

# Calcite straw stalactites growing from concrete structures

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**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 ( $\text{CaCO}_3$ ) 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 ( $\text{CO}_2$ ) 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  $\text{CaCO}_3$  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.

**Key Words:** concrete, straws, calcium hydroxide, calcium carbonate, calthemite, stalactite, pH, hyperalkaline, leachate.

## Introduction

Straw stalactites growing from concrete structures have similarities in morphology to equivalent speleothems growing in limestone caves but there are distinct differences in processes of formation. Straws growing from concrete can grow hundreds of times faster than straw speleothems. This study looks at the relationship between the growth in straw length and the solution drip rates. Several other influencing factors are considered, including air movement, humidity, temperature, atmospheric  $\text{CO}_2$  concentration, solution pH and chemical reactions.

Whereas the majority of straw speleothems in caves are created when  $\text{CO}_2$  is degassed from drip solution, the majority of concrete derived straws are created when  $\text{CO}_2$  is absorbed into hyperalkaline leachate solution. Calcium-rich leachate seeping from concrete structures is associated with degradation of the concrete and has been the focus of many studies (Macleod *et al.*, 1990; Lees, 1992; Ekström, 2001). These secondary



**Figure 1:** Location of straw stalactites on ceiling of supermarket carpark.



**Figure 2: Calthemite stalagmite beneath dripping straw - subject to abrasion from vehicle tyres and pedestrian traffic.**

derived from leaching of waste materials from lime production have precipitated calcium carbonate, including speleothems in Poole's Cavern discussed by Hartland *et al.* (2010) and Newton *et al.* (2015). The chemistry involved at Poole's Cavern parallels that of  $\text{CaCO}_3$  deposition from degrading concrete leachate.

## Study site

A concrete building constructed in Belmont, NSW, Australia during 2008 (6 years old at the time of study) included a partly enclosed undercover car park with supermarket area above. Straw stalactites began growing within months of the building being completed. Solution water originates from minute holes in poorly constructed roof guttering, which trapped rainwater and leaked a constant flow onto the concrete structure. The water then found its way into the concrete, following microscopic cracks and voids, gaining solutes until it emerged from cracks in the car park ceiling where the stalactite straws are growing.

Although the stalactites were in a difficult physical location to undertake measurements because of vehicle movements, the constant supply of solution water all year round made it ideal for a study of growth rates [Fig.1].

## Terminology

The term "speleothem" as introduced by Moore (1952), is derived from the Greek words *spēlaion* 'cave' + *thēma* 'deposit'. As it specifically refers to secondary deposits in caves, the term should not be used to describe straws, stalactites, flowstone and other secondary deposits associated with dissolution of concrete, mortar, lime or calcareous material outside the cave environment.

Many descriptions in published papers circumnavigate the question of a concise term to cover calcite precipitates on man-made structures. Examples from 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.*" As these descriptions are quite cumbersome the term '**calthemite**' is used in this paper to encompass the varied secondary mineral deposits derived from man-made structures that consist primarily of calcium carbonate. They may also contain other trace elements such as iron, copper and zinc, or minerals such as gypsum. 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.

## Methodology

The length and tip diameter of straw calthemites were measured by taking digital photographs of a precision metal ruler calibrated in 0.5 mm increments next to the straw and enlarging the images. Measurement error was estimated at  $\pm 0.15\text{mm}$ . (Figs 3 and 12) Specific attention was paid to angle and subject distance from camera, to eliminate potential parallax errors.

deposits, which commonly resemble speleothems, are of concern to structural engineers as well as being of visual interest.

The aim of this study was to identify the main factors that influence  $\text{CaCO}_3$  deposition and straw growth and to determine the most likely chemical reactions occurring at the study site, by cross referencing solution pH with studies by Ishida and Maekawa, (2000), Ekström, (2001) and Maekawa, *et al.*, (2009).

Deposition of calcium carbonate derived from degrading concrete, is typically associated with hyperalkaline solution of  $\text{pH} > 9$  (Macleod *et al.*, 1990). In the Peak District, England, there are several locations where hyperalkaline solutions



Straws were measured on average once per week. Also, the time of day, external temperature, humidity, solution pH and drip rate were recorded. Records were kept of atmospheric temperature and humidity (attributed to the weather), because they were considered to influence solution evaporation to an extent that might significantly affect deposition rates. Temperature and humidity data were obtained from a meteorological bureau weather app that provided hourly readings for Belmont NSW. Several checks of bureau temperature readings were found to be within one or two degrees of readings from a thermometer held next to the straws.

The wind direction and strength were not recorded because the underside of the building was generally sheltered, but vehicle movements did create significant air movement past the straws.

Drip solution pH at each straw tip was measured using ‘universal pH indicator’ paper ( $\pm 0.5$  pH units). The chemistry of the solution water was not analysed nor the degree of saturation, which may be influenced by the path and flow rate of seepage water through the concrete. As an additional check, fresh rainwater at the study site was tested with ‘universal pH indicator’ paper and found to be pH 7.

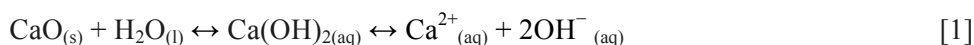
To determine whether vehicle exhaust emissions were aiding  $\text{CaCO}_3$  deposition significantly, the atmosphere at the study site was tested for  $\text{CO}_2$ , using a Dräger tube meter with a lowest detection limit of 0.1% by volume (1000 ppm), and  $\text{CO}_2$  concentration was consistently below detection.

