Calcite Straw Stalactites Growing From Concrete Structures

Garry K. Smith
Newcastle Hunter Valley Speleological Society

Abstract

The growth rates and corresponding drip rates of four stalactite straws derived from a concrete structure were studied over a ten month period. Factors which influence straw growth, including the chemical reactions and solution pH are examined.

The major influencing factors determining calcite deposition, were identified as the supply continuity of solution and the drip rate. Too fast a drip rate and there was insufficient time for deposition at the tip of the straw, too slow and the straw tip calcifies over or just dried up and stopped growing. A constant drip rate of one drop per eleven minutes produced the fastest growth of two millimetres per day. No detectable growth occurred when the solution drip rate was approximately one per minute or faster.

Minute calcite rafts were observed on the solution drop surface. 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 adding to deposition. Rafts can influence the thickness and irregularities of a straw's outside diameter.

Concrete-derived calcite straw stalactites are essentially the same composition and in many respects mimic the shapes and forms of speleothems in limestone caves, however the chemical reaction which allows calcite to be deposited under concrete structures, is usually very different. The solution pH influences which chemical reaction/s are occurring at a particular time to deposit the calcite. This can also have a bearing on the deposition rate. Of the three main reactions, two rely on absorption of CO_2 from the atmosphere for calcite 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 in very old concrete and is essentially the same as the reaction occurring in limestone caves.

A search of literature failed to find a suitable term encompassing the various concrete or mortar derived secondary deposits growing from man made structures, consisting primarily of calcite. 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 paper the term **'Calthemite'** is used to encompass the various decorations mimicking speleothems, derived from cement or lime used in construction. The reasoning behind the introduction of this term is discussed in this paper.

Introduction

A layperson observing straws growing from a concrete structure could at a glance compare them to those growing in limestone caves. Given the right conditions, calthemite straws growing from concrete can grow at amazing rates, many hundreds of times faster than limestone cave straws (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, atmospheric humidity, temperature, atmospheric CO_2 concentration, solution pH and chemical reactions.

There are many chemical reactions occurring within curing concrete and later in its degradation. For the purpose of this study the latter reactions relating to the secondary deposition of calcite are considered. A number of previously published papers look at growth rates of concrete derived straws, such as Allison (1923) and Ver Steeg (1932), whom may have incorrectly concluded that calcite deposition at their study sites, was due to degassing. Later literature by Diamond (1976), Macleod et al. (1990), Borrows (2006a; 2007) and Maekawa et al. (2009), look more closely at the chemistry of concrete and indicate there may be more than one chemical reaction occurring at one time. These later authors conclude that the chemical reactions causing deposition of calcite is due to absorption of CO_2 into solution at the site of deposition.

Given my extensive interest in caves and speleothems, I was fascinated by the appearance of calcite straws at a nearby shopping centre. This interest quickly grew into a quest to know more. What are concrete derived deposits called? What growth rate is possible for a straw? What chemical reaction is occurring when concrete derived straws are created? What determines or influences concrete derived straw growth rate?

A new concrete building constructed in Belmont NSW, during 2008 (now 6 years old) included a partly underground carpark with supermarket area above. Straw stalactites began growing within months of the building being completed. Solution water originates from a minute hole in poorly constructed roof guttering, which trapped rainwater and leaked a constant flow onto the concrete structure. The slow trickle of water then found its way into the concrete structure, following micro cracks and voids, picking up calcium along its path until it emerged from cracks in the carpark ceiling. These drip sites are where the stalactite straws are growing.

Although the stalactites were in a difficult physical location to undertake measurements, due to vehicle movements, the constant supply of solution water all year round, made it ideal for a study of growth rates [Fig. 1]. The aim was to identify the main influencing factors determining growth rate of calthemite straws and identify which chemical reaction is responsible for the deposition of calcite at the study site.

Methodology

A metal ruler was used to measure the length of the stalactites and a digital photo taken of each measurement for verification at a later date. The time of day, temperature, humidity, solution pH and drip rate were all recorded. This was quite time consuming when measuring a very slow drip rate. Temperature and humidity were recorded from a meteorological bureau weather app, which had hourly readings for Belmont NSW. This was found to be consistently within a couple of degrees of a hand held thermometer.

The wind direction and strength was not recorded as the underside of the building was generally sheltered from southerly and easterly prevailing breezes, however vehicle movements did create significant air movement past the straws.

Figure 1. Location of straw stalactite on roof above supermarket carpark.

Figure 2. Measuring stalactites with an engineering metal ruler graduated in 0.5mm increments.

The straw's length and diameter were measure at the very tip by photographing a precision metal engineering ruler (calibrated in 0.5mm increments) next to the straw and at the same distance from the camera lens to eliminate parallax error. The digital photo was then enlarged to measure the exact outside diameter of the straw tip to within ± 0.15mm, using the ruler scale (Figures 2 & 9). This method allowed measurement of the fragile straw without physical contact.

Drip solution pH at each straw tip, was measured using 'universal pH indicator' paper (± 0.5 pH units). The chemistry of the solution water was not analysed nor the degree of calcite 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 pH7 - neutral.

To determine if vehicle exhaust was significantly aiding calcite deposition, the atmosphere at the study site was tested for CO_2 with a Dräger tube meter. The colorimetric tubes used, could measure a CO_2 range between 0.1 to 1.2 % by volume. Measured air samples sucked through the tubes during several occasions did not detect a measurable quantity of CO_2 despite significant vehicle movements.

Chemical reactions creating 'Calthemites' formations on concrete structures

Calthemites in the majority of cases, are created by different chemical reactions than those forming speleothems in limestone caves. A simplistic explanation of the different chemical process occurring to deposit calcite is:

- Speleothems are created when solution water degasses CO_2, resulting in calcite deposition,
- Calthemites are created when atmospheric CO_2 is absorbed into solution water, resulting in calcite deposition.

Before looking at the calthemite chemical reactions, it is prudent to delve a little into what makes up concrete.

