

An applied mineralogical investigation of concrete degradation in a major concrete road bridge

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Abstract

A core of concrete taken from a major road bridge in the Strathclyde Region, Scotland, has been subjected to an applied mineralogical investigation, which involved stable isotope analysis, petrography, X-ray diffraction and scanning electron microscopy.

The structure is actively undergoing severe degradation due to mineral growth which is related to chemical reactions between the concrete and pore fluid. The physical growth of minerals causes disfigurement and structural weakening.

Pyrite and pyrrhotine hosted by dolerite aggregate appear to have been oxidized, providing sulphate for the deposition of ettringite and minor gypsum, in spheroidal cavities within the cement paste. The rainwater which passes through the structure mobilising sulphate from original gypsum in the paste and oxidizing the iron sulphides is also involved in the further leaching of elements from the cement paste and in the deposition of calcite. The isotopic values of calcites forming a crust on the concrete and a stalactite under the bridge are similar with $\delta^{13}\text{C} = -19\text{‰}$ PDB and $\delta^{18}\text{O} = +16\text{‰}$ SMOW. We suggest that atmospheric carbon dioxide was the carbon source. The carbon isotopic fractionation of -12‰ from atmospheric carbon dioxide of $\delta^{13}\text{C} = -7\text{‰}$, (O'Neil and Barnes, 1971) can best be explained as due to a kinetic fractionation related to the hyper-basicity of the pore water. The equilibrium formation temperature of about 45°C calculated from the oxygen isotope values and assuming a $\delta^{18}\text{O}$ value of meteoric water of -8‰ SMOW, is considered unreasonable. The exceptionally low $\delta^{18}\text{O}$ values are attributed mainly to reaction kinetics and the calcite inheriting its oxygen, two-thirds from atmospheric carbon dioxide and one third from the meteoric formation water (O'Neil and Barnes, 1971). A $\delta^{18}\text{O}$ value of atmospheric carbon dioxide of $+41\text{‰}$ SMOW and a $\delta^{18}\text{O}$ value of meteoric water of -8‰ SMOW, lead to a calculated $\delta^{18}\text{O}$ value for the calcites of $+10\text{‰}$ SMOW. The calcites analysed have a value of $+16\text{‰}$ and this may be due to partial re-equilibration towards a calculated value of $+21\text{‰}$ for calcite in equilibrium with the meteoric water at 20°C .

KEYWORDS: concrete deterioration, petrography, ettringite, calcite, stable isotopes.

Introduction

CONCRETE degradation is an endemic problem in the British Isles and throughout the world. The problem of concrete and building stone decay has been investigated by many workers, but they have often been unable to establish any exact mechanisms for the decay reaction processes (Smith *et al.*, 1988). Common causes of concrete decay in Scotland are sulphate mineral growth (sulphate attack), carbonate mineral growth (carbonation), and chloride attack due to the use of

road salt. Samples of a road bridge were made available for study by Strathclyde Region Roads Department. This structure had previously been classified in unpublished reports as having undergone carbonation.

Carbonate mineral growth in concrete structures is a major cause of decay; carbonate mineral growth reduces the alkalinity of the structure allowing encased steel support bars to oxidize and corrode (Minoru, 1968). The structure may also suffer shrinkage related to carbonate mineral

