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Australian Government
Department of Education, Employment and Workplace Relations

The Use of Crystallisation Inhibitors in the Preservation of Heritage Buildings Affected by Salinity

Eoin O'Caoimh

International ISS Institute/DEEWR Trades Fellowship

Fellowship supported by the Department of Education, Employment and Workplace Relations, Australian Government

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Executive Summary

The purpose of the Fellowship was to study the work being undertaken under the auspices of the European Union-funded SALTCONTROL project.

The three-year SALTCONTROL project was established to develop new methods of preventing salt damage by using compounds that inhibit the growth of salt crystals. The project involved applying inhibitors to the building fabric in an attempt to prevent salt crystallisation forming in the stone pores instead of on the surface where the crystallisation of harmless efflorescence takes place.

The overseas component of the Fellowship focussed on the research and development work being done at the University of Granada (UGR) in Spain. The UGR was the ideal destination as this was the venue where many of the large-scale project tests were conducted, including in situ trials. Climatic conditions in Granada are similar to those experienced in Australia.

The SALTCONTROL project was developed in recognition of the fact that new, low cost conservation treatments were needed for built cultural heritage that could both prevent salt damage and improve desalination in stonework. The project has led to the creation of a fully tested, reliable procedure for the use of crystallisation inhibitors for conservation.

The Fellow used the overseas component of the Fellowship to explore the identified skills and knowledge deficiencies and obtain the information necessary to return to Australia better equipped to advise on and promote the use of crystallisation inhibitors. The information and knowledge obtained will be shared through workshops, conferences, educational programs and publications.

The knowledge gained from the Fellowship also has implications for future government funding priorities in conservation and heritage. New methodologies flowing from the SALTCONTROL project also need to be incorporated into relevant training courses and university curricula. These are specified in the Recommendations section of this report.

The Fellowship has resulted in the establishment of a significant international relationship and important skills and knowledge have been gained. It is vital that the skills and knowledge obtained by the Fellow be shared with those best placed to recognise and appreciate their value and to advise on how best to act on the opportunities presented.

Table of Contents

Abbreviations and Acronyms

AICCM	Australian Institute for the Conservation of Cultural Material
ATMP	Amino Trimethylene Phosphonic Acid
CPSISC	Construction and Property Services Industry Skills Council
DECC&W	Department of Environment, Climate Change and Water, NSW
DEEWR	Department of Education, Employment and Workplace Relations
DPCD	Department of Planning and Community Development
DTPMP	Diethylenetriamine penta (methylene phosphonic acid)
HEDP	1-Hydroxyethylidene-1,1-Diphosphonic Acid
ICOMOS	International Council on Monuments and Sites
ISS Institute	International Specialised Skills Institute
ITAB	Industry Training Advisory Board
TAFE	Technical and Further Education
UCL	University College London
UGR	University of Granada, Spain
VET	Vocational Education and Training

Definitions

ATMP	Amino Trimethylene Phosphonic Acid is a phosphonic acid, and is commonly used to prevent scale formation in water systems.
Biomineralisation	This is the process by which living organisms produce minerals, often to harden or stiffen existing tissues.
Design	Design is problem setting and problem solving. Design is a fundamental economic and business tool. It is embedded in every aspect of commerce and industry and adds high value to any service or product—in business, government, education and training, and the community in general. Reference: 'Sustainable Policies for a Dynamic Future', Carolynne Bourne AM, ISS Institute 2007.
DTPMP	Diethylenetriamine penta (methylene phosphonic acid), a nitrogenous organic polyphosphonic acid. It has a better scale and corrosion inhibition effect than other phosphonates.
HEDP	1-Hydroxyethylidene-1,1-Diphosphonic Acid, an organophosphoric acid corrosion inhibitor used in detergents, water treatment, cosmetics and pharmaceutical treatment.
Molar	A measure of the concentration of a solute in a solution.
Phosphonates	Phosphonates or phosphonic acids, are a group of organic compounds. Phosphonates are highly water-soluble while the phosphonic acids are only sparingly soluble.
Skill deficiency	A skill deficiency is where a demand for labour has not been recognised and training is unavailable in Australian education institutions. This arises where skills are acquired on-the-job, gleaned from published material or from working and/or studying overseas. Reference: 'Directory of Opportunities. Specialised Courses with Italy. Part 1: Veneto Region', ISS Institute, 1991. There may be individuals or individual firms that have these capabilities. However, individuals in the main do not share their capabilities, but rather keep the intellectual property to themselves. Over time these individuals retire and pass away. Firms likewise come and go.
XRD	Powder diffraction (XRD) is a technique that uses X-rays to identify unknown substances by comparing diffraction data against a database of known patterns.