The key component of concrete is cement. The mineral composition of ordinary Portland cement paste (cement + water) is roughly 70% C-S-H* gels, 20% portlandite ($Ca(OH)_2$), 7% aluminates and sulpho-aluminates and 3% unhydrated material (Diamond, 1976). There are a number of chemical reactions involved in the hydration of the calcium silicate, aluminate, and aluminoferrite minerals that cause cement mixed with water to go hard or set (also referred to as cure) (Borrows, 2006a, 2007; Macleod, et al., 1990). For the purposes of this paper only the calcium reactions are detailed. Several chemical reactions may be occurring simultaneously at a specific location and the solution pH, (by definition, pH is a measure of the hydrogen ion concentration in solution) has an influence on which reaction/s are occurring (Maekawa, et al., 2009). Refer to [Fig. 3]

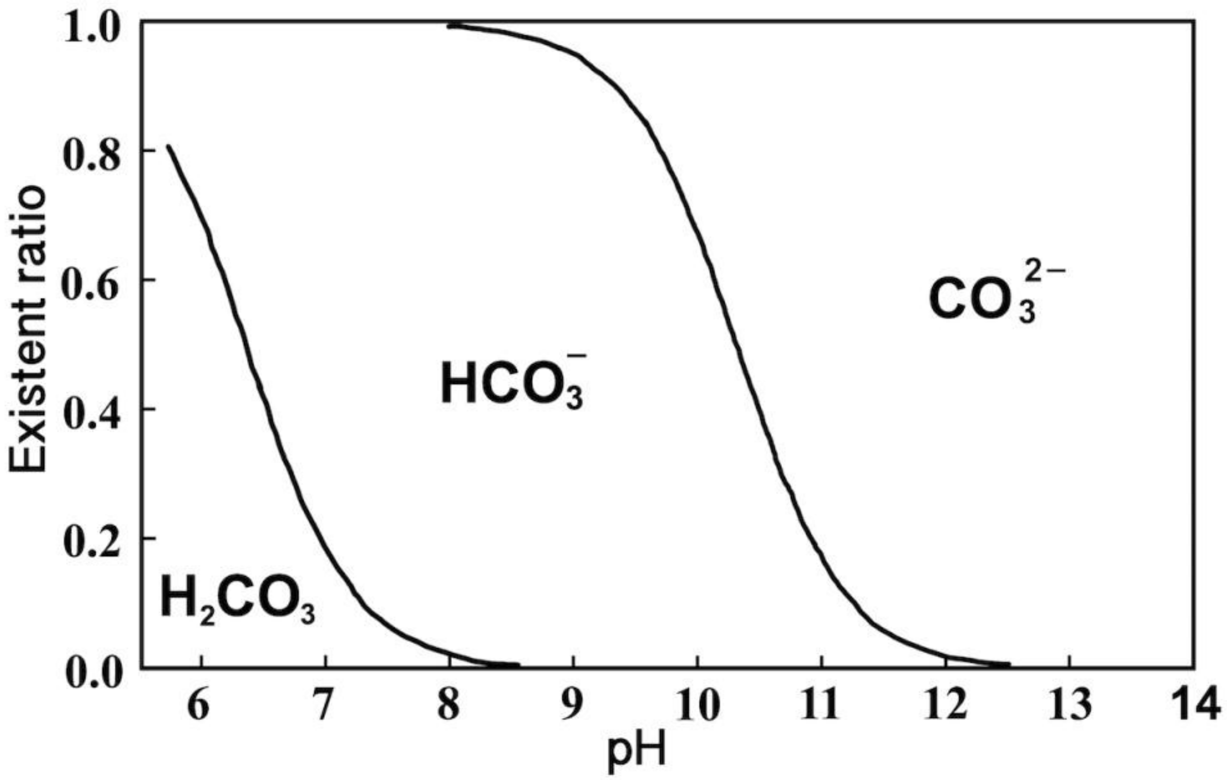

Figure 3. Relationship between equilibrium of Carbonic Acid and pH in solution. Carbonic Acid includes both carbonates and bicarbonates. Graph after Maekawa et al. 2009.

To make concrete, aggregate and sand (which play no part in the chemical reaction), is mixed with cement. When water is added to the mix, it readily reacts with the calcium oxide in the cement to form $Ca(OH)_2$ (calcium hydroxide), which is the 20% portlandite component of cement paste [Eqn. 1]. The chemical reaction is:

$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$ [1]**

Calcium hydroxide solution (lime water) is alkaline, typically pH 7-12. (Maekawa, et. al. 2009). Any carbon dioxide (CO_2) trapped in the mix will readily react with the calcium hydroxide solution to precipitate calcium carbonate ($CaCO_3$) within the concrete structure [Eqn.2]. This overall reaction has been generally termed as “concrete carbonation” (Ho and Lewis, 1987; Papadakis, et. al., 1989, 1991, 1992). The chemical reaction is:

$Ca(OH)_2(aq) + CO_2\ (g) \rightarrow CaCO_3(s) + H_2O(l)$ [2]

Equation [2] is the overall reaction, however in practice the process is more complex and better described by equations 2a and 2b.

$Ca(OH)_2(aq) + CO_2\ (g) \rightarrow Ca(HCO_3)_2(aq) + H_2O(l)$ [2a]

$Ca(HCO_3)_2(aq) + H_2O(l) + CO_2\ (g) \rightarrow CaCO_3(s) + H_2O(l)$ [2b]

Reaction [2] occurs within the concrete matrix until all the available free CO_2 in the mixture is used up. Concrete exposed to the atmosphere containing more CO_2 will allow the 2nd reaction to continue to a shallow depth (often just a few millimetres) from the surface after which atmospheric CO_2 is unable to penetrate and carry on reaction [Eqn. 2] (Ishida and Maekawa, 2000; Borrows, 2006a;). Hence, in set concrete there remains some free calcium hydroxide within its structure.

