Thermodynamic analysis of deterioration of marble and cement buildings functioning as habitat for terrestrial algae

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The phenomenon of secretion of organic acids, primarily oxalic acid \( \text{H}_2\text{C}_2\text{O}_4/\text{C}_2\text{O}_4^{2-} \) from algae growing on buildings/monuments has been reported by some workers. These secretions may cause rapid deterioration of building surfaces. In the present study, using thermodynamic data, the effect of aqueous oxalic acid \( \text{H}_2\text{C}_2\text{O}_4/\text{C}_2\text{O}_4^{2-} \) on the deterioration of marble and portland cement has been estimated. Theoretically, for deterioration at normal pH, the equilibrium activity thresholds of \( \text{H}_2\text{C}_2\text{O}_4 \) (aq) and \( \text{C}_2\text{O}_4^{2-} \) (aq) are of the order of \( 10^{-11} \) to \( 10^{-10} \) M. The required equilibrium activities being so low, the oxalic acid-induced deterioration of buildings seems to be spontaneous in natural environments. Thermodynamic calculations also show that cement buildings deteriorate faster than marble buildings. Moreover, the degree of \( \text{C}_2\text{O}_4^{2-} \) (aq) attack on buildings increases with the fall in pH of the reacting medium.

During the last several years, there has been a growing interest in studying the deterioration of buildings in Europe, North America and Asia\(^{1,4} \). Stones, like marble, sandstone and granite, have long been used in the construction of buildings all over the world. However, present-day buildings are largely made up of concrete of which cement is an important constituent. Studies concerning deterioration of cement buildings are scanty\(^{3,4} \). Dicalcium silicate (DCS, \( 2\text{CaO}\cdot\text{SiO}_2 \)), tricalcium silicate (TCS, \( 3\text{CaO}\cdot\text{SiO}_2 \)) and tricalcium aluminate (TCA, \( 3\text{CaO}\cdot\text{Al}_2\text{O}_3 \)) are the three main constituents of Portland cement, which form a hydrated colloidal gel of unknown composition when cement hardens.

Weathering of stones used in building constructions is due to their interaction with different constituents of the atmosphere (hydrosphere and biosphere). The most typical and important aspect of such weathering is the action of the highly polluted urban atmosphere. Most investigations deal with sulphation of carbonatic surfaces, such as, marble and limestone resulting in the formation of gypsum crusts\(^2 \). Role of other factors, specially of biological origin, causing decay of buildings are not fully explored and have been studied only qualitatively.

Buildings, usually made up of marble, concrete or granite stones, provide an artificial habitat to different species of terrestrial algae, specially in marshy and coastal areas, where the relative humidity is generally very high\(^6 \). These algae grow both epilithically and endolithically. With the growth of algae, specially of perforating species, the building surfaces get rapidly corroded. Through the cell wall, these algae secrete a variety of organic compounds especially organic acids\(^6\). The secretion of oxalic acid from such algae is widely reported\(^8 \). The deterioration of the building surfaces is initiated by the reaction of these acids with building constituents. The amount of secretion from algae varies greatly and it seems that the release is low in sparse populations growing actively, but at high cell density, inhibiting light intensity or limiting \( \text{CO}_2 \) concentrations, the secretion can increase greatly\(^8 \).

The purpose of this paper is to estimate the thermodynamic equilibrium between the oxalic acid (both dissociated and undissociated forms), released from algae, and marble, DCS, TCS and TCA and to present a thermodynamic analysis of the effect of aqueous phase oxalic acid on marble and cement.

The interaction of marble with oxalic acid is well documented. The primary product is usually whewellite\(^7 \) (monohydrate of calcium oxalate, \( \text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O} \)). However, sometimes, though rare, weddellite (dihydrate of calcium oxalate, \( \text{CaC}_2\text{O}_4\cdot2\text{H}_2\text{O} \)) can be formed\(^7 \). High relative humidity and the presence of catalysts in the atmosphere enhance the rate of attack. Both the dissociated (\( \text{C}_2\text{O}_4^{2-} \)) and undissociated (\( \text{H}_2\text{C}_2\text{O}_4 \)) forms of oxalic acid interact with marble. A representative reaction is given below (reaction I):

\[
\text{CaCO}_3 + \text{H}_2\text{C}_2\text{O}_4/\text{C}_2\text{O}_4^{2-} \rightarrow \text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O} + \text{CO}_2 \cdot \text{marble}
\]

