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Deterioration of stone and concrete exposed to bird excreta – Examination of the role of glyoxylic acid

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ABSTRACT

The deterioration of buildings as a result of the deposition of bird excreta is a phenomenon which has been well-documented. A number of mechanisms have been proposed as playing a role in deterioration, some of which involve biological processes. Uric acid in bird excreta is broken down by fungi into urea and glyoxylic acid. This paper examines the effect of exposing stone and cement specimens to glyoxylic acid solutions. These materials were a limestone, a sandstone and two cement pastes – Portland and calcium sulfoaluminate cement. Specimens of these materials were submerged in acid solutions and deterioration characterised using mass loss measurements, micro-CT scanning, and analysis of the solutions at the end of the experiment and the acid-degraded layers at the specimen surface. Attempts were made to synthesise and characterise calcium salts of glyoxylic acid. Additionally, geochemical modelling was conducted to provide further understanding of the deterioration processes. The results indicate that the main processes involved in glyoxylic acid attack of the materials investigated are acidolysis and complex formation. No calcium glyoxylate salts were present in the degraded materials. Instead, a conversion of glyoxylate to oxalate occurred leading to precipitation of calcium oxalate compounds.

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1. Introduction

The deposition of bird excreta possesses the potential to initiate biodeterioration of the fabric of buildings through a number of routes (Spennemann et al., 2017). Mechanisms include the enlargement of cracks and joints by vascular plants deriving from seeds in the excreta (Lisci et al., 2003), and damage from its chemical constituents. Additionally, bird excreta may act as a source of nutrients to micro-organisms, which may lead to biodeterioration through the production of metabolites.

Bird excreta consists of two components – urine and faeces - which are usually voided simultaneously. Urine largely takes the form of fine crystals of uric acid dihydrate ($C_5H_4N_4O_3 \cdot 2H_2O$) dispersed in a small volume of water. Depending on the species of bird, other nitrogen-bearing substances may be present, including urea, ammonium compounds, purines, creatine, creatinine and amino acids (Bernardi et al., 2009). The faecal matter contains the residue of organic material ingested by the bird. It may also contain fragments of inorganic minerals – 'grit' - ingested to aid in the digestion of seed and grain (Gómez-Heras et al., 2004). One study identified other insoluble salts – specifically members of the apatite group ($Ca_{10}(PO_4)_6(OH,F,Cl)_2$) and calcium oxalate (Gómez-Heras et al., 2004). A number of soluble salts were also present: halite (NaCl), sylvite (KCl), aphthitalite ($(Ka,Na)_3Na(SO_4)_2$), and calcium langbeinite ($Ca_2K_2(SO_4)_3$). These salts were present in relatively small quantities.

Uric acid is almost insoluble and so its capacity for causing damage through acidolysis is limited. Whilst it has been observed that repeated dissolution and re-precipitation of uric acid from bird excreta on building surfaces can cause staining (Haag-Wackernagel, 2012), most studies conclude that it does not lead directly to physical damage (Hempel and Moncrieff, 1971; Del Monte, 1986). However, crystallisation pressures exerted by soluble salt constituents during cyclical wetting and drying have been attributed to deterioration of tuffs in the Midas monument in Turkey (Topal and Sözmen, 2003).

Many microorganisms are capable of using uric acid as a source of nitrogen. In particular, fungi degrade uric acid via the pathway:(Vogels and Van der Drift, 1976; Vera-Ponce de Leon et al., 2016)

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Uric acid → Allantoin → Allantoic acid → Ureidoglycolic acid → Glyoxylic acid + Urea

Vogels and Van der Drift (1976) have compiled a list of fungal species found to able to use uric acid. From this, the species identified in the literature as having been isolated from bird excreta are the microfungus *Microascus brevicaulis*, as well as the filamentous fungi *Penicillium chrysogenum*, *Aspergillus fumigatus*, *A. niger* and *Beauveria bassiana*.

A study examining damage resulting from fungal activity found that the surfaces of marble specimens on which bird excreta had been deposited supported the growth of several species of fungi (Bassi and Chiatante, 1976). In separate experiments, two of these species - *Aspergillus repens* and *Penicillium cyclopium* - displayed notably accelerated growth in agar in the presence of pigeon droppings compared to agar alone. These two species were also found to lower the pH of the medium (Czapek solution) in which they were grown. After fungal growth, SEM examination of the marble surfaces found numerous cavities and indentations in the surface, attributed in part to production of acid.

Slight acidification has also been observed during the growth of unidentified mould on pigeon excreta (Spennemann et al., 2017). The pH dropped from a value of 6.0 down to 5.4, over a period of 3 days, but then increased over the next 8 days to a pH of 8.5. The reason for this change was not explored further, but the most likely explanation would be the further degradation of glyoxylic acid (or other organic acids), and of urea to ammonia (Bachrach, 1957). Whilst complete degradation of glyoxylic acid to CO_2 by bacteria is possible (Hutchinson, 1950), formation of oxalic acid is often an intermediate stage in this process, with a proportion being precipitated as oxalate salts (Carlile, 1984). This would also produce an increase in pH.