If rain or other seepage water can penetrate set concrete micro cracks or micropores it will readily carry the calcium hydroxide solution to the edge of the concrete. When it comes into contact with air the chemical reaction [Eqn.2] will takes place. Carbon dioxide in the air reacts with the calcium hydroxide solution and precipitates calcium carbonate to create calthemite straws**.**

Calcium hydroxide is about 200 times more soluble in water than calcite (Sefton 1988), which explains why solution pH is so high and calthemite straws grow faster than speleothem straws in limestone caves.

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, (Ekström, 2001). As a consequence the dominant ion present in new concrete will be CO_3^{2-} (Maekawa, et al., 2009), and the chemical reaction [Eqn. 3] is most likely occurring. The source of the Ca^{2+} being the calcium component of the C-S-H* cement paste gels.

$Ca^{2+}(aq) + CO_3^{2-}\ (aq) \rightarrow CaCO_3(s)$ [3]

It is highly likely that reaction [Eqn. 3] is creating the calthemites at Belmont as the solution drops on the straws remained at pH13 throughout the study.

When the content of potassium and sodium starts to decline in the solution water, the pH falls to about 12.5, while the $Ca(OH)_2$ content starts to rise as Equation [2] becomes more active (Ekström, T, 2001). When the solution pH falls below pH 10, the dominant carbonate species will be HCO_3^- ion [Refer to Fig.3] (Pourbaix, 1974; Maekawa et al., 2009) and Equation [2] will become dominant in the deposition of calcite to create calthemites. As time passes, the available calcium hydroxide will gradually leach from the cement paste and the pH will fall even further. Below approximately pH 6.5, $H_2CO_3^-$ becomes the dominant species (Maekawa, et. al., 2009), and reaction [Eqn. 4] is mainly occurring

---

Foot note

*In cement chemistry a shorthand notation is used to represent complex compounds, e.g. C, calcium oxide; S, silica; H, hydrate; A, alumina. ** (aq) denotes a species in aqueous solution.

Thus solution water emerging from stalactites growing on concrete structures as a result of reaction [Eqn. 4] is very similar to the classic degassing reaction creating speleothems in caves [Eqn. 6]. However, there is no timescale indicated and it could well be that the timespan required to leach all the $Ca(OH)_2$ from the seepage path is over tens or hundreds of years. As previously mentioned there are many factors which play a part in the overall process including: rainfall, porosity of the concrete, rate of seepage, etc. Given that if the solution water found alternative paths through new cracks or micro pores in old concrete, then this could unlock new sources of $Ca(OH)_2$, thus reverting the dominant reaction back to Equation [2].

$2HCO_3^-(aq) + Ca^{2+}(aq) \rightarrow CaCO_3(s) + H_2O(l) + CO_2(g)$ [4]

At the study site, atmospheric CO_2 is ≈0.04% where the rainwater collects in the building roof gutter. It diffuses into the rainwater (to form a weak carbonic acid) with no additional CO_2 from other sources. For reaction [4] to occur at the study site, this weak carbonic acid solution would have to enter the concrete and slowly dissolve calcium from its structure. Given the low calcium ion (Ca^{2+}) carrying capacity of this solution, it is highly unlikely that equation [4] reaction is involved in calthemite deposition at the present study site. An additional check on rainwater at the study site returned a value of pH 7 (i.e. neutral).

As previously mentioned, properly laid concrete and mortar are not very porous and the carbonation reaction [2] occurs mainly in the surface layers often to just a few millimetres deep. Borrows (2006a and 2006b) describes a very simple test using phenolphthalein solution (a pH indicator) to determine the depth of the carbonation layer in freshly broken old concrete, which can be used to determine the age of concrete.

Bear in mind that the strength of the concrete, 'cement to water ratio' and the compaction when being laid down, all play a part in the overall porosity of cured concrete (Lees, 1992). Capillary porosity, gel pores, air voids and micro cracks may allow some water seepage through the concrete structure to facilitate the movement of calcium hydroxide to the concrete surface, and subsequent deposition of calcite.

All the chemical reactions involving calcium are reversible and dependent on the dominant carbonate species, availability of water and pH, so at any one time there may be several reactions occurring at a greater or lesser extent and all of the above mentioned reactions are reversible. 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.

As a comparison, the insert text box detail the chemical reactions [Eqns. 5 and 6] which create speleothems in limestone and other carbonate rock caves.

The chemical reaction which creates speleothems in caves.

Limestone cave speleothems are created by a different chemical reaction than that which creates concrete derived straws and other calthomite decorations.

Rainwater percolating through surface soil, absorbs carbon dioxide and becomes slightly acidic (carbonic acid). This weak acid is able to dissolve calcite from the carbonate bedrock (e.g. limestone or marble) and transport it in solution as calcium bicarbonate. The chemical formula for this reaction is:

$CaCO_3(s) + H_2O(l) + CO_2(aq) \rightarrow Ca(HCO_3)_2(aq)$ [5]

This solution travels through the voids in the bedrock until it reaches an exposed surface. If this is on the cave roof it will begin to create a stalactite straw. When the solution comes into contact with cave air, degassing occurs and CO_2 is released, thus reducing the solutions acidity and calcium carbonate is precipitated out of solution to create speleothems. The chemical reaction is the reverse of that which initially dissolved the Calcium Carbonate into the solution. The reaction is:

$Ca(HCO_3)_2(aq) \rightarrow CaCO_3(s) + H_2O(l) + CO_2(g)$ [6]

The growth rates of stalactites in natural limestone caves has been well documented by repeated measurements in well-known caves. Data show that stalactites in caves never grow much over 2 millimetres a year and may average only a little more than a tenth of a millimetre per year. (Moore and Sullivan. 1997). However, James (2003) says that under ideal condition cave soda straws can grow in the order of centimetres per year.

pH of Solution (Drip Water)

Maekawa et al. (2009) 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, carbonic ions are dominant, whereas carbonic hydroxide ions increase under lower pH conditions”. [Fig. 3]

