' some may say. It is however a concern to structural engineers as it's a sign of degrading concrete. I suspect there are many cavers like myself, who have pondering over the sight of such wonders. This prompted me to take on a study of these secondary calcium carbonate deposits under man-made structures.

The initial focus was to determine how quickly the straws grew and what factors influence their growth and also to identify the chemical reaction causing calcium carbonate ($CaCO_3$) deposition and measure the 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; calthemite.

Location of calthemite straws on the supermarket carpark ceiling. Photo by Sonia Taylor-Smith

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 calcium carbonate 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'.



Measuring calthemite straws with engineering metal ruler graduated in 0.5 mm increments.
Photo by Garry K. Smith

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 this study, the term **'Calthemite'** was used to encompass the various decorations mimicking speleothems, derived from man-made structures containing cement, mortar,

lime or other calcareous material. The word 'calthemite' is derived from the Latin *calx* (genitive *calcis*) 'lime' + Latin < Greek *théma*, '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 a manmade structure outside a cave environment, which includes mines and tunnels, where the secondary deposit may be derived from concrete, lime, mortar, limestone, dolomite or other calcareous material.

For clarification, the term 'speleothem', first used by Moore in (1952) can only be used to describe 'secondary deposits' **inside a cave**. Hill, C A, and Forti, P, (1997) went on to further define 'speleothem secondary deposits' in the excellent publication, *Cave Minerals of the World*, (2nd edition) p13, which specifically disallowed secondary deposits in mines and tunnels as being classed as speleothems.

31-01-14 21-02-14 25-03-14 5-05-14 8-08-14 22-08-14 24-09-14

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

Calthemite Properties

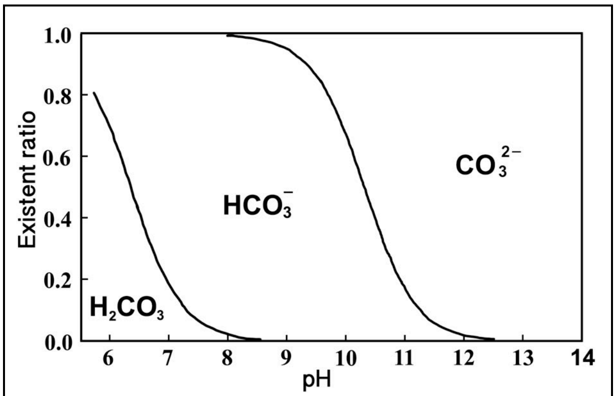
Calthemites consist predominately of calcium carbonate ($CaCO_3$), but may contain other trace elements such as iron, copper and zinc, or minerals e.g. gypsum. These elements and minerals may colour the calthemite when transported by the leaching solution and deposited at the same time as the $CaCO_3$ hence the predominately white calcium carbonate will be stained yellow, orange or red from rusting steel reinforcing bars and copper pipes passing through concrete, which can produce a green or blue copper oxide colour.

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.

Chemistry

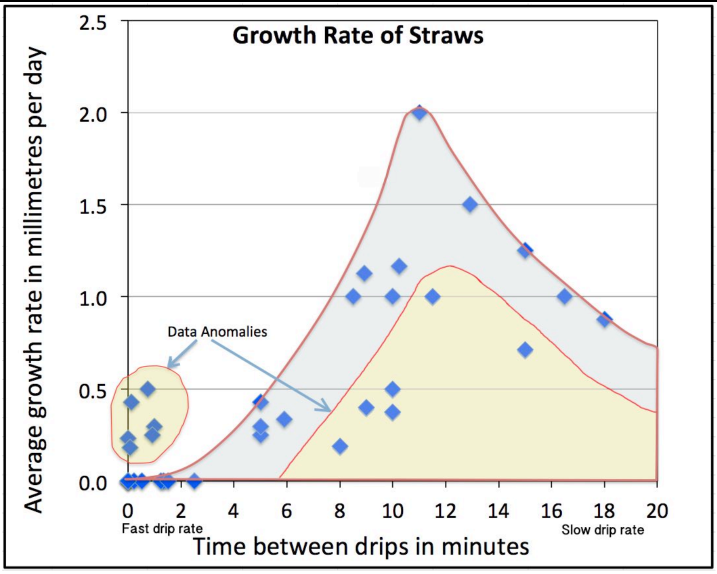
To make concrete, aggregate and sand are mixed with cement. When water is added to the mix it reacts readily with the calcium oxide (CaO) in the cement to form calcium hydroxide ($Ca(OH)_2$), which is a key component in the chemistry creating calthemites.