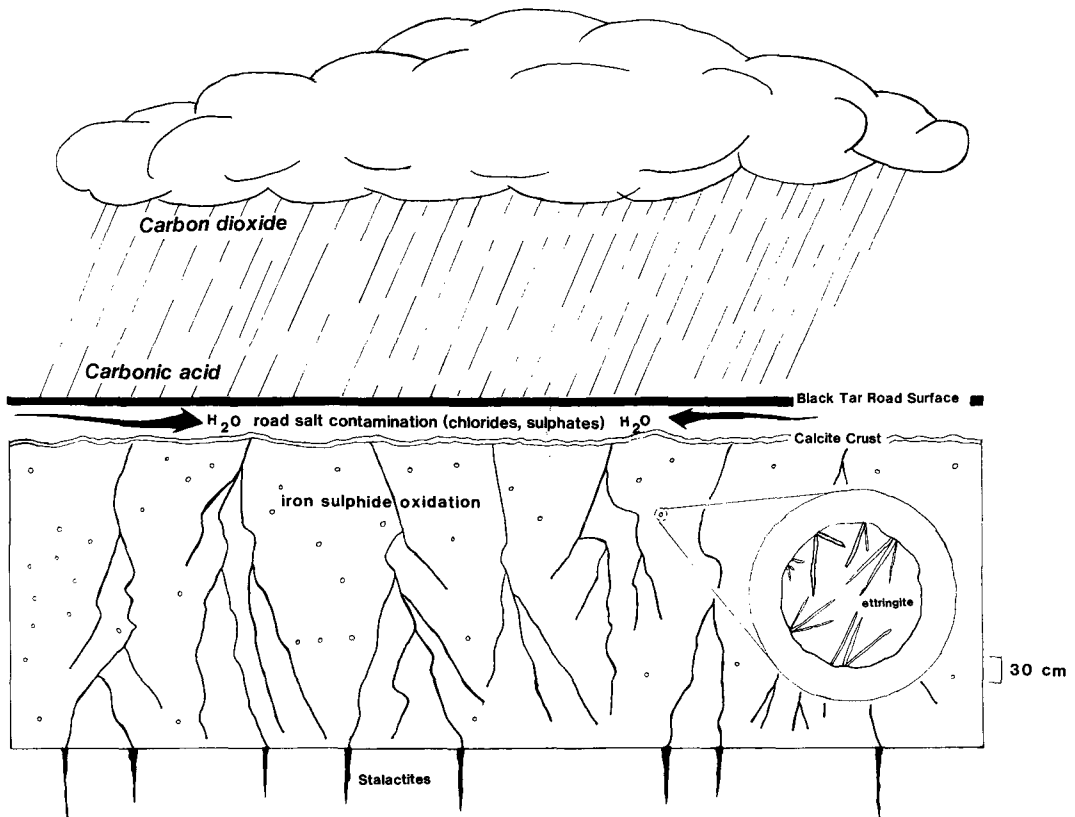


FIG. 1. A schematic diagram to display the proposed environmental and chemical system that has deposited the calcite and ettringite, causing the concrete deterioration.

growth (Lea, 1970). The carbonate mineral growth in concrete is thought to be mainly related to the reaction of the hydration product portlandite ($\text{Ca}(\text{OH})_2$) with atmospheric carbon dioxide (Lea, 1970). Carbonate mineral growth may also disfigure decorative structures, and stalactitic growths are not uncommon. The carbonate minerals themselves are susceptible to leaching by aggressive acidic waters and this leaching leads to further structural damage and decorative disfigurement (Smith *et al.*, 1988).

The predominant carbonate mineral found growing in concrete is calcite (CaCO_3), but other less common carbonates have been reported, trona ($\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) and thermonatrite ($\text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$) (Charola and Lewin, 1979). Often these occur as efflorescent growths on the external surface of the structure. Sulphate minerals are produced by various mechanisms, the most common being the invasion of the structure by groundwaters enriched in sulphate. Common minerals deposited in concrete are gypsum

($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) and the complex sulphocarbonate thaumasite ($\text{Ca}_6\text{Si}_2(\text{SO}_4)_2(\text{CO}_3)_2(\text{OH})_{12} \cdot 24\text{H}_2\text{O}$).