“Free” carbonic acid is H_2CO_3 but this is really a hypothetical species as carbonic acid is always in aqueous solution, where the pH determines which of the ions (H_2CO_3, HCO_3^-, CO_3^{2-}) is the dominant species. On the far right of Figure [3] the graph shows CO_3^{2-} as the dominant ion at a high solution pH, thus Equation [3] reaction is dominant. The center portion of Figure [3] is HCO_3^-, which indicates Equation [2] reaction is dominant. The lower left is H_2CO_3 indicates Equation [4] reaction is dominant. i.e (At solution pH11 there is approximately 17% HCO_3^-, [Eqn. 2] reaction and 83% CO_3^{2-} [Eqn. 3] reaction)

At the study site, approximately 10 straw drips were measured on a regular basis with ‘universal pH indicator’ (this included some not being monitored for length) and all were pH 13 throughout the study. Hence [Eqn.3] is creating the calthemites at the study site. Note; It is not advisable to have the drip solution come in contact with bare skin as a pH of between 11 and 14 is considered a strong alkaline solution and can cause burns.

A Swedish lab study of leach water found that new concrete produced highly alkaline solutions (pH 13.3) and decreased to about 12.5 after some time. This is because the first leaching removes potassium and sodium, which created the stronger alkaline solution (Ekström, T. 2001).

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.

The straw stalactite No. 1, [Fig. 4] had the best calcite deposition rate and consistently grew in length throughout the study. There were a few periods between measurements, when this stalactite grew an average of 0.714mm/day in a 14 day period and 0.875mm/day in a 16 day period, however 1mm/day growth rate was more common. In one measurement period this straw grew at an average rate 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 re-recommenced at the following reading date, then continued till the end of the study.

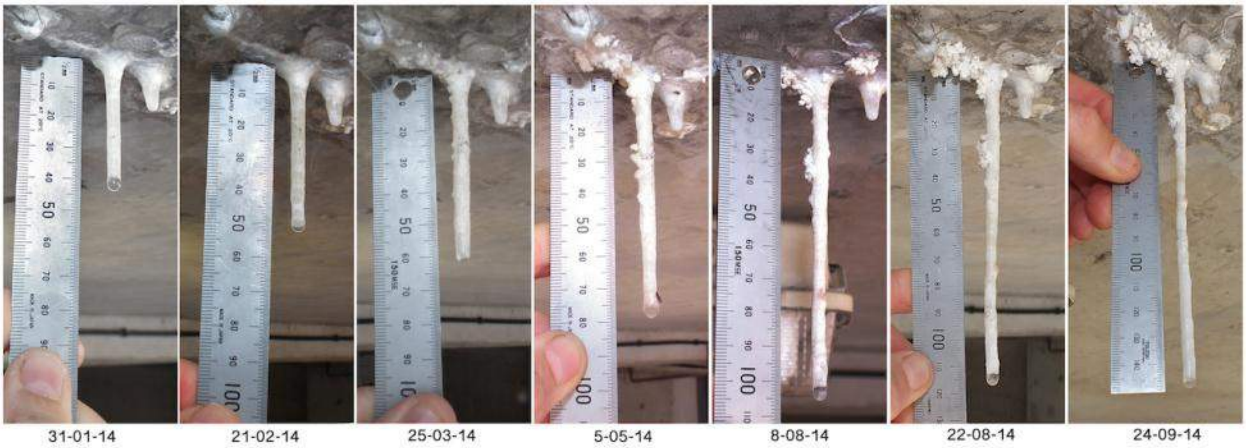

Figure 4. Growth of stalactite straw No.1. The sequence above shows the growth of 104mm in 237 days. When there was only one drip every 11 minutes, this straw grew an incredible 2mm per day. Note that the small straw on the right of straw No.1 has calcified over and not grown at all during measurement period. The date below each image relates to date of measurement recording.

Two of the straws (No.2 and No.3) had periods of sporadic activity before completely drying up just 2 months into the study, and no growth recorded thereafter. Other straws began growing at a fast rate just a few centimetres away from the now dormant straws. [Fig. 5a and 5b]. This indicates that the solution originally flowing to No.2 and No.3 had found another path to escape from the concrete.