Acknowledgements

Eoin O'Caoimh would like to thank the following individuals and organisations who gave generously of their time and their expertise to assist, advise and guide him throughout the Fellowship program.

Awarding Body – International Specialised Skills Institute (ISS Institute)

The International Specialised Skills Institute Inc is an independent, national organisation that for over two decades has worked with Australian governments, industry and education institutions to enable individuals to gain enhanced skills and experience in traditional trades, professions and leading-edge technologies.

At the heart of the Institute are our Fellows. Under the **Overseas Applied Research Fellowship Program** the Fellows travel overseas. Upon their return, they pass on what they have learnt by:

1. Preparing detailed reports to government departments, industry and education institutions.
2. Recommending improvements to accredited educational courses.
3. Offering training activities including workshops, conferences and forums.

Over 180 Australians have received Fellowships, across many industry sectors.

Recognised experts from overseas also conduct training activities and events. To date, 22 leaders in their field have shared their expertise in Australia.

According to Skills Australia's 'Australian Workforce Futures: A National Workforce Development Strategy 2010':

> Australia requires a highly skilled population to maintain and improve our economic position in the face of increasing global competition, and to have the skills to adapt to the introduction of new technology and rapid change.
>
> International and Australian research indicates we need a deeper level of skills than currently exists in the Australian labour market to lift productivity. We need a workforce in which more people have skills, but also multiple and higher level skills and qualifications. Deepening skills across all occupations is crucial to achieving long-term productivity growth. It also reflects the recent trend for jobs to become more complex and the consequent increased demand for higher level skills. This trend is projected to continue regardless of whether we experience strong or weak economic growth in the future. Future environmental challenges will also create demand for more sustainability related skills across a range of industries and occupations.[1]

In this context, the Institute works with Fellows, industry and government to identify specific skills in Australia that require enhancing, where accredited courses are not available through Australian higher education institutions or other Registered Training Organisations. The Fellows' overseas experience sees them broadening and deepening their own professional practice, which they then share with their peers, industry and government upon their return. This is the focus of the Institute's work.

For further information on our Fellows and our work see www.issinstitute.org.au.

[1] Skills Australia's 'Australian Workforce Futures: A National Workforce Development Strategy 2010', pp. 1-2 http://www.skillsaustralia.gov.au/PDFs_RTFs/WWF_strategy.pdf

Acknowledgements

Fellowship Supporter

This Fellowship has been supported by the Department of Education, Employment and Workplace Relations (DEEWR).

DEEWR provides national leadership and works in collaboration with the States and Territories, industry, other agencies and the community in support of the Government's objectives. DEEWR aims to touch the lives of all Australians in a positive way, working towards a vision of creating a productive and inclusive Australia. Eoin O'Caoimh would like to thank them for providing funding support for this Fellowship.

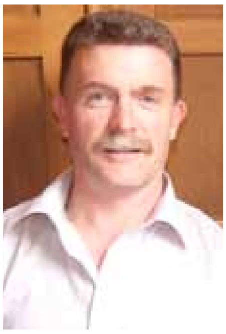
Supporters

- Philip Morey, Research and Development Manager, Austral Bricks NSW
- Alan Ross, Chief Executive Officer, Construction and Property Services Industry Skills Council
- Allan Nicholson, Principal Salinity Officer, NSW Department of Environment, Climate Change and Water
- Professor Clifford Price, Institute of Archaeology, University College of London
- Professor Carlos Rodriguez-Navarro, Department of Mineralogy and Petrology, University of Granada, Spain