To our knowledge, no detailed mineralogical study involving $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ stable isotopes has been reported on a concrete structure that is undergoing active degradation. There appears to be a missing link between chemical and engineering studies, and applied mineralogical studies of concrete deterioration. The road bridge investigated has a dual carriageway passing on top and a double railway track passing below. A core of concrete was obtained from below the tar surface perpendicular to the bridge deck (see Fig. 1). The technique of stable isotope analyses was employed to aid in the identification of sources of carbon and of depositional processes. The core was also subjected to mineralogical investigation, using established techniques such as petrography, scanning electron microscopy and x-ray diffraction spectrometry.

Mineralogical composition of concrete

Concrete is composed of two materials, cement paste and aggregate. The paste is produced by hydrating cement powder which, in an exothermic reaction, produces hydrous cementitious minerals. The aggregate consists of sand-sized particles grading into rock fragments and may be monomineralic, but more commonly aggregate consists of rock fragments. The types of minerals and their abundance vary with each batch and type of concrete. The cement paste studied in the structure is a paste produced from an Ordinary Portland Cement. The mineral composition of Ordinary Portland Cement paste is thought to be 70% C-S-H gels, 20% portlandite ($\text{Ca}(\text{OH})_2$), 7% aluminates and sulpho-aluminates and 3% unhydrated material (Diamond, 1976). The portlandite present in cement paste is in the form of hexagonal platelets that concentrate at the paste-to-aggregate interface in a complex double aureole. It is portlandite that is thought to provide the bond strength in concrete (Lea, 1970). The mineralogy of the C-S-H gels is complex; they have a morphology similar to the phyllosilicates and both their crystal structure and chemistry is variable. Examples of these so called gel minerals are tobermorite, gyrolite and reyerite (Komarneni and Guggenheim, 1988; Merlino, 1988*a, b*). The hydrated alumina minerals present are most usually in the form of hydrogarnet ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$) which is randomly dispersed through the paste along with a small amount of the mineral ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3 \cdot (\text{OH})_{12} \cdot 26\text{H}_2\text{O}$). The microstructure of the C-S-H gel consists of microscopic pores of diameters in the range of 2 nm, linked by similarly minute tubercles (Neville and Brooks, 1987). For a more detailed study of the chemistry and structure of cement paste see Ramachandran *et al.*, 1981.

Hand specimen analysis

Examination of the core by naked eye and below a binocular microscope revealed three zones in the core. The first zone occurs on the outermost surface of the core closest to the tar surface of the road. It consists of a cream coloured precipitate with patches of brown staining; the concrete itself is pitted and friable. This zone extended to half a centimetre in depth from the top of the core. The second zone extended from 0.5 cm to 2 cm depth in the core and consisted of cement paste and aggregate; the paste has a cream coloration and is pitted. The third zone extended from the base of the second zone to the base of the core, a distance of 15 cm. This zone consisted of reasonably fresh concrete with

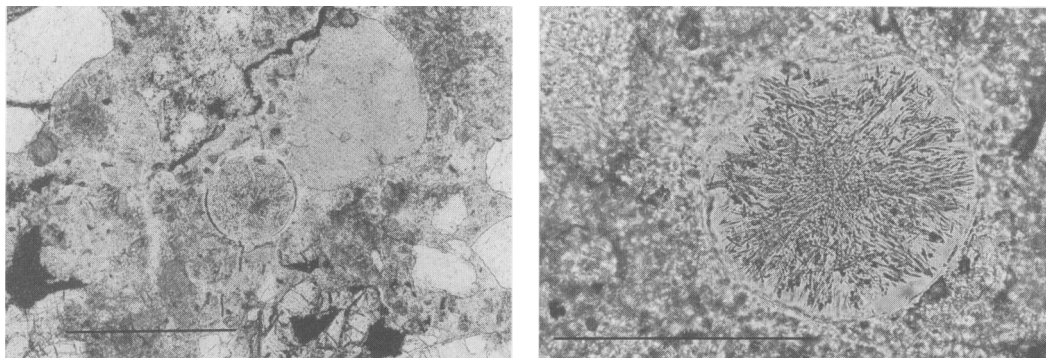
unaltered aggregate. Observation of the core under a binocular microscope revealed the ubiquitous presence of white spheres in the cement paste; the spheres were present in all three zones and ranged in diameter from 1 mm to 4 mm. Similar-sized spherical cavities could also be seen throughout the cement paste. It was apparent that the white material had preferentially grown within the spherical voids. Observation of the aggregate in the concrete indicated that some of the aggregate fragments had undergone alteration in the cement paste. Staining of fragments and occasional brown haloes around aggregate fragments were noted.