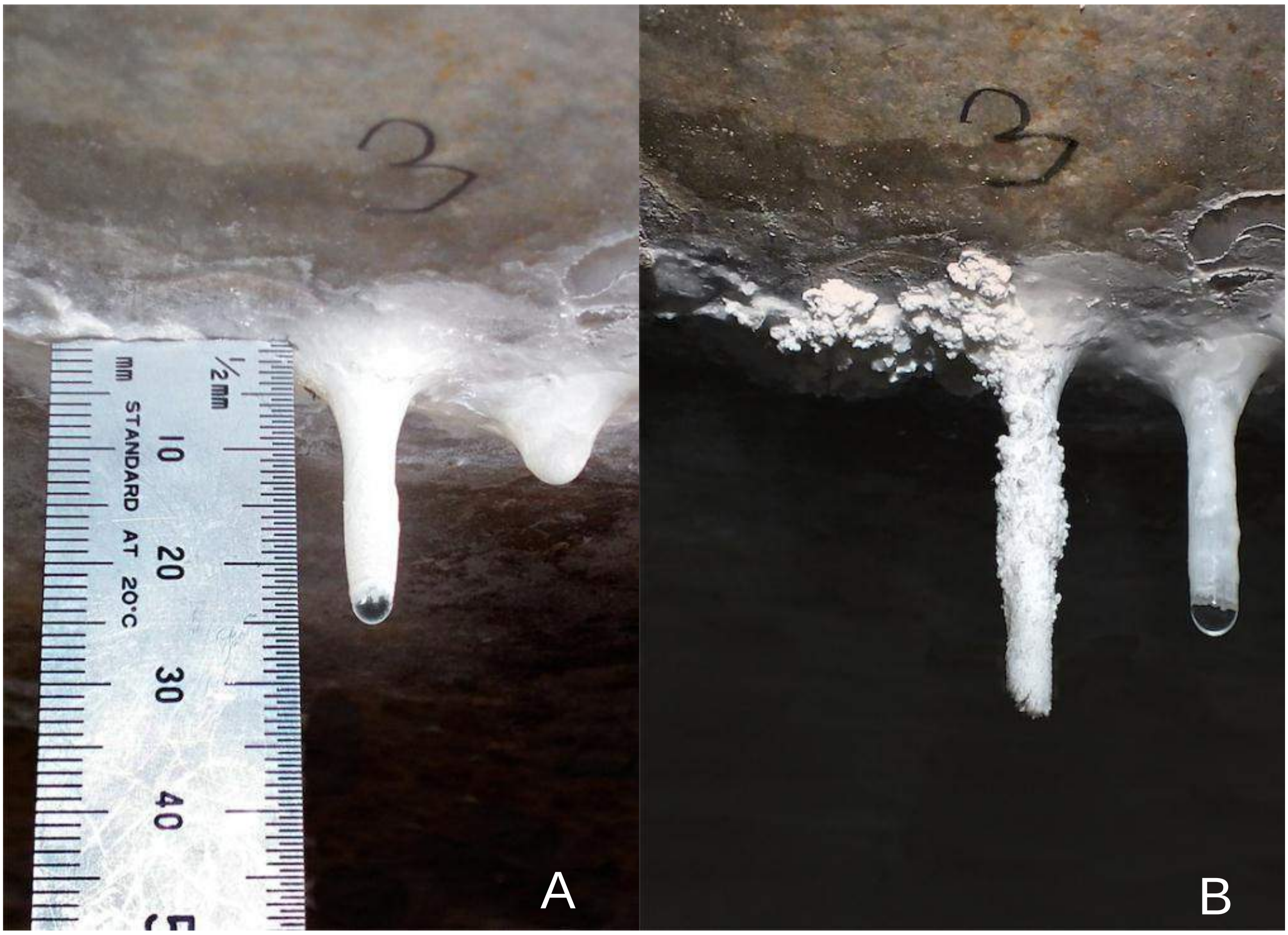

Figure 5a. Straw No.3 on the far left was dripping at the start of the study. The beginning of a small straw next to it is completely dry and calcified over.

Figure 5b. Two months after starting study, straw No.3 has dried up completely and the previously dormant straw next to it has become very active and is **growing** rapidly.

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 has been very useful in identifying the limitation on growth rate, which is associated with fast dripping seepage solution.

Growth and Drip Rates of Straws

Analysis of the data indicate almost no deposition occurs at the straw's tip when solution drip rate is approximately one or more drops per minute.

When the drip rate was slower than one drip per minute, deposition begins to occur at the straw tip and an increase in length resulted. For drip rates between 8 to 17 minutes, the corresponding growth rates was generally over 1mm per day. [Fig. 6]

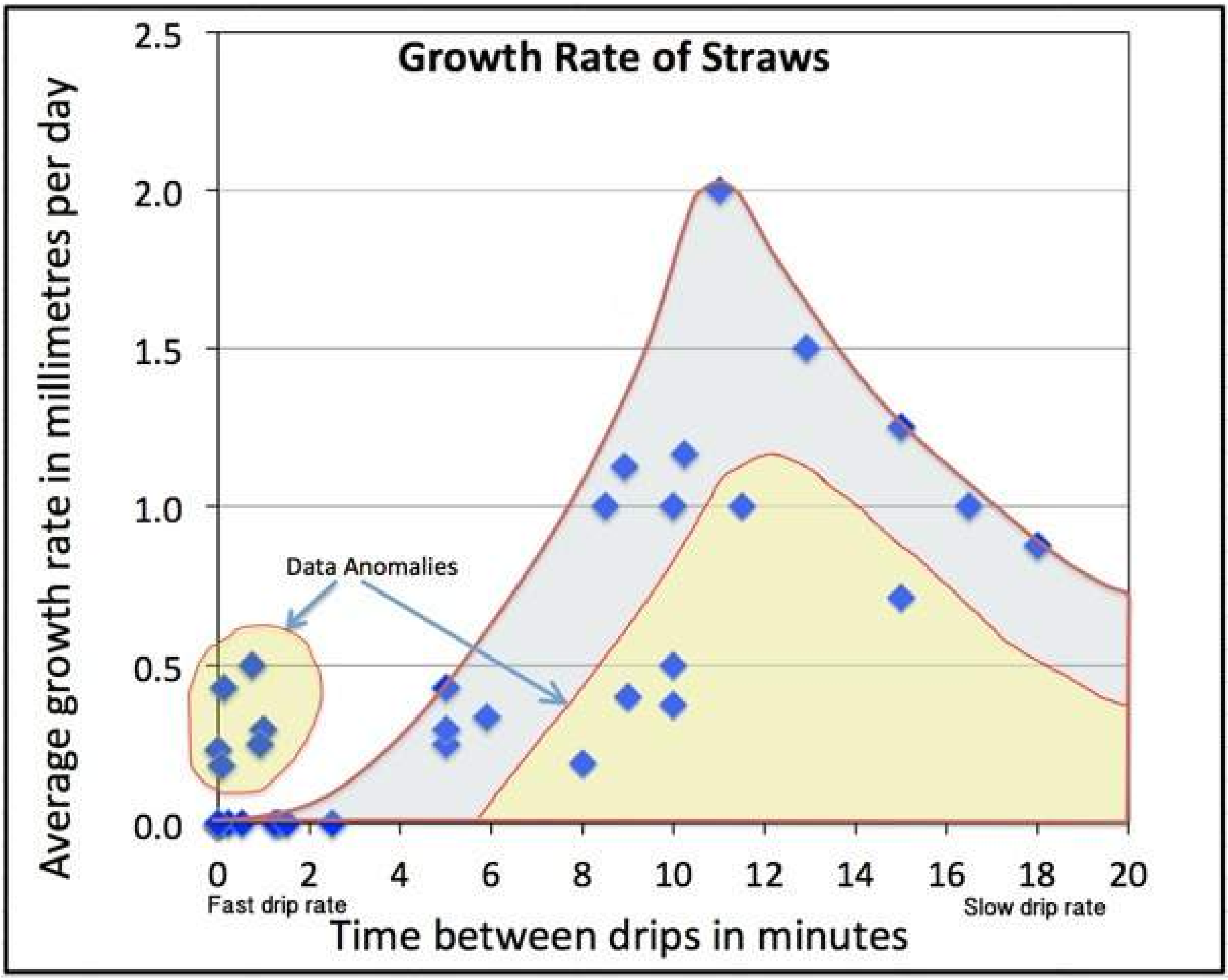

Figure 6. Plotted points showing straw average growth rates between periods of data recording, measured in millimetres per day in conjunction with solution drip rate in minutes. Note, the ‘Data Anomalies’, which occur when drip rate changes dramatically between recording periods.