Specialized analytical equipment was not available to determine which polymorph of calcium carbonate is deposited to create calthemites, but it is hypothesized that calcite is precipitated from solution in preference to the other, less stable, polymorphs aragonite and vaterite.

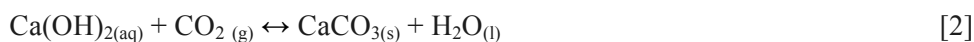
## Chemical reactions creating calthemites

Concrete chemistry is summarized briefly below. A number of chemical reactions occur that cause cement mixed with water to cure (Macleod, *et al.*, 1990; Borrows, 2006a, 2007), but for the purposes of this paper only the calcium reactions are detailed. All are reversible and several may occur simultaneously at a specific location, influenced by solution pH (Maekawa, *et al.*, 2009). Refer to Figure 4.

To make concrete, aggregate and sand are mixed with cement. When water is added to the mix it reacts readily with the calcium oxide ( $\text{CaO}$ ) in the cement to form calcium hydroxide ( $\text{Ca(OH)}_2$ ), which can further dissociate to form  $\text{Ca}^{2+}$  and hydroxide ( $\text{OH}^-$ ) ions. [Equation 1].



Any carbon dioxide ( $\text{CO}_2$ ) trapped in the mix will readily react with the  $\text{Ca(OH)}_2$  to precipitate  $\text{CaCO}_3$  within the concrete structure [Equation 2]. This overall reaction has been generally termed as “concrete carbonation” (Ho and Lewis, 1987; Papadakis, *et al.*, 1989, 1991, 1992).



Reaction [2] occurs within the concrete matrix until all the available free  $\text{CO}_2$  in the mixture is used up. Setting concrete exposed to the atmosphere containing more  $\text{CO}_2$  will allow reaction [2] to continue to a

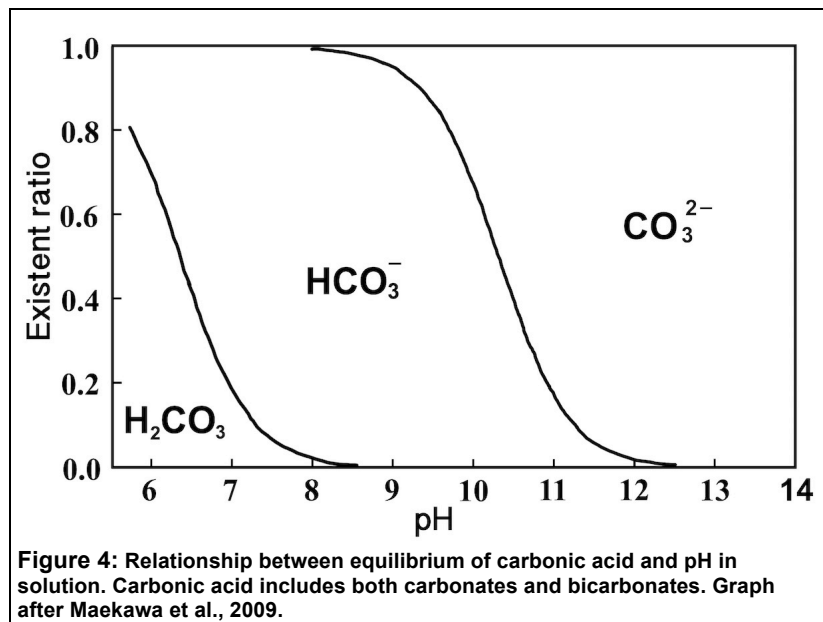
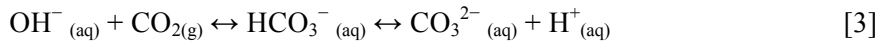


**Figure 3: Measuring calthemite straws with engineering metal ruler graduated in 0.5mm increments.**

shallow depth (commonly just a few millimetres) from the surface after which atmospheric CO<sub>2</sub> is unable to penetrate and carry on the reaction [Equation 2] (Lees, 1992; Ishida and Maekawa, 2000; Borrows, 2006a, 2006b). Hence, free Ca(OH)<sub>2</sub> remains within the structure of set concrete.

If rain or seepage water from other sources penetrates into microscopic cracks, gel pores and air voids in set concrete it will readily carry the Ca(OH)<sub>2</sub> in solution to the edge of the concrete. When this leachate comes into contact with air containing CO<sub>2</sub> the Equation [2] reaction takes place and precipitates calcium carbonate, to create calthemite straws.

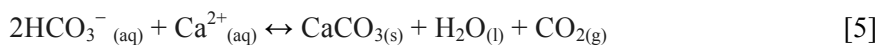
To complicate the issue, there is a period when the presence of potassium and sodium in new concrete will support a higher solution alkalinity of about pH 13.2 – 13.4 (Liu, and He, 1998; Ekström, 2001). The hyperalkaline solution becomes supersaturated with Ca<sup>2+</sup> (Liu, and He, 1998) compared to a mildly alkaline solution. When the hyperalkaline leachate emerges from beneath the concrete structure, CO<sub>2</sub> is absorbed into the solution from the atmosphere [Equation 3] resulting in the dominant ion CO<sub>3</sub><sup>2-</sup> reacting with Ca<sup>2+</sup> to precipitate CaCO<sub>3</sub> (Macleod *et al.*, 1991; Maekawa, *et al.*, 2009). [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. (Ekström, 2001). While the pH steadily drops further, the Ca(OH)<sub>2</sub> content starts to rise and Equation [2] becomes more active (Ekström, 2001). Below pH 10.3, the dominant carbonate species will be HCO<sub>3</sub><sup>-</sup> ion [Fig.4] (Pourbaix, 1974; Maekawa *et al.*, 2009; Lichtfouse *et al.*, 2012; Newton *et al.*, 2015) and Equation [2] will become dominant in the deposition of CaCO<sub>3</sub> calthemites.