X-ray diffraction studies

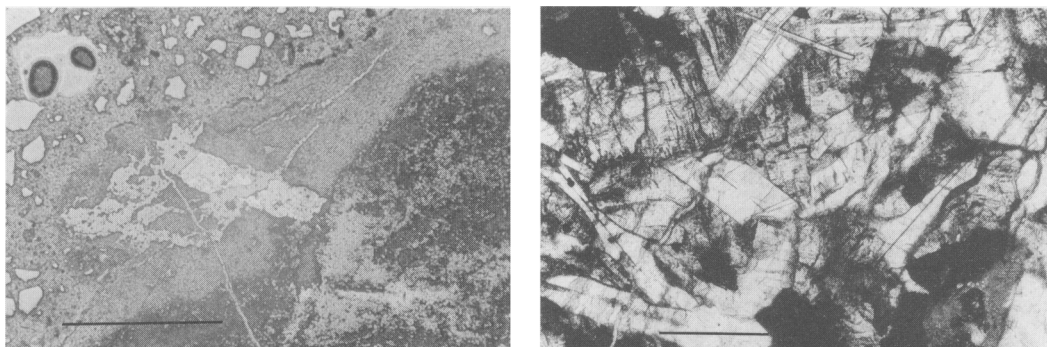
Material from the two upper zones was found by powder X-ray diffractometry to be composed of calcite, quartz and C-S-H gel. The cream coloration of the top of the core is undoubtedly due to calcite growth. Quartz was present in the form of sand grains added as fine aggregate to the cement paste. The cementitious minerals are of the C-S-H gel type. All the samples analysed from the upper two zones of the concrete were depleted in the mineral portlandite ($\text{Ca}(\text{OH})_2$). One of the white spheres was picked out and found to consist of ettringite with a minor presence of gypsum. Non-carbonated cement paste revealed a depletion in the hydration mineral hydrogarnet ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$). Similarly, portlandite is in lower concentrations than would be expected. The hydrous cementitious minerals found in cement paste give poor diffractograms due to their lack of crystallinity. However, in the non-carbonated cement paste it appeared that these minerals were less crystalline than would be expected. The lack of crystallinity of the components and the depletion of hydrogarnet suggests that water may have passed through the paste, leaching chemical species and altering minerals.

Petrography

A suite of polished thin sections was prepared from the core. The cementitious minerals found in cement paste are usually too fine-grained to be observed under a normal light microscope, but it is occasionally possible to identify portlandite grains (Powers and Hammersley, 1978) and unhydrated clinker grains. Within the cement paste studied it was difficult to observe any cementitious minerals. However, throughout the paste there are usually abundant spherical cavities ranging in diameter from <1 mm to 6 mm. The cavities are occasionally empty, but are commonly filled with acicular needle-like growths that



FIGS. 2 and 3. FIG. 2 (*left*). Transmitted light photomicrograph (ppl) of cement paste, showing a spherical cavity filled with ettringite. Note also the fracture passing through the paste. Scale bar = 800 μm . FIG. 3 (*right*). A transmitted light photomicrograph (ppl) showing more detail of one of the spherical cavities. Note the ettringite whiskers nucleating on the side of the cavity. Scale bar = 600 μm .