The most rapid growth rate of 2 mm per day, occurred when the drip rate was one drop every 11 minutes.

The growth rates of the studied straws, was taken to be the increase in length between data collection periods, divided by the number of days elapsed. The drip rate was timed when each length measurement was recorded. Unfortunately it was beyond the scope of this study to continuously monitor the drip rate, which may well have varied between measurement periods. As Allison (1923) observed, “*one can hardly expect to secure uniformity in results from stalactites and stalagmites growing under diverse conditions*.”

The relationship between the growth rate of straws and their drip rate is shown in Figure 6. 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.6)

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 mechanism for water flow through the concrete matrix is surface tension, capillary and gravitational forces, which combine to pull the solution through the concrete cracks and micro pores (Macleod, et al., 1990; Maekawa, et al., 2009). As water travels through the concrete structure, it leaches out calcium ions and calcium hydroxide.

When the first mineral-laden drop of water comes into contact with the atmosphere, it absorbs CO_2 and calcite is deposited in a thin ring around the base of the drip where it is attached to the supporting structure. Each subsequent drop deposits more calcite onto the previously deposited ring of crystals. Eventually, these rings form a very narrow (4 mm), hollow tube often referred to as a "soda straw" stalactite.

On straw No.1, microscopic calcite rafts were continually forming on the surface of the suspended solution drop. [Figures 7 and 8]. A long period between drips (≈ 5 minutes or more), was sufficient time for absorbed CO_2 to cause calcite to precipitate out of solution and form microscopic rafts (up to 0.5mm across).

Figure 7. - Drip with latticework of calcite rafts forming on very slow dripping straw (≈ >12 minutes between drops) on a day with no wind or car movements.

Figure 8. - Calcite rafts are broken up and moving around drip surface quite fast due to lots of air movement

During periods of almost no air movement when the drip rate was very slow (i.e. ≈ >12 minutes between drips), calcite rafts were seen to form a latticework pattern over the drop surface [Figure 7]. A random injection of water from the straw tube would shatter this lattice work into small rafts [Figure 8]. Similar observations were reported by Allison (1923). Any additional pulse of water into the drop, caused rafts to be thrust upward, spinning toward the straw rim where occasionally they attached to the straw’s outer surface. Often these minute rafts would remain attach to the straw rim when the drop eventually fell. This observation has not been recorded in any other papers obtained in literature searches.

On days with greater air movement due to vehicles and/or atmospheric wind, calcite rafts on straw No.1, would be turbulently spinning 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 calcite rafts whirling around the surface of the straw drop. On occasions violent spinning would shear some calcite 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 are allowing 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 outside surface.

Allison (1923) studied straws growing from a concreted section of a coal mine roof in Pennsylvania, 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 calthemites straws growing at the study site, as the active straws retained a thin film of moisture over much of their outer surface.

At the study site the solution drop diameter averaged between 4mm - 4.3mm. Straws with slower drip rates of approximately 15 minutes or more had a slightly larger straw drop diameter (up to 5mm diameter) and created a corresponding diameter straw [Fig. 9]. This may be due to the increased time for precipitation to occur when the drop is slowly growing in size and the diameter is slightly larger when the solution drop is partly formed, due to surface tension having less weight to hold up. Once the drop grows too heavy for the surface tension to hold the weight of solution, 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. Consequently, it is the drop diameter, which determines the diameter of the straw (Ver Steeg, 1932), regardless of the length of stalactite.