As time passes, the available Ca(OH)<sub>2</sub> will leach from the cement paste along the seepage path and the pH will fall even further. If the pH falls below approximately pH 9 carbonic acid (H<sub>2</sub>CO<sub>3</sub>) will start to appear (Maekawa *et al.*, 2009; Hagelia, 2011) and the chemical reaction will change to a similar process to that which occurs in limestone caves. This transition can be facilitated within old concrete when meteoric water or CO<sub>2</sub>-rich groundwater forms H<sub>2</sub>CO<sub>3</sub>, which seeps through old solution paths to dissolve CaCO<sub>3</sub> from its structure. Thin-layer sprayed concrete, such as that used for rock support in tunnels, appears to be more susceptible (Hagelia, 2011). The weakly alkaline leachate has a low Ca<sup>2+</sup>-carrying capacity (compared to hyperalkaline leachate) (Newton *et al.*, 2015) and CaCO<sub>3</sub> deposition occurs under concrete structures when CO<sub>2</sub> is degassed from solution [Equation 5] (Macleod *et al.*, 1990). Calthemites “known to have undergone such a further evolution and morphological change are those found in the cellars of the Urbino castle (built 1470–75), central Italy” (Hill and Forti, 1997, p.225) and evaporation of solution might aid CO<sub>2</sub> degassing.

The chemistry dealing with the creation and presence of H<sub>2</sub>CO<sub>3</sub> and 2HCO<sub>3</sub><sup>-</sup> in leachate is well documented by Ishida and Maekawa, (2000); Hartland *et al.*, (2009) and Newton *et al.*, (2015).



However, there is no timescale indicated and it could well be that the timespan required to leach all the Ca(OH)<sub>2</sub> from the seepage path is tens or hundreds of years. Factors that can play a part in the overall process and timescale include: supply of leachate, concrete porosity, seepage path and flow rate. Also, leachate can find alternative paths through new cracks or micro-pores in old concrete, to unlock new

sources of  $\text{Ca}(\text{OH})_2$ , thus reverting the dominant reaction back to Equation [2].

Within a concrete structure there will be a water pressure gradient and the leaching process creates calcium concentration gradients in layers between the concrete surface and its core. These layers affect the chemical equilibrium of the hydration products calcium hydroxide, calcium aluminium hydrates and calcium aluminium iron hydrate. It is a very complex process due to the many chemical reactions involved.

Calcium hydroxide is about 200 times more soluble than calcite in water (Sefton 1988), and therefore facilitates the rapid growth of calthemite straws compared to normal speleothem straws in limestone caves.

### pH of leachate at study site

Maekawa *et al.* (2009, p.230) demonstrate that calculations can determine the relationship between the pH value in solution and the ratio of carbonic acid, bicarbonate ion and carbonate ion. In the high pH range, carbonate ions are dominant, whereas bicarbonate ions increase under lower pH conditions. [Fig.4]. The graph produced by Maekawa *et al.* provides an excellent visual reference to which chemical reaction(s) are likely to occur across a range of drip solution pH values.

At the study site, drips on approximately 10 straws were measured on a regular basis with ‘universal pH indicator’ (this included some straws that were not being monitored for length) and all remained at pH 13 throughout the study. Additional checks of rainwater in the roof guttering returned a value of pH 7 (i.e. neutral).

Therefore, consistent with the findings of Macleod *et al.* (1990), Hartland *et al.* (2010) and Newton *et al.* (2015) it can reasonably be assumed that the reaction described by Equation [4] is creating the calthemites at the study site.

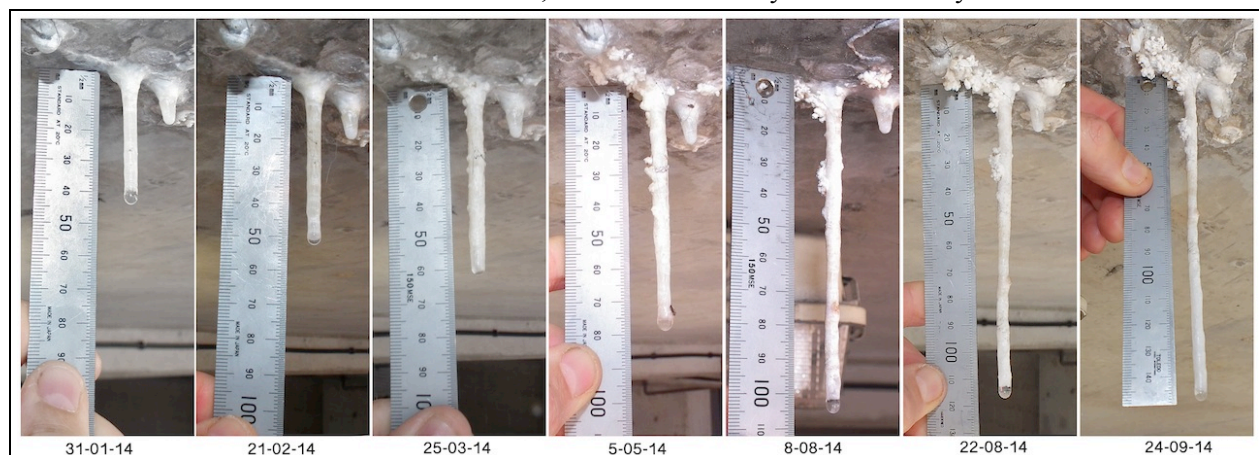
### Straws under study

Over a period of 10 months the growth rates of four straw stalactites were documented. The growth rates of the fastest and slowest ‘active’ straws (with a constant supply of seepage solution), varied considerably. A plot of the straw length in millimetres versus time in elapsed days is shown in Figure 7.