FIGS. 4 and 5. FIG. 4 (*left*). A reflected light photomicrograph showing a large pyrrhotine grain in an aggregate. Scale bar = 1250 μm . FIG. 5 (*right*). Transmitted light photomicrograph (ppl) showing iron staining around feldspar grains and in fractures in the grains in a dolerite aggregate due to iron sulphide oxidation. Scale bar = 500 μm .

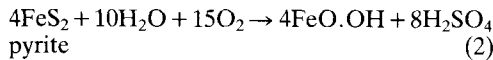
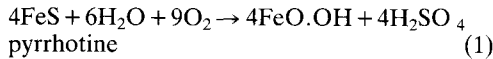
radiate into the pore space, presumably having nucleated on the side of the pores (Fig. 2). The mineral grains are extremely fine ($<4 \mu\text{m}$) and almost whisker like; they were identified by powder x-ray diffraction as ettringite (Fig. 3). Isolated ettringite needles can also be seen in the cement paste and it is presumed that they are original ettringite produced as the cement powder hydrated. It is obvious that the ettringite found growing in the abundant cavities is a secondary alteration product. The filling of air cavities with ettringite has been noted previously (Powers and Hammersley, 1978), and is noted in the American Society for Testing and Materials standard for concrete petrography (ASTM C856).

The most common aggregate is dolerite, but gabbro, lava, sandstone and schist fragments are also present. Exotic aggregate included wood

fragments, coal particles, rose quartz, mudstone and limestone. None of these aggregate fragments had obviously reacted with the cement paste; however, surrounding a solitary limestone fragment is a yellow reaction rim which may be due to reaction with the cement paste or fluids percolating through the structure.

In transmitted light the dolerite aggregate fragments (1 cm to 10 cm), can be seen to contain an abundance of opaque minerals. The grains, when studied in reflected light, were revealed as the iron sulphides pyrite and pyrrhotine (Fig. 4), as well as the iron-titanium oxide phases, ilmenite and magnetite. In the chemical environment found in concrete, iron-titanium oxides are not potentially reactive but pyrite and pyrrhotine are undesirable as they may oxidize easily to produce sulphuric acid (Shayan, 1988).

A dolerite aggregate that had iron staining was picked out and a polished thin section prepared (Fig. 5). It could be seen that in the iron-stained area of the fragment pyrrhotine and pyrite were absent and in the unstained area they were present. The iron staining is probably due to the oxidation of pyrrhotine and pyrite producing sulphuric acid (Shayan, 1988), and leaving a residual iron hydroxide (Eqns. 1 and 2). Water and oxygen are required for the oxidation of pyrite and pyrrhotine and the oxidation staining observable in numerous aggregate fragments indicates that fluids have percolated through the structure.



Scanning electron microscopy

Samples of paste and aggregate were picked out from the core and observed by an SEM equipped with energy dispersive X-ray analysis facilities. Paste from the top 0.5 cm of the core was rich in calcite distributed as fine-grained material throughout the paste. Microfractures in the paste are lined with a white gel-type material that was rich in silicon, aluminium, potassium and sulphur. The material was similar in morphology to a gel, and it is possible that it is a symptom of alkali silica reaction (Lea, 1970). SEM obser-

vation of the cement paste allowed the spherical cavities to be studied in greater detail. The often perfect sphericity of the cavities suggests that they are air bubbles that have been trapped in the cement paste as it cured, and their abundance indicates that the concrete may have been a poorly prepared concrete. The cavities are often filled with spherical masses of acicular needles of ettringite. The needles radiate outwards apparently nucleating on the side of the cavity. Gypsum crystals nestle within the needles along with crystals of an unidentified chlorine-rich phase (Fig. 6).

Stable isotopes

We are not aware of previously published carbon and oxygen stable isotope studies on minerals produced during the degradation of concrete. Two samples of calcite were analysed for $\delta^{13}\text{C}$ PDB and $\delta^{18}\text{O}$ SMOW in the standard manner (McCrea, 1950). The results are listed in Table 1, along with the formation temperatures of the calcites calculated using an assumed meteoric water $\delta^{18}\text{O}$ value of -8‰ SMOW. The first sample was taken from the calcitic crust at the top of the core and the second from a stalactite, one of several growing on the underside of the bridge deck (Fig. 1). Both samples have very similar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values.