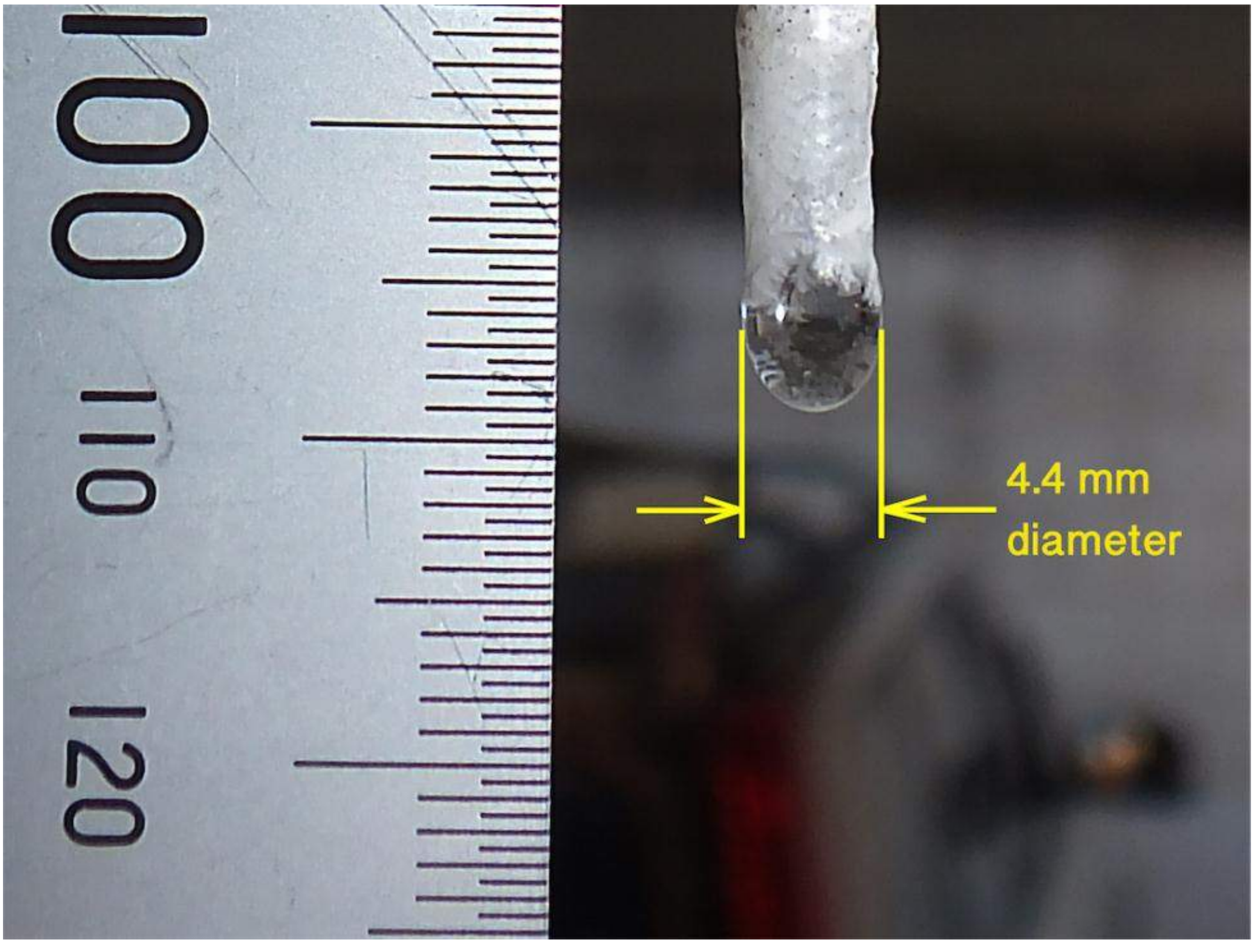

Figure 9. Method of measuring the straw diameter at the growth rim is by photographing a 0.5 calibrated engineering ruler next to the straw, at the same optical distance to the camera. The diameter of the straw can then be remotely measured from the digital image without the need to physically contact the fragile straw rim.

Ver Steeg, (1932) points out that the rate of vertical growth of stalactites, in the early stages of development during his study of above ground stalactites, compare closely with those studied by Allison (1923) of stalactites growing from concrete in a mine tunnel. Ver Steeg expected the aboveground stalactites to grow faster in conditions with lower relative humidity, increased air circulation and higher air temperatures, resulting in more evaporation than is typically experienced underground. However, Ver Steeg's recorded growth rates were very similar to Allison's.

The straws growth data recorded in the Belmont site study when related to atmospheric temperature and humidity confirmed Ver Steeg's observations that evaporation of solution had very little influence on the calcite deposition/growth rate at the straw tip.

Comparison of macro photos taken just a day apart, showed growth of calcite crystals was lengthening the straw in addition to attachment of microscopic rafts from the surface of the drop.

On fast dripping straws, no calcite rafts were visible to the naked eye, nor macro photography images. Atmospheric CO_2 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 was remaining in solution and falling to the ground where depositing occurred as a stalagmite beneath the drip point. [Fig. 10]

Figure 10. Stalagmite about 8mm high, growing under one of the fast dripping straws.

Stalagmite Growth

While the aim of this study was primarily to look at the growth rate of straw stalactites, it was noted that the growth of stalagmites below the fast dripping stalactites (more than 1 drop per minute) was far greater than the slow dripping stalactites. These stalagmites are broad in diameter (approx. 150mm diameter) and the tallest was just 15mm high. Vehicle tyres and pedestrian traffic constantly pass over the damp stalagmites resulting in mechanical abrasion and dispersal of the calcite laden water from the drip site. This reduces the full potential for stalagmite growth. As a consequence it would have been pointless to consider studying the growth of these stalagmites over a period of time.

Calthemites containing other trace elements

Calthemites stained various colours by elements such as iron or copper are commonly observed under manmade concrete structures. Steel bars are used in concrete structures as reinforcing to add tensile strength to concrete. The drawback is that if water penetrates the set concrete and changes the pH balance around the reinforcing bars, it may facilitate oxidation of the steel. The resulting iron oxide, expands and cracks the concrete. Also the iron oxide can be leached out with the same solution seepage water which creates the calthemites. Hence the predominately white calcite, will be stained orange [Fig. 11].

Figure 11. Orange coloured Calthemite formation containing traces of iron from reinforcing bars within the concrete. This example is at the study site.

Copper pipes passing through or near concrete – while less susceptible to oxidation, can produce a green or blue copper oxide which discolours calthemites [Fig. 12].

Figure 12. Aqua coloured Calthemite formations containing traces of copper, deposited in conjunction with calcite. This example is at an underground carpark, 0.5km from the study site.

Terminology Discussion

The author had much deliberation as to whether the calcite soda straws and other formations (secondary deposits) associated with concrete or mortar, should be classed as 'speleothems' or possibly 'concrete speleothems'. References in notable publications define the term 'speleothem' as encompassing all secondary mineral deposits formed within a cave, most commonly **calcite**, however may be **aragonite** or **vaterite** or other secondary mineral. Therefore all cave straws, stalactites, shawls, flowstone, coral, stalagmites etc, which occur in caves are classed as speleothems. The formal definition of "speleothem" as introduced by Moore (1954) is derived from the Greek words *spēlaion* ‘cave’ + *théma* ‘deposit’.

Borrows, (2007) refers to the term ‘urban dripstone’ which implies that concrete derived secondary deposits only occur in the urban environment. However, they occur in many location away from the urban environment wherever there is concrete or mortar.

Hill and Forti, (1997) refer to “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.” While all these descriptions get the message across, they became quite cumbersome to use on a constant basis.