The three main constituents of portland cement (DCS, TCS and TCA) also interact with aqueous phase oxalic acid (\( \text{H}_2\text{C}_2\text{O}_4/\text{C}_2\text{O}_4^{2-} \)) in the same fashion. While whewellite is the main product in case of DCS and TCS, the interaction of TCA may result in the formation of whewellite and kaolinite (dihydrate of aluminium pyrosilicate, \( \text{Al}_2\text{Si}_2\text{O}_7\cdot2\text{H}_2\text{O} \)). Both whewellite and kaolinite are insoluble compounds with high thermodynamic stability. A representative reaction is given below (reaction II):

\[
\frac{2\text{CaO}\cdot\text{SiO}_2 + 3\text{CaO}\cdot\text{Al}_2\text{O}_3}{\text{cement}} + \text{H}_2\text{C}_2\text{O}_4/\text{C}_2\text{O}_4^{2-} \rightarrow \text{CaC}_2\text{O}_4\cdot2\text{H}_2\text{O} + \text{Al}_2\text{Si}_2\text{O}_7\cdot2\text{H}_2\text{O} \]

Under thermodynamic equilibrium conditions, the standard Gibbs free energy depends on the equilibrium constant \( K \)

\[
\Delta G^\circ = -RT \ln K \quad (1)
\]
where \( T \) is the temperature and \( R \) is the gas constant (1.987 cal mol\(^{-1}\) K\(^{-1}\)). At 298 K (1) becomes:

\[
\Delta G^o = -1.36 \times 10^3 \log K 
\] (2)

The mass balance equations for the reaction of marble with oxalic acid (\( HC_2O_4^- / C_2O_4^{2-} \)) can be written from reaction I. Similarly reaction II helps in the formulation of specific balanced equations for the interaction of DCS, TCS and TCA with both \( H_2C_2O_4 \) and \( C_2O_4^{2-} \) species. These equations are as follows:

\[
CaCO_3 (s) + H_2C_2O_4 (aq) \rightarrow CaC_2O_4 s, H_2O (s) + CO_2 (g) \] (3)

\[
2CaO.SiO_2 (s) + 2H_2C_2O_4 (aq) \rightarrow 2(CaC_2O_4.s, H_2O) (s) + SiO_2 (s) + H_2O (l) \] (4)

\[
3CaO.SiO_2 (s) + 3H_2C_2O_4 (aq) \rightarrow 3(CaC_2O_4.s, H_2O) (s) + SiO_2 (s) + 2H_2O (l) \] (5)

\[
3CaO.Al_2O_3 (s) + 3H_2C_2O_4 (aq) + 2SiO_2 (s) \rightarrow 3(CaC_2O_4.s, H_2O) (s) + Al_2 SiO_3 s, 2H_2O (s) \] (6)

\[
CaCO_3 (s) + C_2O_4^{2-} (aq) + 2H^+ (aq) \rightarrow CaC_2O_4 s, H_2O (s) + CO_2 (g) \] (7)

\[
2CaO.SiO_2 (s) + 2C_2O_4^{2-} (aq) + 4H^+ (aq) \rightarrow 2(CaC_2O_4.s, H_2O) (s) + SiO_2 (s) + H_2O (l) \] (8)

\[
3CaO.SiO_2 (s) + 3C_2O_4^{2-} (aq) + 6H^+ (aq) \rightarrow 3(CaC_2O_4.s, H_2O) (s) + SiO_2 (s) + 2H_2O (l) \] (9)

\[
3CaO.Al_2O_3 (s) + 3C_2O_4^{2-} (aq) + 2SiO_2 (s) + 6H^+ (aq) \rightarrow 3(CaC_2O_4.s, H_2O) (s) + Al_2 SiO_3 s, 2H_2O (s) \] (10)

Using thermodynamic data\(^{11} \) (Table 1), the standard Gibbs free energy for the reaction between marble and oxalic acid (\( H_2C_2O_4 \)) can be calculated from (3):

\[
\Delta G^o = \Delta G^o_{u} (products) - \Delta G^o_{u} (reactants) = -25.21 \text{ (kcal mol}^{-1}\text{)}.
\]

Similarly from (4) to (10) the standard free energies of other reactions can be calculated. Values obtained are shown in Table 2.

The equilibrium constant for the reaction between marble and oxalic acid (\( H_2C_2O_4 \)) is:

\[
K = \frac{p(CO_2)}{a(H_2C_2O_4)},
\] (11)

where \( p(CO_2) \) and \( a(H_2C_2O_4) \) are, respectively, the partial pressure of \( CO_2 \) in the atmosphere and the activity of \( H_2C_2O_4 \) in the aqueous layer supporting the algal growth on the stone surface. The equilibrium constants derived for other reactions are shown in Table 3. Values of the equilibrium constants under standard thermodynamic condition (298 K, 1 atm), can be calculated from (2), employing \( \Delta G^o \) data presented in Table 2. These results are also shown in Table 3.