Table 1. Isotope analyses and calculated formation temperature.

SAMPLE	$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{SMOW}}$	FORMATION TEMPERATURE
crust	-18.5‰	+16.6‰	45°C
stalactite	-19.2‰	+16.4‰	46°C

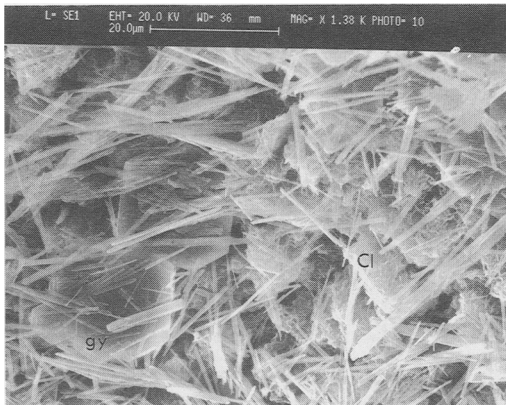
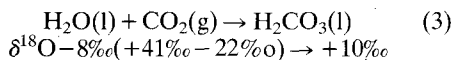


Fig. 6. Scanning electron photomicrograph of a spherical mass of ettringite. Note the gypsum crystals (gy) and the chlorine-rich phase (Cl) nestling in the ettringite whiskers.

In order to make an intelligible interpretation of the results a comparison had to be made with a similar natural process. The pore fluids of concrete are extremely alkaline and often attain pH values of 12 or more (Glasser, 1986). Carbon dioxide reacts rapidly with alkaline water possibly due to an affinity of OH^- for the carbon dioxide molecule. The formation of travertine deposits by the deposition of calcite scums in highly alkaline fresh water pools is analogous to the concrete growth system in chemical terms. During the deposition of such calcites the $\delta^{13}\text{C}$ value is fractionated by at least -10‰ (O'Neil and Barnes, 1971). This value coincides approximately with fractionation expected from a kinetic process with an inverse square root of mass dependence (e.g. diffusion velocity). Similarly a kinetic

variation of the cement paste allowed the spherical

fractionation of the oxygen isotope value of the carbon dioxide would be -22‰ but the $\delta^{18}\text{O}$ value for the calcite is thought to be obtained by a mixture of one third oxygen from the meteoric formation water and two-thirds from the atmospheric carbon dioxide involved in the reaction Eqn. 3 (O'Neil and Barnes, 1971).



Assuming the carbon dioxide involved in the calcite growth in the concrete is atmospheric ($\delta^{13}\text{C} = -7\text{‰}$), then the expected $\delta^{13}\text{C}$ values for the samples are at least -18‰ PDB. The $\delta^{13}\text{C}$ values (Table 1) are slightly lighter than expected and this could be related to the high pH of the water. The precipitation of the calcitic scums studied by O'Neil and Barnes (1971) is extremely rapid and as a result the calcites are out of oxygen isotopic equilibrium. The calcites found within this concrete structure may not have been so rapidly deposited, but they are certainly not in isotopic equilibrium as the calculated formation tempera-

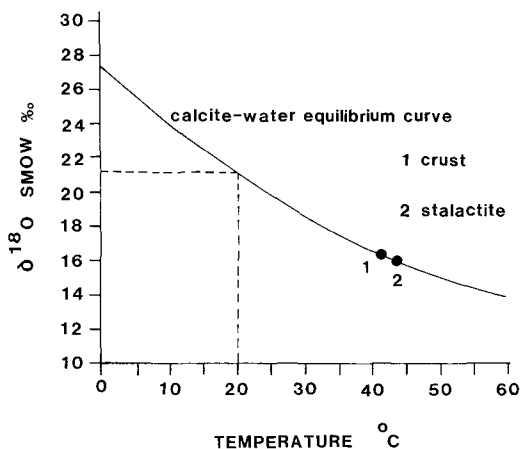


Fig. 7. Plot of temperature against $\delta^{18}\text{O}$, the calcite-water equilibrium curve has been plotted to allow equilibrium formation temperatures to be noted. The more realistic formation temperature of 20°C has been marked for reference.