The solution pH, influences which chemical reaction/s are occurring at a particular time to deposit the $CaCO_3$. This can also have a



Relationship between equilibrium of carbonic acid and pH in solution. Carbonic acid includes both carbonates and bicarbonates. Graph after Maekawa et al., 2009.

bearing on the deposition rates and growth of straws. Of the three main reactions, two rely on absorption of CO_2 from the atmosphere for $CaCO_3$ deposition to occur, as opposed to cave straws (speleothems) where deposition occurs due to degassing of CO_2 from solution. The third reaction 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.



Plot of calthemite straw averaged growth rates between periods of data recording, measured in mm/day vs solution drip rate in minutes. The 'Data Anomalies' are measurements recorded in periods when the drip rate changed dramatically between recordings.

There is of course the circumstances where mine shafts, vehicle and train tunnels are cut through limestone, dolomite or other calcareous rock and the secondary deposits – the calthemites in them - are precipitated by the same chemistry as 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 (April 2016) or search Wikipedia for Calthemite.

Rafts Observed on 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 straw's outside diameter.


Drip with calcite rafts latticework formed on a very slow-dripping calthemite straw (=>12 minutes between drops) on a day with no wind or vehicle movement. Photo by Garry K. Smith


Calcite rafts are broken up and spinning around the drip surface, influenced by air movement. Photo by Garry K. Smith

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

Summary of Findings

Calthemite stalagmite beneath dripping straw – subject to abrasion from vehicle tyres and pedestrian traffic. Photo by Naomi Baxter.

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 calthemite straw's growth rate.
3. No straw growth occurs if the drip rate is more frequent than 1 drip/min
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 straws is typically pH > 9 and commonly reaches pH 13.5, which can easily burn human skin.
7. Deposition of calcium carbonate occurs when atmospheric CO_2 diffuses into the drop solution, as opposed to normal cave speleothem chemistry where CO_2 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.

Background to Study

The study concept evolved from a wild brainstorm while loading my car with groceries at the local supermarket and pondering what I could do to contribute to the ASF's 2015 Biennial Conference, which was still 18 months away at the time. Looking up I saw about 30 active stalactites of various lengths hanging from the concrete building above. This raised many questions in my mind. How quickly do they grow? What chemistry is involved? Has anyone studied non-cave stalactites before? What are they called if the term 'speleothem' can only be used to describe secondary deposits in caves?

All these unanswered questions certainly sparked my interest. I remembered seeing these straws and stalactites growing within a very short period of the buildings completion six years earlier and many were still very actively growing.

After many nights at the computer scouring the internet, I only had some answers and not very comprehensive ones at that. The next day I was down at the shopping centre and up a ladder after the supermarket closing time. The months rolled by with weekly and often daily return visits to measure, photograph and record data such as temperature, humidity, atmospheric CO_2 concentration, solution pH and drip rates.

A short period into the study I was unable to do the measurements after closing time, so put on a fluro vest and took the readings during the shopping centre opening hours. It is surprising how a fluro vest makes a person look official. I was never questioned by staff nor security personnel while making the measurements.

Ten months of collecting data allowed me to gain a pretty good grasp of growth rates and how it related to the drip rate. I must admit that staring up at a straw drip waiting for it to drop can be time consuming, especially when there may be 20 minutes or more between drips.

The rest is history. I was able to present the study at the ASF's 30th Biennial Conference in Exmouth WA, 21st – 26th June 2015. It has been a very time consuming task, but very rewarding in that I have personally learnt a lot from the exercise.

Acknowledgements
A special thanks to Dr Ken Turner whom I consulted on many occasions for advice on the chemistry, and Dr Andrew C Baker and Jodie Rutledge for critical reviews of the paper.

The following is the abstract from the peer reviewed paper published in 'Cave and Karst Science', Vol.43, No.1 (April 2016)

Abstract: 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 (pH > 9) as opposed to the near neutral pH to mildly alkaline solutions (pH 7.5 – 8.5) that commonly deposit speleothems.

Aqua-coloured calthemite formations containing traces of copper, deposited in conjunction with calcite. Example at an underground carpark, 0.5km from the study site. Photo by Garry K. Smith

Orange-coloured calthemite flowstone containing traces of iron from reinforcing bars within concrete. This example is at the study site. Photo by Garry K. Smith