Organisations Impacted by this Fellowship

- Australian Department of Environment, Water, Heritage and the Arts
- Australia International Council on Monuments and Sites (ICOMOS)
- Australian Institute of Architects
- Australian Institute for the Conservation of Cultural Material (AICCM)
- Australian Stone Advisory Association
- Construction and Property Services Industry Skills Council (CPSISC)
- Department of Environment, Climate Change and Water, NSW Government
- Department of Environment and Heritage, South Australian Government
- Department of Planning and Community Development (DPCD), Victorian Government
- Firms including stonemasons, bricklayers, heritage architects
- Heritage Council of Victoria
- Heritage Victoria
- Housing Industry Association
- Local councils
- Master Builders Association
- National Trust of Australia (Victoria)
- NSW Heritage Office
- TAFE institutes
- Suppliers including brick companies
- University Architectural and Heritage Conservation Faculties

About the Fellow



Name: Eoin O'Caoimh

Employment

- Head Teacher, Western Sydney Institute of TAFE

Qualifications

- Bachelor of Education, Trinity College, Dublin, 1985
- Masters Degree in Education (Literacy Education) University of Western Sydney, 1994

In 1998 the Fellow was seconded temporarily to TAFE NSW Construction and Transport Training Division where he was employed as a curriculum coordinator responsible for supervising the development of new construction industry curriculum. During this time he also coordinated the re-write of both the NSW Bricklaying and Stone Masonry courses.

In 2007 the Fellow was commissioned to research and write a training program and accompanying information booklet for the NSW Department of Environment, Climate Change and Water titled 'Building in a Saline Environment' as part of a salinity awareness course for the NSW building industry.[2] The Fellow presented the training program to the 2007 Urban Salt Conference in Sydney.

The Fellow continues to be involved in raising awareness about salinity and its impact on the built environment. While his training programs to date focus on what is yet to be built, the Fellow anticipates that his Fellowship will lead him to training in cost effective, practical conservation methods suitable for use on built cultural heritage.

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[2] *The information booklet Building in a Saline Environment* (ISBN 978 0 7347 5970 2) is available from the NSW Department of Environment, Climate Change and Water at www.sydney.cma.nsw.gov.au

Aims of the Fellowship Program

The aims of the Fellowship program were as follows:

- Establish the exact methodology and processes undertaken by the SALTCONTROL project partners leading to the creation of a tested, reliable procedure for the use of crystallisation inhibitors for conservation.
- Further understand the methodology and processes involved by examining the initial testing of the method in laboratory conditions.
- Identify European methods of collecting, recording and analysing data on presenting salt types, salt concentrations and related environmental information from in situ masonry members.
- Learn about the pre-application testing processes by discussion with and demonstration by SALTCONTROL project team members.
- Participate in the creation of salt-specific crystallisation inhibitors.
- Learn new techniques in the application of salt-specific crystallisation inhibitors.
- Identify European methods of determining and testing optimum, salt-specific crystallisation inhibitors that will best prevent further crystallisation-induced damage.

The Australian Context

The conservation of Australia's built heritage environment is facing a looming crisis. Our heritage building stock is under threat due to the mechanical breakdown of masonry members, including brick and stone, caused by accumulated concentrations of salts in the fine pore structures of the masonry units.

Salts are readily dissolved in water. When the salt solution comes into contact with porous and permeable building material it can be readily absorbed into the building's fabric. When the salt solution evaporates the salts remain by returning to their solid or crystal state and expanding in the fine pores of the masonry member. As the cycle is repeated the concentration of salt crystals in the material's pores increases.

In many cases natural and manufactured masonry members are unable to withstand the expansionary forces of the re-crystallisation process over time and atomic level mechanical breakdown of the material occurs. Masonry members are now routinely destructively tested post-manufacture or on extraction and graded according to their capacity to withstand repeated exposure to salt re-crystallisation cycles. Unfortunately, because this testing and grading process is a relatively recent development, it has come too late for many of Australia's heritage and domestic building stock.

The Australian landscape and climate combine to produce a salt cycling nightmare. Large amounts of windblown salts are dissolved by rains and the resulting solutions then exposed to rapid evaporation. While Australia's European-built cultural heritage is relatively young, the frequency of salt cycling due to the Australian climate means that our unprotected buildings constructed using non-exposure grade masonry materials are substantially 'older' than equivalent buildings in Europe because of salt weathering.