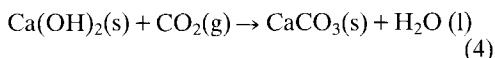
ture of approximately 45°C is too high (Fig. 7). Reasonable temperatures for the calcite to have formed at are around 20°C and if they formed in equilibrium with the formation water $\delta^{18}\text{O} = -8\text{‰}$ they would be expected to have a $\delta^{18}\text{O}$ SMOW value of $+21\text{‰}$. The oxygen values for the calcites confirm that they were not deposited in equilibrium (Table 1), but they also do not

match the value calculated by the non-equilibrium kinetic reaction. Re-equilibration of the kinetically fractionated carbon dioxide takes place on dissolving in water due to carbonate speciation and this process will increase the $\delta^{18}\text{O}$ value of the calcite from $+10\text{‰}$ towards the equilibrium value of $+21\text{‰}$. Also, the $\delta^{18}\text{O}$ value of the formation water may be different to that of local meteoric water or oxygen being contributed to the system from other minerals such as portlandite (see Eqn. 4) perhaps by isotope exchange.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the two samples are very close and this suggests that they were formed by one fluid with a similar isotopic composition and a similar reaction process.

Proposed model for mineral deposition

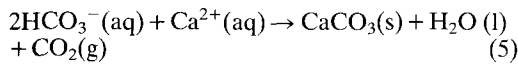
A calcitic crust occurs on the upper side of the bridge deck below the tar surface. Stalactitic growths composed of calcite are abundant on the underside of the bridge deck. Within the concrete structure there is no calcite growth, except as occasional fine-grained fracture linings. Most of the calcite growth is due to water percolation through the structure. The mineral portlandite ($\text{Ca}(\text{OH})_2$) is concentrated in concrete structures at the surface of the structure and at the interface between the cement paste and aggregate fragments (Lea, 1970). Undoubtedly the portlandite at the surface of the bridge deck reacted immediately with atmospheric carbon dioxide to produce calcite (Eqn. 4). It is highly likely that the reaction at the concrete surfaces took place as it cured.



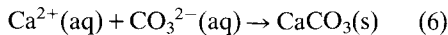
This initial reaction must have left a fine coating of calcite on the surface of the concrete. The fine grained coating of calcite would act as a nucleus for the growth of calcite from the predominantly aqueous system. Rainwater with hydrated carbon dioxide and various dissolved carbon species has flowed along the roads on either side of the bridge below the tar surface, and collected on the bridge deck. The bridge deck is topographically lower than the roads on either side. As the water flows it corrodes the concrete and leaches calcium hydroxide from the cement paste. The water may attain a pH of 12 and the dominant carbon species is the CO_3^{2-} ion (Pourbaix, 1974). With a solid carbonate coating already present and with water rich in leached calcium and carbonate ions a calcitic crust is produced on the upper side of the deck.

The deck itself is composed of large concrete blocks joined together by vertical mortar-sealed

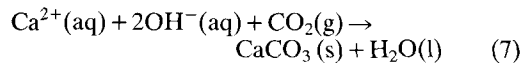
joints. The blocks are also fractured and intricate patterns of fractures cross-cut the blocks. The pools of water collecting on the upper side of the bridge deck percolate downwards through the joints and fractures (Fig. 1), the driving mechanism for the water flow being surface tension and gravitational forces. As the water passes through the deck at a fairly rapid rate it interacts with the mortar and cement paste leaching calcium hydroxide. As time passed the available calcium hydroxide will gradually have been leached from the cement paste, and as a result the pH of the water would have fallen. At pH values of 6 to 10, the dominant carbon species is the HCO_3^- ion (Pourbaix, 1974). As water emerges on the underside of the bridge deck stalactites may be formed in the classic degassing fashion (Eqn. 5).