Thus, the production of glyoxylic acid via fungal degradation of uric acid in bird excreta would appear to be a potential deterioration mechanism for materials on the exterior of buildings. Damage to construction materials by organic acids does not always occur solely as a result of acidolysis. Firstly, complex formation between the organic acid and metal ions from the material may exacerbate the process of acidolysis, by increasing the concentration of ions that can be accommodated in solution, potentially leading to faster rates of deterioration. Secondly, insoluble salts can be formed with metal ions in the material. In some cases, these occupy a much larger volume than the original solid compounds, leading to expansion and cracking (Larreur-Cayol et al., 2011).

Glyoxylic acid ($OCHCO_2H$) is a highly soluble acid. In solution, the glyoxylate ion undergoes hydration in the presence of water:

$$OCHCO_2^- + H_2O \rightleftharpoons (HO)_2CHCO_2^-$$

With regards to complex formation, considering the inorganic, non-metallic components encountered in the outer fabric of buildings, the most common constituent chemical elements are likely to be calcium, silicon, aluminium, magnesium and iron, plus oxygen, carbon and hydrogen. The ability of glyoxylic acid to form complexes with these elements has not been explored thoroughly. However, the stability constants of strong complexes formed by aluminium and iron (III) have been determined (Table 1). Stability constants for iron (III) complexes have also been determined by Vincze (1999). The methods used by this researcher concluded that four complexes existed (1:1 to 1:4), and attributed very different stability constants. The stability constants adopted here were favoured on the grounds that a technique for estimating stability constants based on the affinity of metal ions for the hydroxide ion (Hancock and Martell, 1989) gave a value for the aluminium glyoxylate complex with a metal ligand ratio of 1:1 close to the experimentally determined value.

The formation of salts by glyoxylic acid is also an under-explored area, but work carried out in the 19th century identified two calcium salts of low solubility (Debus, 1904). These were calcium glyoxylate ($Ca(C_2HO_3)_2 \cdot 2H_2O$), which forms at pH conditions around neutrality, and a basic calcium glyoxylate $Ca(OH) \cdot C_2HO_3 \cdot H_2O$ which was found to form under higher pH conditions. The second of these compounds decomposed to calcium oxalate and calcium glycolate, with elevated temperatures accelerating this process. The solubility products of the two salts are given in Table 2. It should be noted that the solubility of the basic salt is estimated based on the conventional interpretation of the term 'sparingly soluble': the solubility was assumed to be 0.1 g in 100 ml. While other salts of glyoxylic acid exist, they are more soluble. Tables 1 and 2, also contain data for oxalic acid and glycolic acid, the significance of which will become clear later in this paper.

This paper examines the behaviour of stone and concrete exposed to glyoxylic acid solutions, with the view to answering the following research questions: (i) How damaging is glyoxylic acid attack, and are some materials more vulnerable than others? (ii) To what extents do acidolysis, complex formation and the precipitation of glyoxylate salts play a role in the deterioration of stone and concrete exposed to glyoxylic acid? (iii) Based on the deterioration mechanisms, what measures are best suited to limiting glyoxylic acid attack?

The approach adopted was to initially examine the influence of the acid on two types of stone (a sandstone and a limestone) and two types of hardened cement. This was done in terms of mass loss and pH measurements from specimens submerged in acid solutions, CT scans of specimens after exposure, analysis of the altered solutions, and chemical and mineralogical analysis of the deteriorated materials. Geochemical modelling was employed to further explore the mechanism of deterioration.

2. Materials and methods

The approach adopted in investigating the effect of glyoxylic acid on stone and cement was to expose selected materials to solutions containing glyoxylic acid at two different concentrations, and to monitor deterioration via mass loss measurements and micro-CT scanning. Since acid attack was anticipated to leave behind residual constituents of the original materials, and possibly glyoxylate salts, it was decided that chemical and mineralogical analysis of the acid degraded layers would also shed light on the mechanisms involved. In addition, analysis of the solutions after the experiments would assist in elucidating the chemical reactions occurring.

A series of geochemical models were developed using the geochemical modelling computer program PHREEQC (Parkhurst and Appelo, 2013) to further understand the mechanisms of deterioration. Part of the interpretation of these results was anticipated to involve an understanding of the nature of the calcium glyoxylate salts, and, specifically, the likely effects of their precipitation on the volume stability of stone and cement. This requires knowledge of the crystal structure of the compounds, of which nothing was known. For this reason, it was also decided to synthesise and then attempt to determine the structure of these compounds using powder X-ray diffraction.

2.1. Materials and chemical reagents

2.1.1. Stone and cement specimens

Four materials were studied. These were a limestone, a sandstone, and two hardened cement pastes prepared from Portland and calcium aluminate cements.

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