Straw stalactite No.1, [Fig.5] had the highest calcite deposition rate and grew consistently in length throughout the study. On average this straw grew at approximately one millimetre per day with a maximum of 2mm per day. On the 237th day of the study, it was noted that the end of straw No.1 had been broken off – cause unknown. Hence the growth rate for this straw had to be recommenced at the following reading date and then continued until the end of the study.

Two of the straws (No.2 and No.3) had periods of sporadic activity before drying up completely just 2 months into the study, and no growth was recorded thereafter. Other straws began growing at a fast rate just a few centimetres away from these now dormant straws. [Figs 6a and 6b]. This suggests that the solution originally flowing to No.2 and No.3 had found another path to escape from the concrete.

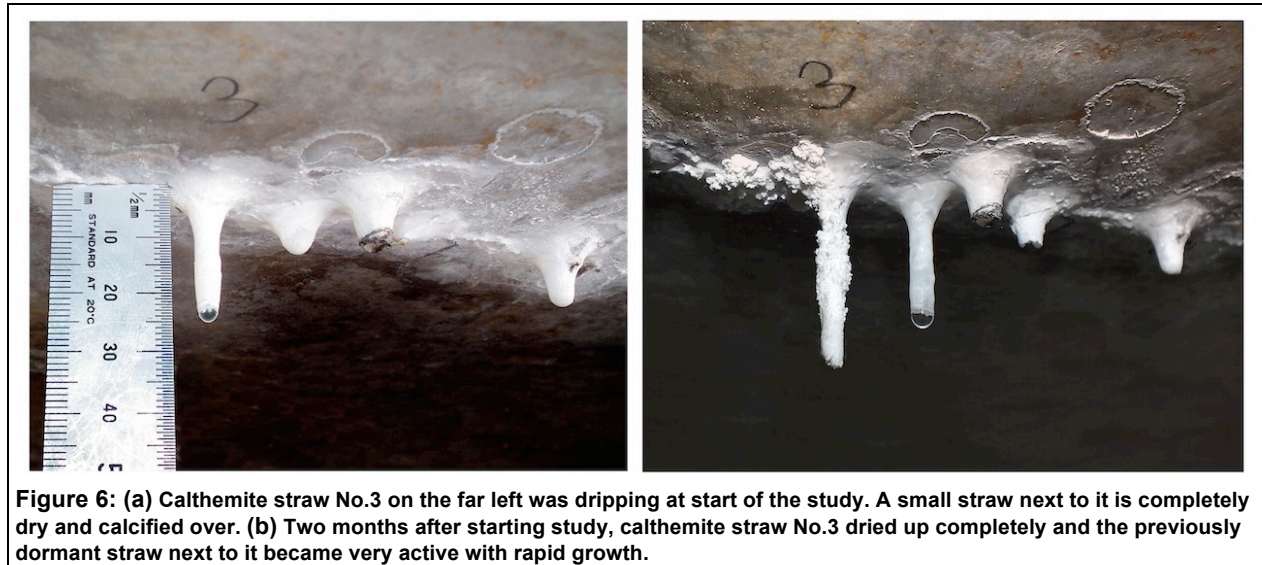
Straw No.4 began growing about the time of starting the study. During the third month into the study it was decided to record data from this straw, which consistently remained very active. This straw was



**Figure 5:** 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.

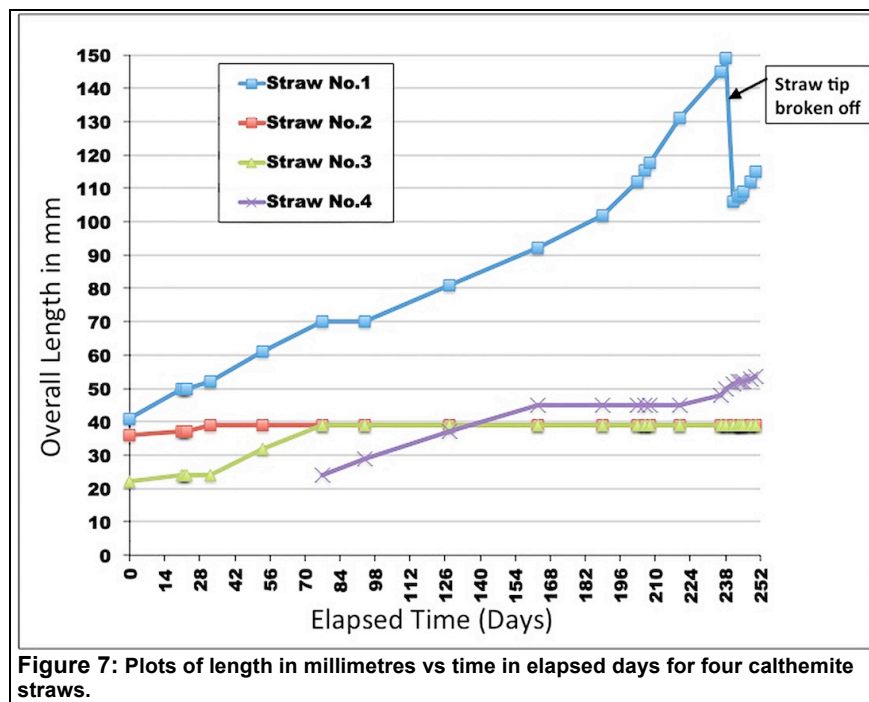


particularly useful in identifying the limitation of growth rate, associated with fast dripping seepage solution.