Traditional conservation and repair treatments have tended to focus on removing existing moisture and preventing the entry of rising or falling damp into a building's fabric. Consequently, conservation efforts in Australia have been directed at restoration and the creation of damp proof barriers below (and often above) masonry members in the belief that this will eliminate the possibility of further salt-induced mechanical breakdown.

However, the elimination of observable moisture is not a viable long-term answer. The accumulated salt load that remains in a building's fabric after a damp proof barrier is repaired or created can be reactivated by humidity and precipitation. This has led to attempts at desalinating masonry members using a variety of washing and poulticing techniques. Poulticing materials in the form of clays are repeatedly applied to masonry surfaces to draw the accumulated salts from the fabric. Unfortunately, as a result of the repeated salt crystallisation cycling many general-purpose (non-exposure grade) masonry members are too fragile for even some of the less destructive paper-based poulticing materials that have recently come on the market.

In many cases, heritage conservators are forced to make budget-based decisions about what they can realistically afford to conserve and maintain. Traditional treatments of the problem are expensive and time consuming, as well as being resource intense. In many cases current treatment methods can have such a deleterious effect on masonry that the original fabric is permanently lost.

Identifying the Skills Deficiencies

1. **Recognise salt-laden in situ masonry members and associated actual or potential salt crystallisation-induced mechanical breakdown.**

- Determine the construction method, position, composition and historical and current uses of the masonry member; the historical regional weather data, such as maximum and minimum temperatures and rainfall averages; the estimated length of time the masonry member has been in service; and the types and concentrations of salts available in the location.

  Aim: To become skilled in understanding the environmental conditions that result in the accumulation of concentrated salts within a masonry member.

2. **Identify European methods of collecting, recording and analysing data on salt types, salt concentrations and related environmental information from in situ masonry members.**

- Observe in situ sampling and review data additives that have been applied. Observe data collection processes.

  Aim: To learn about the key data and variables required to be analysed before attempts can be made to find the site-specific solution required to inhibit further crystallisation and to allow possible natural desalination to commence in the masonry member.

3. **Assess the electron microscopy technique of environmental scanning used to examine salt crystallisation dynamics and kinetics.**

- Observe samples taken from project research sites. Discuss methodology, interpretations and recommendations with the field study group at the University of Granada (UGR).

  Aim: To understand the methodology used to precisely analyse samples before in situ application of organic compounds takes place.

4. **Identify European methods of determining and testing optimum, site-specific crystallisation inhibitors that will best prevent further crystallisation-induced damage.**

- Analyse the methodology used in the selection of the most appropriate type of additive for a specific substrate and salt type. Visit laboratories to observe testing. Interview the doctoral team responsible for solution preparation and refinement. Review results of initial trials carried out on comparable source material.

  Aim: To gain an understanding of the processes involved in matching an organic additive to specific site conditions and to learn about the steps involved in applying the results of successful in situ trials to major conservation projects of built cultural heritage.

5. **Identify, observe and record European methods of applying crystallisation inhibitors to duplicate masonry members in the laboratory**.

- Review results of final trials carried out on in situ heritage masonry; and, if possible, subsequent project scale applications of the methodologies developed during the research and trials. Focus, in particular, on the trials carried out with sodium chloride, sodium sulphate- and magnesium sulphate-affected masonry members.

  Aim: To become knowledgeable about the sampling and testing processes required before large-scale application of organic compounds can take place.

Identifying the Skills Deficiencies

6. **Identify, observe and record European methods of applying crystallisation inhibitors to masonry members on site.**

- Speak with members of the research team where large-scale applications of crystallisation inhibitors have taken place. Where possible, participate in the application processes of organic compounds to inhibit crystallisation of existing salts.

  Aim: Learn about the application methods used for a successful large-scale application of organic compounds to take place.

7. **Identify factors related to assessing and prioritising appropriate use of organic compounds in relation to the salinity-affected heritage and non-heritage building stock.**

- Visit current and proposed projects where the application of organic compounds is being considered.

  Aim: Learn from custodians of European-built heritage about the benefits and limitations of crystallisation inhibitor application methodologies, including financial and logistical considerations. Determine the practicalities involved in adopting these methodologies for use on Australia's built heritage.