Taking the logarithm of (11), we have:

\[
\log K = \log p(CO_2) - \log a(H_2C_2O_4).
\] (12)

Under equilibrium conditions \( (\Delta G = 0) \) and employing the value of equilibrium constant from Table 3, we get:

\[
\log a(H_2C_2O_4) = \log p(CO_2) - 18.54.
\] (13)

Background concentration of \( CO_2 \) in the atmosphere is 325 ppm (325 \times 10^{-6} atm) (ref. 12). Hence, the calculated required equilibrium activity of the undissociated...
Table 3. Equilibrium constant \( K \) for the reactions of marble, DCS, TCS and TCA with H\(_2\)C\(_2\)O\(_4\) (aq) and C\(_2\)O\(_4^{2-}\) (aq) at 298 K and 1 atm

<table>
<thead>
<tr>
<th>Reacting surface</th>
<th>( K ) (at 298 K and 1 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marble</td>
<td>( \frac{P(CO_2)}{P(H_2C_2O_4)} ) 18.54</td>
</tr>
<tr>
<td></td>
<td>( \frac{P(CO_2)}{P(acC_2O_4^{2-})a(H^+)} ) 18.54</td>
</tr>
<tr>
<td>DCS</td>
<td>( \frac{1}{a(H_2C_2O_4)} ) 101.87</td>
</tr>
<tr>
<td></td>
<td>( \frac{1}{a(C_2O_4^{2-})a(H^+)} ) 101.87</td>
</tr>
<tr>
<td>TCS</td>
<td>( \frac{1}{a(H_2C_2O_4)} ) 187.27</td>
</tr>
<tr>
<td></td>
<td>( \frac{1}{a(C_2O_4^{2-})a(H^+)} ) 187.27</td>
</tr>
<tr>
<td>TCA</td>
<td>( \frac{1}{a(H_2C_2O_4)} ) 206.57</td>
</tr>
<tr>
<td></td>
<td>( \frac{1}{a(C_2O_4^{2-})a(H^+)} ) 206.57</td>
</tr>
</tbody>
</table>

Interactions with H\(_2\)C\(_2\)O\(_4\) (i) and C\(_2\)O\(_4^{2-}\) (ii).

p: partial pressure; a: activity.

form of oxalic acid, for its interaction with marble is 9.44 \( \times \) 10\(^{-23} \) atm. Similarly the values of required equilibrium activities of oxalic acid (H\(_2\)C\(_2\)O\(_4\)) for its interaction with DCS, TCS and TCA can be calculated. Results are shown in Table 2.

The application of the above described thermodynamic treatment on (7)–(10) leads to the following equations:

\[
\log a(C_2O_4^{2-}) = 2 \text{pH} - 22.03,
\]

\[
\log a(C_2O_4^{2-}) = 4 \text{pH} - 50.94,
\]

\[
\log a(C_2O_4^{2-}) = 6 \text{pH} - 62.42,
\]

\[
\log a(C_2O_4^{2-}) = 6 \text{pH} - 68.86.
\]

For the interaction of marble, DCS, TCS and TCA with C\(_2\)O\(_4^{2-}\), (14)–(17) respectively, give the relationship between pH and the activity of C\(_2\)O\(_4^{2-}\). The straight line plots defined by these equations are shown in Figure 1, which indicate that the required equilibrium activity of C\(_2\)O\(_4^{2-}\) is a function of the concentration of H\(^+\) ion in the reacting medium.

The negative values of Gibbs free energies for the reactions of H\(_2\)C\(_2\)O\(_4\) and C\(_2\)O\(_4^{2-}\) species of oxalic acid with marble, DCS, TCS and TCA indicate that these reactions are thermodynamically feasible. The required equilibrium activities of H\(_2\)C\(_2\)O\(_4\) and C\(_2\)O\(_4^{2-}\) for the above interactions are of the order of 10\(^{-15}\)–10\(^{-68}\) M. The amount of oxalic acid secreted by different species of algae varies in different environments and the activity of oxalic acid in the reacting medium also depends on the activity coefficient which, in turn, is a function of the ionic strength of the medium. Owing to these difficulties the activities of oxalic acid species in stone-algae environments cannot be generalized. However, the extremely low required equilibrium activities of H\(_2\)C\(_2\)O\(_4\) and C\(_2\)O\(_4^{2-}\) probably indicate that their interactions with marble, DCS, TCS and TCA are spontaneous in the natural atmosphere. In an environment of heavy acid rain, \( \Delta G < \Delta G_{\text{nomal}} < 0 \), so the deterioration of buildings is accelerated. Moreover, the standard free energy changes are more negative in the case of DCS, TCS and TCA than in marble. Hence, oxalic acid induced deterioration of cement buildings is much more severe than those made of marble.