An extensive search of available literature failed to identify an existing term which encompassed the varied forms of secondary calcite deposits mimicking speleothems and growing under man-made concrete structures. A simple term which covers all concrete and mortar–derived secondary deposits regardless of the formation shape, would reduce the need for lengthy roundabout description.

Therefore the term **‘calthemite’** or plural **‘calthemites’**, is proposed to encompass the varied secondary deposits derived from man made structures, consisting primarily of calcite and may contain other trace elements such as iron, copper, zinc etc. or minerals e.g. gypsum. The word ‘calthemite’ being derived from the Latin *calx* (genitive *calcis*) “lime” + Latin < Greek *théma*, “deposit” meaning ‘something laid down’, (also Medieval Latin *thema,* “deposit”) and the Latin –ita < Greek -itēs – used as a suffix indicating a mineral or rock.

In coming to a decision for an all-encompassing term, many combinations of Latin and Greek words were considered. Among them were; efflorescence, concretions, limonite, calcrete and caliche to name a few, however these words are currently in use to describe specific geological forms of calcite and as such could not be used.

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 saturated seepage solution and drip rate. Evaporation of solution due to atmospheric conditions, had no detectable affect on calcite deposition. The formation of calcite rafts on the drop surface, can influence the outside diameter of a calthemite straw.

Calthemites can grow much faster than cave speleothems. At the study site one calthemite straw achieved an average growth rates of 2mm per day over two days, when there was 11 minutes between drips. Too fast a drip rate, results in very little or no growth and too slow a drip rate caused the straw to calcify over and block up.

Given the number of variables which affect calcite deposition (growth of straws), it is almost impossible to predict the exact age of a calthemite straw by measuring its length or solution drip rate at a particular time.

The solution creating the calthemites at the study site is pH 13. This indicates that the predominant chemical reaction creating the calthemites is, $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$ and to a lesser extent $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$. Deposition of calcite occurs in both these chemical reactions when atmospheric CO_2 diffuses into the drip solution.

While outside the scope of this study, it can be assumed that straws at other sites may achieve greater deposition rates at faster drip rate, if the atmosphere in contact with the solution, contained a higher concentrations of CO_2. Also a longer seepage path through concrete may allow solution water to leach a higher concentration of calcium ions and calcium hydroxide and carry it to the deposition site.

Acknowledgements

The author would like to especially thank Dr Ken Turner (Ken Turner Consulting) regarding very helpful and constructive comments on the chemistry surrounding deposition of calcite derived from concrete.

A special thankyou to Dr Andrew Baker, New South Wales – National Parks and Wildlife Service (NPWS) Landforms and Rehabilitation Team (formerly Karst and Geodiversity Unit) and Jodie Rutledge for critically review of this paper.

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*. September 2007, Vol.44(5), 134 The Royal Society of Chemistry, Cambridge, UK.

Borrows, P, 2006a. Chemistry Outdoors, *School Science Review – Outdoor Science*, March 2006, Vol.87(320), 24-25. Published by the Association of Science Education, College Lane, Hartfield, Herts, UK.

Borrows, P, 2006b. Concrete Chemistry, Letters - November 2006, Royal Society of Chemistry, Cambridge, UK - http://www.rsc.org/education/eic/issues/2006Nov/Letters.asp

Diamond, S, 1976. Cement paste microstructure - an overview at several levels, in: Hydraulic cement pastes; their structure and properties, Tapton Hall, University of Sheffield, 2-30.

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&recordOId=1273303fileOId=1766469.

Hill, C A, and Forti, P, 1986, 1997. 'Cave Minerals of the World', 1st & 2nd editions. Published by National Speleological Society Inc. 2813 Cave Ave, Huntsville, Alabama, 35810, USA.

Ho DWS, Lewis RK, 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 Waterbased on Mass Transport and Chemical Equilibrium Theory". Translation from Proceedings of Japan Society of Civil Engineers (JSCE), No.648/Vol.47, May 2000

James, J, 2003. "The Crystal Gallery Finlayson". *Beneath the Surface: A Natural History of Australian Caves.* Published by UNSW Press. ISBN 0 868405957 (p. 65)

Khokhar, A, 2010. Cotutelle PhD Thesis, Ecole Centrale de Nantes, (France) and the Free University of Brussels (Belgium). "Optimisation of concrete mix design with high content of mineral additions: Effect on microstructure, hydration and shrinkage".

Lees, T P, 1992. Deterioration Mechanisms, Chapter 2. *Durability of Concrete Structures Investigation, repair, protection*. Edited by Geoff Mays, E & FN Spon Press 1990, Print ISBN: 978-0-419-15620-8

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

Maekawa, K, Ishida, T, and Kishi, T, 2009. *Multi-Scale Modeling of Structural Concrete*. Published by Taylor and Francis, 2 Park Square, Milton Park, Abingdon, Oxford OX14 4RN.

Moore, G W, and Sullivan, G N, 1997. *Speleology: Caves and the Caves Environment*, Revised Third Edition, Published by Cave Books with assistance from the National Speleology Society, ISBN 0-939748-46-0 (p. 52).

Papadakis, V G, Vayenas, C G, Fardis, M N, 1989. A reaction engineering approach to the problem of concrete carbonation. AIChE J 35:1639–1650

Papadakis, V G, Vayenas, C G, Fardis, M N, 1991. Fundamental modeling and experimental investigation of concrete carbonation. ACI Mater J 88:363–373

Papadakis, V G, Vayenas, C G, Fardis, M N, 1992. Hydration and carbonation of pozzolanic cements. ACI Mater J 89 : 119–130.

Pourbaix, M. 1974. 2nd edition. Atlas of electrochemical equilibria in aqueous solutions. Pergamon Press.

Sefton, M, 1988. "Manmade" speleothems; South Africa Speleological Assoc. Bull., Vol.28, 5-7.

Ver Steeg, K, 1932. "An Unusual Occurrence of Stalactites and Stalagmites". *The Ohio Journal of Science.* March 1932. Vol.32(2), 69-83.