  European research and development has resulted in a cost-effective method of slowing, or perhaps halting altogether, the impacts of the salt crystallisation cycle. Current methods in dealing with salinity-affected masonry in Australia are not only expensive and labour intensive, but can also be detrimental to the long-term conservation of the building. The SALTCONTROL project provides an effective and cost-effective alternative to address salt crystallisation in Australia's heritage stock.

The International Experience

The Fellow visited the United Kingdom and Spain. In London the Fellow met with Professor Clifford Price, of the Institute of Archaeology, University College London. In Spain Professor Carlos Rodriguez-Navarro at the Department of Mineralogy and Petrology at the University of Granada (UGR) was the Fellow's host.

The UGR was a principal research partner in the European Union-funded SALTCONTROL project. This project was established in response to the need for new, low-cost, conservation treatments for built cultural heritage that would both prevent salt damage and improve desalination in stonework.

Over a three-year period The SALTCONTROL project involved the development of inhibitors that prevent salt crystallisation in stone pores and cause salts to form on the stone surface where the crystallisation of harmless efflorescence takes place. The project evaluated inhibitors in atomic scale studies, larger-scale tests and in situ trials.

The project also included research into how salt crystals develop and behave. The SALTCONTROL team believes their work has led to the creation of a fully-tested, reliable procedure for the use of crystallisation inhibitors for conservation purposes.

The Fellow examined how the techniques developed during the project are impacting on European heritage conservation practices.

United Kingdom

University College, London (UCL)

Contact: Professor Clifford Price, Emeritus Professor of Archaeological Conservation

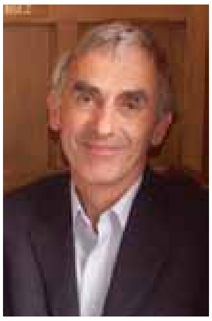

Figure 1

Professor Price (shown in Figure 1) is UCL's representative on the SALTCONTROL project. His principal interests are in the conservation of historic buildings, ancient monuments and archaeological sites. He also has an interest in the prevention of salt damage in porous materials, such as stone, plaster and mud-brick.

As the coordinator of a European Commission project that modelled the thermodynamic properties of aqueous salt solutions, Professor Price was closely involved in the development of a computer program capable of predicting the environmental conditions needed to minimise salt damage in buildings or artefacts.

Professor Price was responsible for the development and international patenting of the commercial stone preservative, Brethane. He currently chairs the Fabric Council at Lincoln Cathedral, and he is a member of the committee tasked with the conservation of Westminster Abbey's Cosmati Pavement.

The International Experience

Professor Price provided invaluable background into the work of the SALTCONTROL project, the principal objective of which was:

> …to develop a new method for the prevention of salt damage based on the use of compounds that inhibit the growth of salt crystals. When inhibitors are applied, salt crystallization within the pores of the stone is prevented, allowing the salts to form as non-disruptive efflorescences along the stone surface…[3]

Spain

University of Granada (UGR)

Contact: Professor Carlos Rodriguez-Navarro, Department of Mineralogy and Petrology

On arrival at UGR Professor Rodriguez-Navarro gave the Fellow a tour of the Department of Mineralogy and Petrology and introduced him to a number of his colleagues and doctoral students. The Fellow was also provided research documents relating to the work of UGR and others in the field of crystallisation inhibitors. One of the documents provided was a report on research undertaken by the team at UGR into the potential of phosphonates as crystallisation inhibitors for sodium sulphate. Sodium sulphate is one of the most damaging soluble salts in historic buildings and sculpture.[4] The damage is caused when expansive pressure is generated within the stone's pore by the crystallising salts and this then exceeds the rupture modulus of the material's pores.

UGR's research focused on three previously identified organic additives: 1-Hydroxyethylidene-1,1-Diphosphonic Acid (HEDP); Amino Trimethylene Phosphonic Acid (ATMP) and Diethylenetriamine penta (methylene phosphonic acid) (DTPMP). During laboratory testing, variations to pH were introduced and the effects recorded. The aim of the research was to develop a method of promoting the growth of harmless surface efflorescence on sodium sulphate-laden porous ornamental stone while preventing the growth of damaging sub-efflorescence within the stone.