It is more probable that if the fluid is at a higher pH, the stalactites may be produced by the reaction of carbonate and calcium ions in the solution forming calcite (Eqn. 6). This reaction is probably the most dominant in the formation of stalactites on the bridge.



At very high pH (>12) the very rapid reaction of carbon dioxide and alkaline solution could take place according to Eqn. 7.



The stable isotope analyses of the calcite crust and stalactite, supports the theory that atmospheric carbon dioxide is the source of the carbon for the calcite, and that the calcites have been deposited from hyper-basic aqueous solutions.

The hyper-basic solution that has percolated through the concrete depositing the calcite has permeated into the cement paste itself. Surface tension and capillary forces combine to pull the fluid into micro pores and tubercles in the cement paste. The fluid is continually reacting with minerals and aggregate fragments in the cement paste, and could be mobilizing sulphate from gypsum within the paste. The fluid may leach aluminium from hydrogarnet in the cement paste and it undoubtedly plays a vital role in the oxidation of pyrite and pyrrhotine in doleritic aggregate fragments. Thus the fluid becomes enriched in dissolved sulphur species. Calcium will also be leached from the tobermorite-type minerals present and calcium enrichment will occur as portlandite, concentrated around aggregate fragments, is taken into solution. The pH of the fluid passing

through the micro-porous system is unlike the carbonate depositing fluids, in the sense that it probably has a fixed pH of around 12. At such a pH the dominant species are Ca^{2+} , Al^{3+} , SO_4^{2-} and $\text{OH}^-(\text{aq})$ (Pourbaix, 1974). Within the micropores in the cement paste the capillary forces pulling the fluid through the minute tubercles ensure that the fluid is under a slight pressure. It is possible that as the fluid passes through the micropores it flows into the spherical cavities in the cement paste. As the fluid emerges into the spherical cavities from the micro-porous system ettringite nucleates and grows. With time, as fluid flows towards and through the spherical cavities the whisker like grains of ettringite are propagated. It is feasible that once ettringite has nucleated in a cavity, diffusion will take place. Calcium, aluminium and sulphate ions could migrate through the micropores in the cement paste towards an ettringite growth point. Some ions diffuse into the cavity, and other ions diffuse out of the cavity and eventually out of the underside of the bridge deck in solution.

To confirm the proposed mechanism an attempt was made to compare the $\delta^{34}\text{S}$ isotope value of the pyrite, pyrrhotine and ettringite. Unfortunately a suitable amount of ettringite could not be collected to allow a reliable sulphur isotope analysis. With the only other possible sources of sulphate being acid rain or environmental input such as groundwaters, it is possible to attribute the major sulphate input as being internally discharged to the system by oxidizing iron sulphides and remobilization of gypsum. Microscopic observation of the pyrite and pyrrhotine in dolerite fragments tends also to suggest that wide scale oxidation has taken place. The presence of the gypsum crystals amongst the ettringite needles suggests that the system may be running out of aluminium or that the aluminium content of the fluid varies. The lack of aluminium discourages the deposition of ettringite, and gypsum grows. A lack of hydrogarnet, the aluminium bearing mineral found in cement paste, has been confirmed by X-ray diffraction.

Thus, by studying this concrete core it has been proved that stable isotope analyses coupled with mineralogy can contribute significantly to understanding the deterioration of a concrete structure. The intricate relationships between the mineral depositional systems and the chemical corrosion of the concrete can be more readily explained by a combination of geochemistry and mineralogy.

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