### Growth and drip rates

Analysis of the data indicates that almost no deposition occurs at the straw's tip when the solution drip rate is approximately one or more drops per minute i.e. fast drip rate. When the drip rate was slower than one drip per minute deposition began to occur at the straw tip, resulting in increased length. For drip rates of one every 8 to 17 minutes the growth rate was generally more than 1mm per day. The most rapid growth rate of 2mm per day occurred when the drip rate was approximately one drop every 11 minutes. It

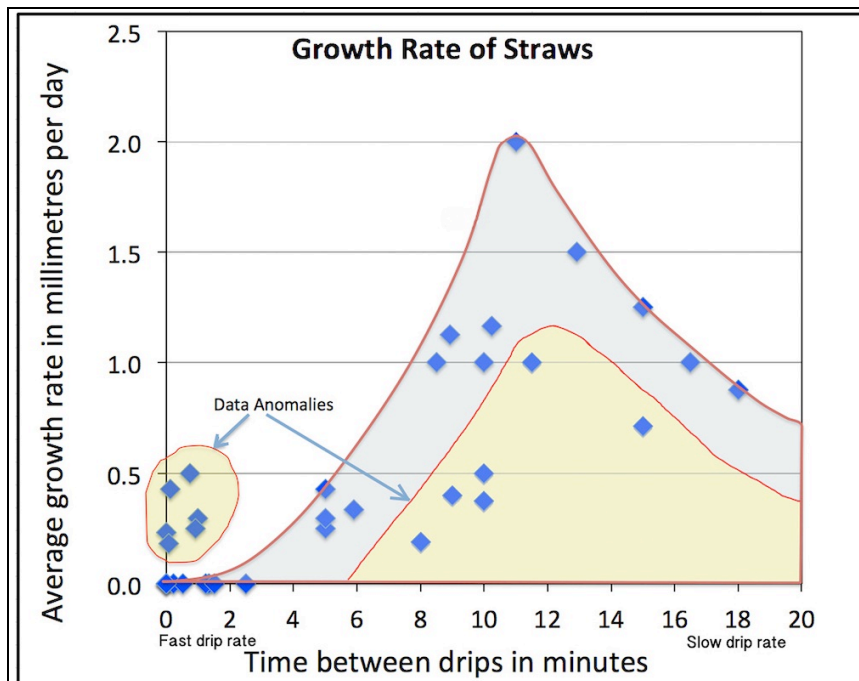


is conjectured that at the study site when the drip rate was slower than about 30 minutes between drips, deposition possibly aided by solution evaporation, causes the straw tip to calcify over, preventing further growth. Certainly a total lack of solution supply causes the straw to dry up and stop growing.

Growth rates of the studied straws were taken to be the increase in length between data collection sessions divided by the number of days elapsed. The drip rate of each straw was timed when its length measurement was recorded. Drip rates might

have varied between measurement sessions but, unfortunately, continuous monitoring was beyond the scope of the study.

The relationship between the growth rate of straws and their drip rate is shown in Figure 8. Closer analysis of data points outside the bell curve, labelled as 'data anomalies', revealed that these growth rates were during periods when the drip rates had changed dramatically from a slow drip rate at the previous reading to a fast drip rate at the time of data recording. The reverse is the case for the data points in the shaded section beneath the bell-shaped curve. Because there were large drip rate variations influencing each data point labelled as 'data anomaly', they should not be considered as a true representation of growth rate relating to drip rate (Fig.8).