At very low concentrations and moderate pH the oxalic acid largely exists as C\(_2\)O\(_4^{2-}\) and (14)–(17) indicate that the interactions of C\(_2\)O\(_4^{2-}\) with marble, DCS, TCS and TCA are pH dependent, with low pH favouring the deterioration process. This is in agreement with earlier observations\(^{3,4}\) on the effects of other atmospheric pollutants on building surfaces. The end products of the interaction of oxalic acid with marble and cement are insoluble compounds, but they lack mechanical strength and cannot substitute for marble and cement as building construction material. Moreover, their interaction with atmospheric SO\(_2\) and H\(^+\) ions of rain water, resulting in the formation of some water-soluble species cannot be ruled out. Such reactions will accelerate the decay process and simultaneously make the attack of oxalic acid on the building surface more severe.

Thermodynamic calculations thus show that: (1) reactions of aqueous oxalic acid (H\(_2\)C\(_2\)O\(_4\)/C\(_2\)O\(_4^{2-}\)) with marble and cement are possible in the atmosphere; (2) oxalic acid-induced deterioration of cement is faster than that of marble; (3) with the fall in pH of the aqueous reacting phase, the rate of attack of C\(_2\)O\(_4^{2-}\) species increases.

Atmospheric deterioration of buildings/stone surfaces is a world-wide phenomenon\(^{12,13-15}\), despite the fact that
some ancient structures have survived the onslaught of atmospheric corrosion until now. Most studies deal with decay of buildings caused by atmospheric $SO_2$, $NO_x$ and $HCl$, completely ignoring the contributions from other atmospheric constituents, specially of biological origin. The growth of algae on rocks and concrete surfaces are widely reported\(^8\) and only intermittent precipitation or moisture derived from dew is sufficient enough to enable motile stages of the life cycle to function. Some algae occur more frequently on acid rock surfaces, e.g. *Stigonema minutum*, *Desmid* spp., *Eunotia* spp., *Pinularia borealis*, whilst on alkaline surfaces *Aphanocapsa* spp., *Schizothrix* spp., only one *Desmid* spp. and *Melosira roeseliana* are common. *Gloeocapsa kuttingiana* produces small pits in the surface when growing on calcite crystals and on marble in quarries, however, these algae occur in close association with fungal hyphae and it is not clear to what extent fungal or algal action produce pitting. Bare rock surfaces within \(\ldots\) where sufficient light penetrates, are also colonized by *Cyanophyta*. On old church walls and grave stones, *Gloeocapsa sanguinea*, *G. kuttingiana*, *G. compacta* and *Scytonema mycrocus* are very common and in many sites they are probably contributing to the breakdown of the stone. Where some water percolates over the surface, *Stichococcus* spp., *Gloeocystis* spp., *Coccomyxa* spp. and *Chlorococccus* spp., occur and these powdery green growths are found on buildings of all kinds, but are most obvious on the more ancient monuments, where time and the breakdown of the surface stone has yielded a favourable habitat. Such growths are of much concern to conservationists in Italy and Greece\(^7\).

Thus, it seems that the deterioration of buildings in many places is mainly through the reactions of oxalic acid secreted from algae, the theoretical feasibility of which has been clearly shown in the present study. Finally it should be stated that the correct prediction of any process needs both thermodynamic and kinetic study of the systems considered. I expect that our conclusions in this paper will be supported by laboratory-controlled experimental kinetic data, which I hope to obtain soon.


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Mechanism of ATP synthesis by protonmotive force

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ATP synthase (or $F_1$,$F_0$ ATPase) is the central enzyme in biological energy conversion that is almost three billion years old and is present in the membranes of mitochondria, chloroplasts and bacteria with amazingly similar structure and function in different species. It couples proton translocation through its membrane-embedded, hydrophobic domain, $F_0$ to the synthesis of the energy carrier molecule, ATP in its soluble, hydrophilic headpiece, $F_1$. In the absence of a high-resolution structure for $F_0$, the complete mechanism of ATP synthesis by protonmotive force has never been elucidated. Here we propose such a mechanism. The proposed mechanism is supported by a number of independent experimental evidences.

ADENOSINE triphosphate synthase (ATP synthase or $F_1$,$F_0$ ATPase) is the central enzyme in energy conversion in mitochondria, chloroplasts and bacteria, synthesizing ATP from ADP and inorganic phosphate using energy derived from a transmembrane electrochemical potential difference. The multisubunit assembly consists of a globular domain, $F_1$ (with composition $\alpha_6\beta_2\gamma_{10}d_e$) and an intrinsic membrane domain, $F_0$ (with composition $ab_{13}c_{13}$) linked by a slender stalk 4.5 nm long. The catalytic binding sites are predominantly in the $\beta$ subunits at the $\alpha-\beta$

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