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Salt damage in porous materials: a threat to the cultural heritage Clifford Price

Salt damage is one of the most pervasive threats to the longterm survival of historic and prehistoric structures and artefacts. Basic research at the Institute on the processes leading to salt damage is helping to ameliorate the problem.

he growth of salt crystals within porous materials is a major cause of decay. It can cause serious surface loss, or even structural collapse, in materials as diverse as stone, ceramics, mudbrick, mortar and plaster. For example, wall paintings, stone monuments, earthen architecture (Fig. 1), and artefacts in museums may all beatrisk.

The salts that cause the damage may come from a wide variety of sources, including air pollution (Fig. 2), the soil, sea spray, de-icing materials, and unsuitable cleaning materials. The damage occurs when salt crystals grow in size within the pore system, as a result of either crystallization or hydration. The growing crystals are able to exert enough force on the pore walls to cause both loss of cohesion and disintegration. The growth is triggered by changes in temperature and humidity, and may be repeated over and over again under the influence of fluctuating environmental conditions. Damage is not restricted to materials that are exposed to the rain; it can occur both indoors and outdoors.

Preventing salt damage

In some instances, it may be possible to remove the salts and thereby prevent further damage. This approach is most likely to succeed with relatively small objects that can be brought into the laboratory for treatment, although even here it may not be



Figure 2 Decayed apostle, Wells Cathedral. The limestone reacts with acidic air pollutants to give salts, which then cause further damage.

possible to extract the salts without further damaging an already weakened surface. In many other instances, salt removal is wholly impracticable, and other solutions have to be sought.

One possible approach, which warrants further research, is the use of growth inhibitors that affect the size and shape of the growing crystals. A more common approach aims to minimize damage through environmental control. Again, this may not always be practicable outdoors, although good use may sometimes be made of protective shelters or vegetation. If only a single salt is present, then the requirements for environmental control are straightforward, at least in principle. At a given temperature, a pure salt picks up moisture from the air (and dissolves in it) whenever the relative humidity exceeds a certain critical value. When the relative humidity subsequently falls below this value, the salt crystallizes out again. Crystallization damage may thus be avoided by maintaining the ambient relative humidity at a value well away from this critical value. If the ambient relative humidity is permanently above the critical value, the salt is permanently in solution; if the humidity is permanently below the critical value, the salt is always solid. Either way, damaging crystallization cycles are avoided. Similar considerations apply to hydration damage. In practice, however, it is very rare for a material to be contaminated with just one salt; it is much more usual to find a cocktail consisting of many cations and anions.

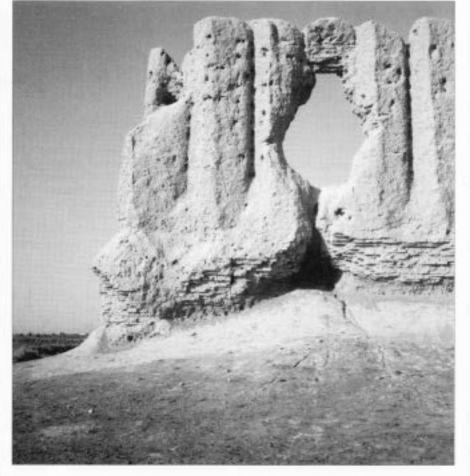


Figure 1 Mudbrick walls of one of the medieval buildings at Merv, Turkmenistan, undermined by salt damage.

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The problem of salt mixtures

Unfortunately, the behaviour of salt mixtures is much more difficult to predict than the behaviour of a single salt. Crystallization and hydration no longer take place at fixed relative humidities but over a range. In order to predict the precise ranges, classical thermodynamics must be used to model the interactions of all the relevant ions present in solution. This approach was developed simultaneously by two independent teams: by Michael Steiger at the University of Hamburg,¹ and by the author at the Institute of Archaeology and Simon Clegg and Peter Brimblecombe at the University of East Anglia.² Both teams showed, for example, that a mixture of sodium nitrate and sodium chloride crystallized over the range 68-75 per cent relative humidity, even though the critical relative humidity of each individual salt was 75 per cent at 20°C. Another example, of importance in polluted marine environments, was the discovery that calcium sulphate in the presence of sodium chloride would crystallize out across the range 75-100 per cent relative humidity; on its own, its critical relative humidity is 100 per cent.

The four researchers have now come together under the aegis of a European Commission research project (contract ENV4-CT95-0135), in order to take the approach further. The team's present research extends the existing model to include all the ions that are likely to be encountered in archaeological materials. This entails searching the chemical literature for existing data on some salts, and making the necessary measurements of solubilities and vapour pressures where these have not previously been made. The extended thermodynamic model is to be fronted by an expert system, currently under development at the Institute of Archaeology. At its simplest, the resulting program will allow the user to input the ionic analysis of the salt mixture in question, and thereby obtain the range of ambient conditions that would minimize salt damage. The expert system will be able to compare its recommendations with existing environmental conditions, and suggest any necessary changes. At a deeper level, it will be capable of querying any imbalances in the ionic data and proposing appropriate assumptions. It will guide decisions over the structure of data input, and provide intelligent searches of its databases for relevant advice, references, and visual material such as photographs and graphs. Subject to approval from the European Commission, and after evaluation in the field, the program will be made available via the World Wide Web.

How fast does damage occur?

As every chemist knows, thermodynamics says nothing about kinetics. In other words,

the proposed model will predict what should happen, given enough time; it will not be able to say anything about the rate at which crystallization and hydration take place. For example, it will not predict whether a wall painting in a church will be affected by the changes in temperature and relative humidity that accompany a service, or whether the painting will respond only to diurnal or even seasonal changes in the environment. Recent research indicates that the kinetics are influenced by the nature of the substrate as well as the identity of the salts.³ This is the subject of continuing research at the Institute of Archaeology, supported by a Natural Environment Research Council Studentship.

Notes

- 1. M. Steiger, "Crystallisation properties of mixed salt systems containing chloride and nitrate" (paper presented at EC Workshop on *Research on the conservation of brick masonry monuments*, Leuven, Belgium, 24–26 October 1994).
- C. A. Price & P. Brimblecombe, "Preventing salt damage in porous materials", in *Preventive conservation: practice, theory and research*, A. Roy & P. Smith (eds), 90–93 (London: International Institute for Conservation, 1994).
- 3. F. Pique, L. Dei, E. Ferroni, "Physicochemical aspects of the deliquescence of calcium nitrate and its implications for wall painting conservation", *Studies in Conservation* 37, 217–27, 1992.