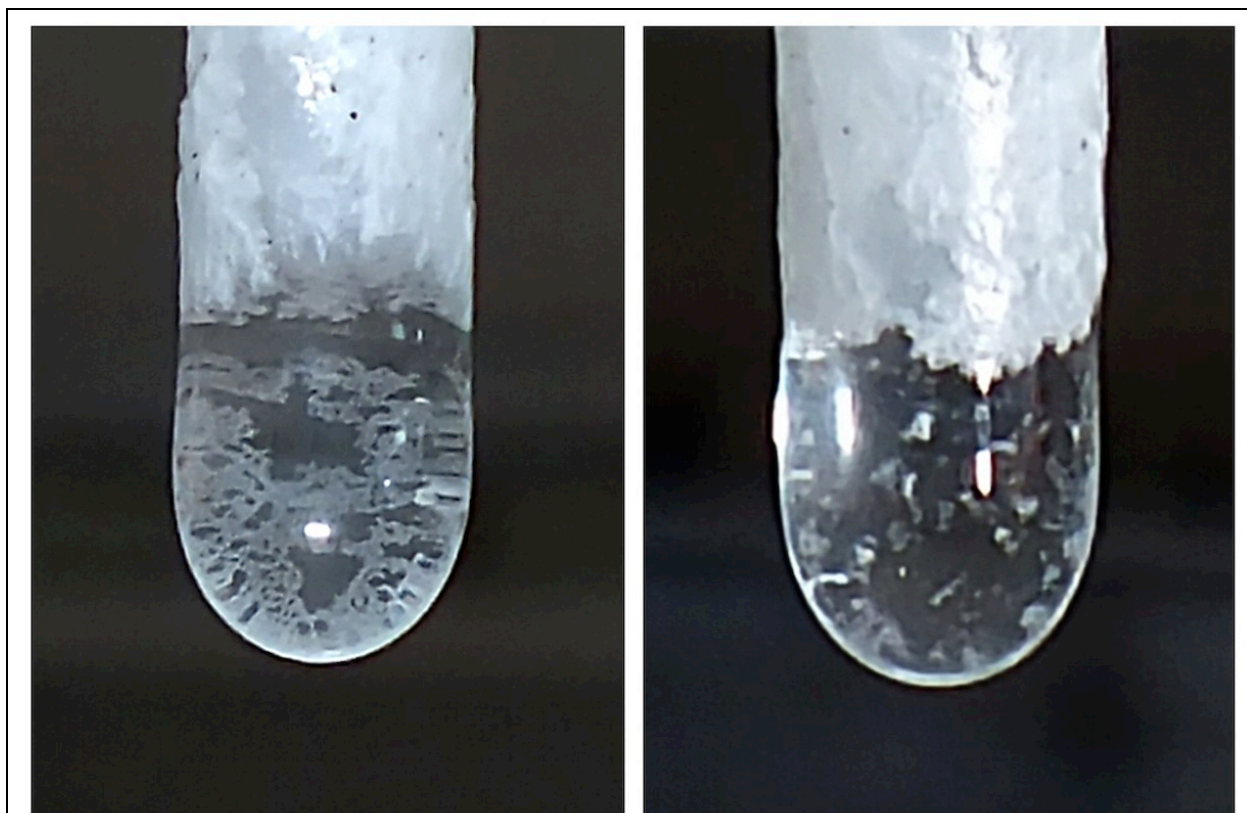
**Figure 8:** Plot of calthemite straw average growth rates between periods of data recording, measured in mm/day vs solution drip rate in minutes. The 'Data Anomalies', are measurements recorded in a period when the drip rate changed dramatically between recordings.

## Mechanism for calcite deposition as a straw

Many factors influence the porosity and cracking of concrete, including water to cement ratio, mineral additions and curing history (Ekström, 2001; Khokhar, 2010). The driving mechanisms for water flow through the concrete matrix are surface tension, capillary forces and gravitational forces, which combine to pull the solution through the concrete cracks and micro pores (Macleod *et al.*, 1990; Mackawa, *et al.*, 2009).

As water travels through the concrete structure, it leaches out  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions. When the first mineral-

laden drop of water comes into contact with the atmosphere, it absorbs  $\text{CO}_2$  resulting in deposition of  $\text{CaCO}_3$  in a thin ring around the base of the drip where it is attached to the supporting structure. Each subsequent drop deposits more  $\text{CaCO}_3$  onto the previously deposited ring of crystals. Eventually, these rings form a very narrow (commonly about 4mm), hollow tube, commonly referred to as a "straw"



**Figure 9:** Drip with calcite rafts lattice work formed on a very slow-dripping calthemite straw ( $\approx >12$  minutes between drops) on a day with no wind or vehicle movement.

**Figure 10:** Calcite rafts are broken up and spinning around the drip surface, influenced by air movement

stalactite.

On straw No.1, microscopic  $\text{CaCO}_3$  rafts were continually forming on the surface of the suspended solution drop (Figs 9 and 10). A long period between drips ( $\geq 5$  minutes) was sufficient time for absorbed  $\text{CO}_2$  to cause precipitation of  $\text{CaCO}_3$  from solution and form rafts visible to the naked eye (up to 0.5mm across).

During periods of almost no air movement when the drip rate was very slow ( $>12$  minutes between drips),  $\text{CaCO}_3$  rafts were seen to create a latticework pattern over the drop surface (Fig.9). A random injection of water from the straw tube would shatter this lattice work into small rafts (Fig.10). The occurrence of rafts was also reported by Ver Steeg (1932). Any additional pulse of water into the drop caused rafts to be thrust upwards, spinning towards the straw's rim where they occasionally attached to the straw's outer surface. Often some of these minute rafts would remain attached to the straw's rim when the drop eventually fell.

On days with greater air movement resulting from vehicle motion and/or atmospheric wind, calcite rafts on straw No.1, would spin turbulently around the surface of the solution drop. The spinning direction of rafts could change in seconds from horizontally around the drop to an almost vertical orbit of the drop or a total direction reversal. A 34-second video was recorded of  $\text{CaCO}_3$  rafts whirling around the surface of the straw drop. On occasions violent spinning would shear some rafts from the drop's surface water tension and push them up onto the outer surface of the straw where rafts would stay attached in a film of solution. This could partly explain some bumps and irregularities in diameter down the length of straws. The sheared-off micro rafts allowed a film of solution to be drawn several millimetres further up the outside of the straw and complete the cementing of micro rafts to the straw's outer surface. Similar observations have not been recorded in any other paper obtained during literature searches.

A short video of the  $\text{CaCO}_3$  rafts spinning on the drip surface can be viewed on Youtube at [https://www.youtube.com/watch?v=G-gm\\_kN5Xes](https://www.youtube.com/watch?v=G-gm_kN5Xes)

Allison (1923, pp.108–109) studied straws growing from a concreted section of a coal mine roof in Pennsylvania and noted that: *"The increase in diameter is effected partly by the creeping of the lime solution up over the rim of the stalactite and partly by the lime solution percolating from the inside of the tube outward through small channels in the stalactite wall"*. There is no doubt that this mechanism is also occurring on the calthemite straws growing at the study site, as the active straws retained a thin film of moisture over much of their outer surface.