Their research into the effectiveness of crystallisation inhibitors is focussed on dealing with conservation of stone *after* the presence of sodium sulphate has established itself. Such research is not to be confused with techniques designed to prevent sodium sulphate or any other potentially damaging salts from entering the material in the first place.

Professor Rodriguez-Navarro organised a set of activities to better assist the Fellow's understanding of the work of his team. The activities included a controlled laboratory experiment to demonstrate the effectiveness of a particular crystallisation inhibitor and create both a statistical and photographic record of the results, a visit to UGR's field trials, and the collection and analysis of on-site salt samples replicating UGR's methodologies.

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[3] *Global Change and Ecosystems*, EU Research and the Environment, Catalogue of projects funded during the Sixth Framework Program, pp. 439, Environment Directorate, European Commission, Directorate-General for Research, Directorate I – Environment, B-1049 Brussels.
Available at http://www.euresearch.ch/fileadmin/documents/PdfDocuments/media-2007/AllFP6ENVprojects.pdf

[4] *Sodium Sulfate Crystallization in the Presence of Phosphonates: Implications in Ornamental Stone Conservation*, Encarnación Ruiz-Agudo, Carlos Rodriguez-Navarro and Eduardo Sebastián-Pardo, Departamento de Mineralogía y Petrología, Universidad de Granada, Fuentenueva s/n, 18002 Granada, Spain.

Experiment to Demonstrate the Effectiveness of Crystallisation Inhibitors

The controlled laboratory experiment took the form of a traditional accelerated destructive test of three masonry samples. Three pieces of stone measuring approximately 250 x 40 x 12 millimetres were selected:

- Sample A – Sandstone
- Sample B – Limestone
- Sample C – Limestone

The main focus of the experiment was to demonstrate the effectiveness of the use of crystallisation inhibitors. In order to do this it was decided to conduct a simple 'with' and 'without' scenario where, with the exception of the addition of the inhibitor to one sample, all other variables, including material being tested, temperature and concentration levels of solutions would be equal.

Because of time limitations it was decided that the tests would be conducted on limestone rather than sandstone, as this would achieve faster observable and measurable results. Sample A is sandstone and was included to provide an additional observation opportunity. Samples B and C were the main focus of the demonstration.

A saturated solution of sodium sulphate ($Na_2 SO_4$) was prepared using deionized water. The resultant solution was then decanted to remove any undissolved crystals.

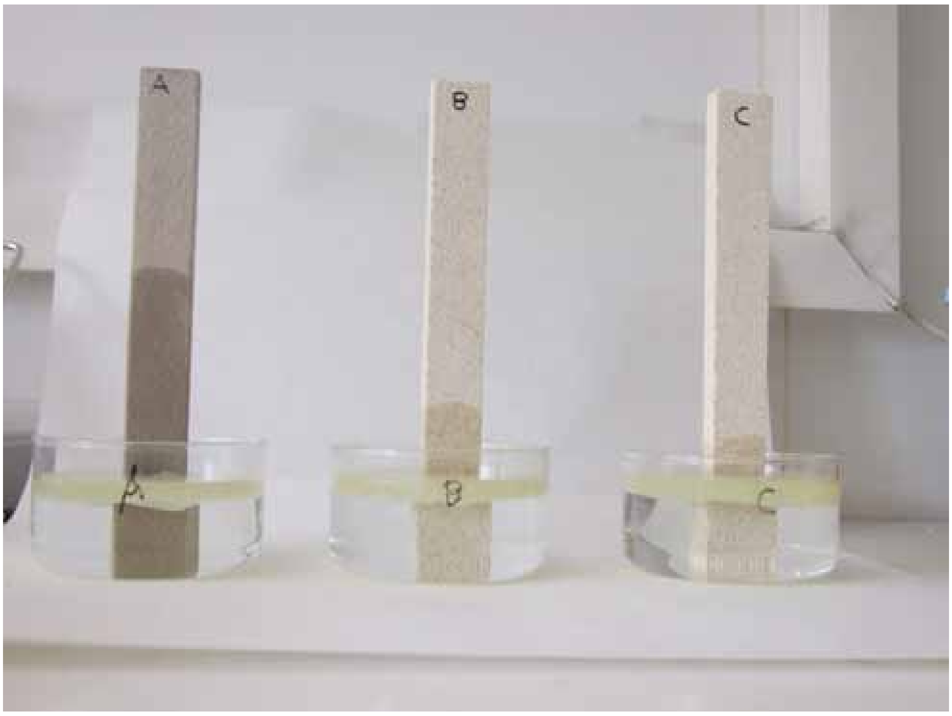

Figure 2. This image was taken five minutes after initial contact with the solution. The speed of the capillary rise is evident, the initial rise being much higher in the sandstone sample A.