**Figure 11:** Drip on a fast-dripping straw (No.4) within the study site, showing no sign of calcite rafts. Typical for drip rates of one drip per minute or faster.

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At the study site the solution drop diameter averaged 4 – 4.3mm. Straws with slower drip rates of approximately one drop every 15 minutes or more had a slightly larger straw drop diameter (up to 5mm diameter) and created a corresponding diameter straw (Fig.12). This might be due to the increased time for precipitation to occur when the drop is growing slowly in size and the diameter is slightly larger when the solution drop is partly formed, hence surface tension has less weight to support. Once the drop grows too heavy for the surface tension to hold its weight, it begins to lengthen and stretch (reducing in diameter at the attachment point on the end of the straw) until the weight is too much for the surface tension to support and the drip falls (Fig.11). Consequently, it is the drop diameter that determines the diameter of the straw (Ver Steeg, 1932), regardless of the



length of the stalactite.

Studying stalactites growing from a bridge containing concrete, Ver Steeg (1932) found that the growth rates compared closely with those of stalactites growing from concrete in a mine tunnel studied by Allison (1923). From the same study, Ver Steeg (1932) expected the above-ground stalactites to grow more quickly in conditions with lower relative humidity, increased air circulation and higher air temperatures, resulting in more evaporation than is typically experienced underground. However, at the time of their studies, it was not known to the authors that degassing rather than evaporation was the most common mode of speleothem formation and nor were they aware of CO<sub>2</sub> hydroxylation reactions involved

in secondary deposition from concrete. The straw growth data recorded at the Belmont study site, when related to atmospheric temperature and humidity, confirm Ver Steeg's observations that evaporation of solution had minimal influence on the calcite deposition/growth rate at the tip of the straw.

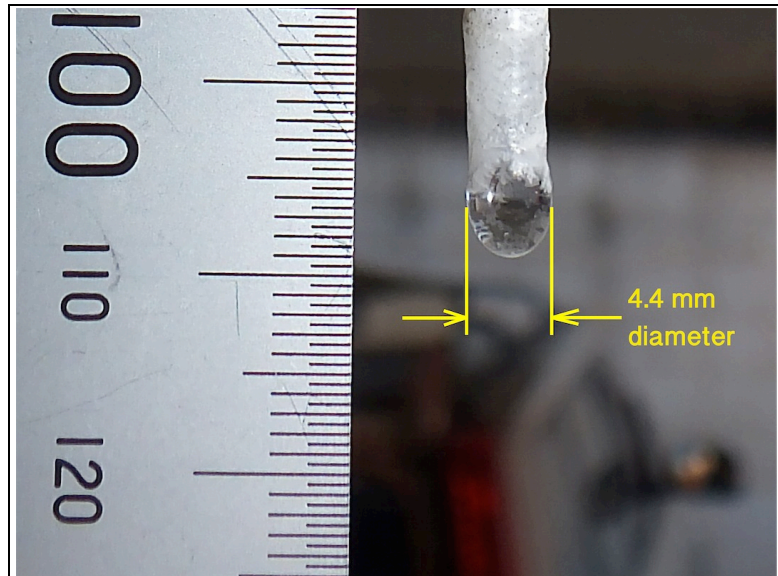
Comparison of macro-photos taken only one day apart showed that carbonate crystal growth was lengthening the straw in addition to attachment of microscopic rafts from the surface of the drop.

On straw No.4 and other fast-dripping straws no rafts were visible to the naked eye or on macro-

photography images (Fig.11). Atmospheric CO<sub>2</sub> could not diffuse quickly enough into the drop for deposition to occur at the straw rim nor to form visible micro rafts. Hence the calcium being transported in solution to the straw tip remained in solution and fell to the ground where deposition occurred as a low profile stalagmite beneath the drip point (Fig.2).

### Calthemites containing other trace elements

Calthemites stained various colours by elements such as iron or copper are commonly observed under man-made concrete structures. Steel bars are used in concrete structures as reinforcing to add tensile strength to concrete. However, if water penetrates the set concrete and changes the pH balance around the reinforcing bars, it may facilitate oxidation of the steel. Any resulting iron oxide expands and cracks the concrete. Also the iron oxide can be leached out with the same solution seepage water that creates calthemites. Hence the predominately white calcium carbonate will be stained orange (Fig.13). Copper pipes passing through or near concrete, while less susceptible to oxidation, can produce a green or blue



**Figure 12: Measuring calthemite straw diameter at the growth rim by photographing a 0.5 mm calibrated engineering rule next to straw. Specific attention is paid to angle and subject distance from camera, to eliminate parallax error. Straw diameter and length can then be measured remotely, from the digital image, without physical contact with the fragile straw rim.**



**Figure 13: Orange-coloured calthemite flowstone containing traces of iron from reinforcing bars within concrete. This example is at the study site.**

copper oxide that discolours calthemites (Fig.14).

## Conclusion

The growth rate of calthemite straws can vary considerably due to a wide range of chemical and physical conditions. The most influential factors are the continuity of leachate solution and drip rate. Evaporation of solution due to atmospheric conditions had no detectable effect on  $\text{CaCO}_3$  deposition when drip rates were more frequent than one every 20 minutes. The formation of  $\text{CaCO}_3$  rafts on the drop surface was found to influence the outside diameter of a calthemite straw when subjected to sufficiently strong air movement.

Calthemites precipitated from hyperalkaline solution can grow much faster than normal cave speleothems. At the study site one straw achieved an average growth rate of 2mm per day, when drips were 11 minutes apart. Too fast a drip rate results in minimal or no growth and too slow a drip rate can cause the straw to calcify over and block up.

Given the number of variables that can effect calcium carbonate deposition, it is impossible to predict the exact age of calthemite straws by measuring their length or the solution drip rate at a particular time.

The solution creating calthemites at the study site is pH 13. This indicates that the predominant chemical reaction creating the calthemites is,  $\text{Ca}^{2+}_{(\text{aq})} + \text{CO}_3^{2-}_{(\text{aq})} \rightarrow \text{CaCO}_{3(\text{s})}$ . Deposition of calcium carbonate occurs when atmospheric  $\text{CO}_2$  diffuses into the drip solution, as opposed to normal cave speleothem chemistry where  $\text{CO}_2$  is degassed from solution.

Whereas they are outside the scope of this study, it can be assumed that straws at other sites may achieve greater deposition rates at a faster drip rate if the atmosphere in contact with the solution contains a higher concentration of  $\text{CO}_2$ . Also, a longer seepage path through concrete may allow leachate to gain more solutes and carry them to the deposition site.

## Acknowledgements

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## References

- Allison, V C, 1923. The growth of stalagmites and stalactites. *Journal of Geology*, Vol.31, 106–125.
- Borrows, P, 2007. Chemistry Trails. *Education in Chemistry*. Vol.44(5), p.134 [Cambridge, UK: The Royal Society of Chemistry.]
- Borrows, P, 2006a. Chemistry Outdoors. *School Science Review – Outdoor Science*, Vol.87(320), 24–25. [Hartfield, Herts, UK: Association of Science Education.]
- Borrows, P, 2006b. Concrete Chemistry. Letters. [Cambridge, UK: Royal Society of Chemistry.] <http://www.rsc.org/education/eic/issues/2006Nov/Letters.asp>



**Figure 14: Aqua-coloured calthemite formations containing traces of copper, deposited in conjunction with calcite. Example at an underground carpark, 0.5km from the study site.**

- Ekström, T, 2001. *Leaching of concrete: Experiments and modelling*. (Report TVBM-3090). Lund Institute of Technology Division of Building Materials. Retrieved from <http://lup.lub.lu.se/luur/download?func=downloadFile&recordId=1273303fileId=1766469>.
- 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.
- Hagelia, P, 2011. Deterioration Mechanisms and Durability of Sprayed Concrete for Rock Support in Tunnels. Doctoral thesis presented at Technische Universiteit Delft, Netherlands.
- Hill, C A, and Forti, P, 1986, 1997. *Cave Minerals of the World*, 1<sup>st</sup> & 2<sup>nd</sup> editions. [Huntsville, Alabama: National Speleological Society Inc.]
- Ho, D W S and Lewis, R K, 1987. Carbonation of concrete and its prediction. *Cement and Concrete Research*, Vol.17, 489–504.
- Ishida, T and Maekawa, K, 2000. “Modeling of pH profile in pore water based on mass transport and chemical equilibrium theory”. Translation from *Proceedings of Japan Society of Civil Engineers (JSCE)*, No.648/Vol.47.
- Khokhar, A, 2010. “Optimisation of concrete mix design with high content of mineral additions: Effect on microstructure, hydration and shrinkage”. Cotutelle PhD Thesis, Ecole Centrale de Nantes, (France) and the Free University of Brussels (Belgium).
- Lees, T P, 1992. *Deterioration Mechanisms*. 10–36 [Chapter 2] in Mays, G C (Ed.), *Durability of Concrete Structures Investigation, repair, protection*. [E & FN Spon Press.] Print ISBN: 978-0-419-15620-8.
- Lichtfouse, E, Schwarzbauer, J and Robert, D, 2012. *Environmental Chemistry for a Sustainable World*. Vol. 2: *Remediation of Air and Water Pollution*. [Springer.] 562pp.
- Liu, Z and He, D, 1998. Special speleothems in cement-grouting tunnels and their implications of the atmospheric CO<sub>2</sub> sink. *Environmental Geology*, Vol.35(4), 258–262.
- 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.
- Maekawa, K, Ishida, T and Kishi, T, 2009. *Multi-Scale Modeling of Structural Concrete*. [Oxford, UK: Taylor and Francis.]
- 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.
- Moore, G W, 1952. Speleothems – a new cave term. *National Speleological Society News*, Vol.10(6), p.2.
- Papadakis, V G, Vayenas, C G and Fardis, M N, 1989. A reaction engineering approach to the problem of concrete carbonation. *American Institute of Chemical Engineers Journal*, Vol.35:1639–1650.
- Papadakis, V G, Vayenas, C G, Fardis, M N, 1991. Fundamental modeling and experimental investigation of concrete carbonation. *American Concrete Institute Materials Journal*, Vol.88, 363–373.
- Papadakis, V G, Vayenas, C G, Fardis, M N, 1992. Hydration and carbonation of pozzolanic cements. *American Concrete Institute Materials Journal*, Vol.89(2), 119–130.
- Pourbaix, M, 1974. *Atlas of electrochemical equilibria in aqueous solutions*. 2<sup>nd</sup> English edition. [Houston, TX: National Association of Corrosion Engineers.]
- Sefton, M, 1988. Manmade” speleothems. *South African Speleological Association Bulletin*, Vol.28, 5–7.
- Ver Steeg, K, 1932. An unusual occurrence of stalactites and stalagmites. *The Ohio Journal of Science*, Vol.32(2), 69–83.