To improve the quality of the photographic record by allowing for easier visual discrimination a black and blue background was added at the start of day 2.

Then 250 millilitres of the saturated $Na_2 SO_4$ solution was added to each of three labelled and sterilised glass containers. While nothing further was added to the solutions in containers A and B, ATMP in the form of Sodium Salt 2100 was added to the solution in container C at a concentration of 10^{-1} molar.

The individual stone samples were all weighed. They were then stood upright in the sterilised glass containers and melted wax was floated on the surface to keep the samples upright. This also limited evaporation from the solution's surface. As soon as the wax had set each individual sample, complete with container, wax, and solution was weighed and the weights were recorded together with the date and time.

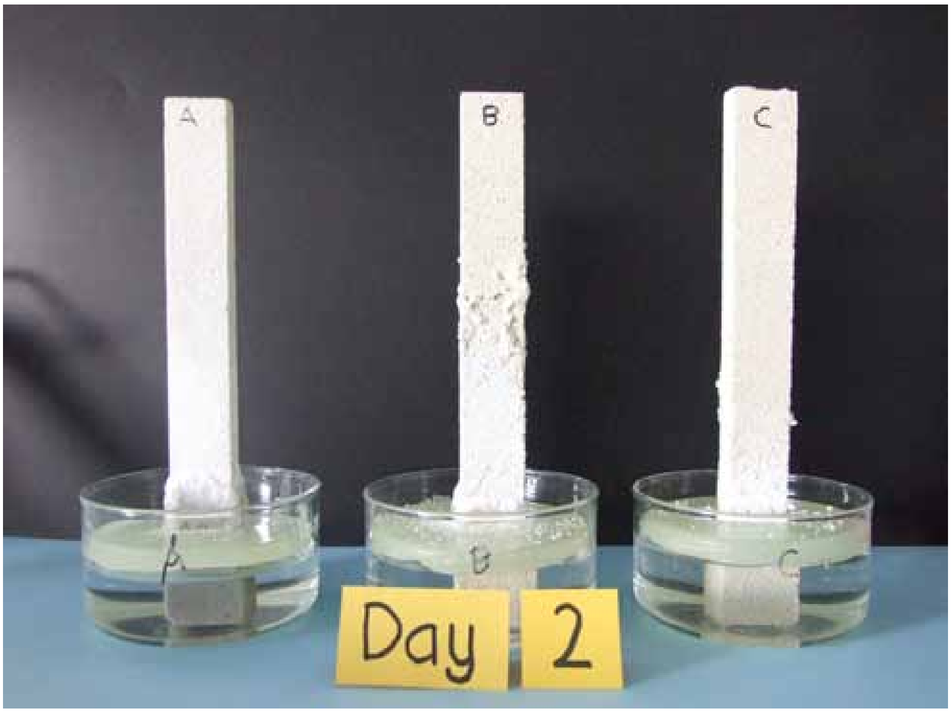

Figure 3. 24 hours after contact with the solution and already significant crystallisation is present on sample B

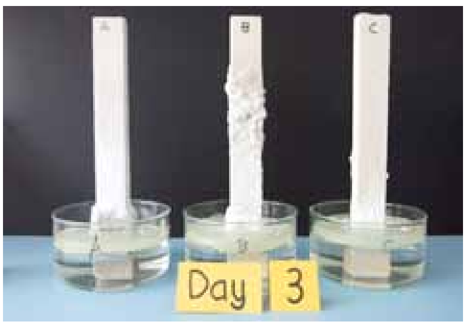

Figure 4. 48 hours after contact and significant crystallisation and some damage is observed on sample B

Figure 5. 96 hours after contact with the solution and sample B is experiencing significant material loss

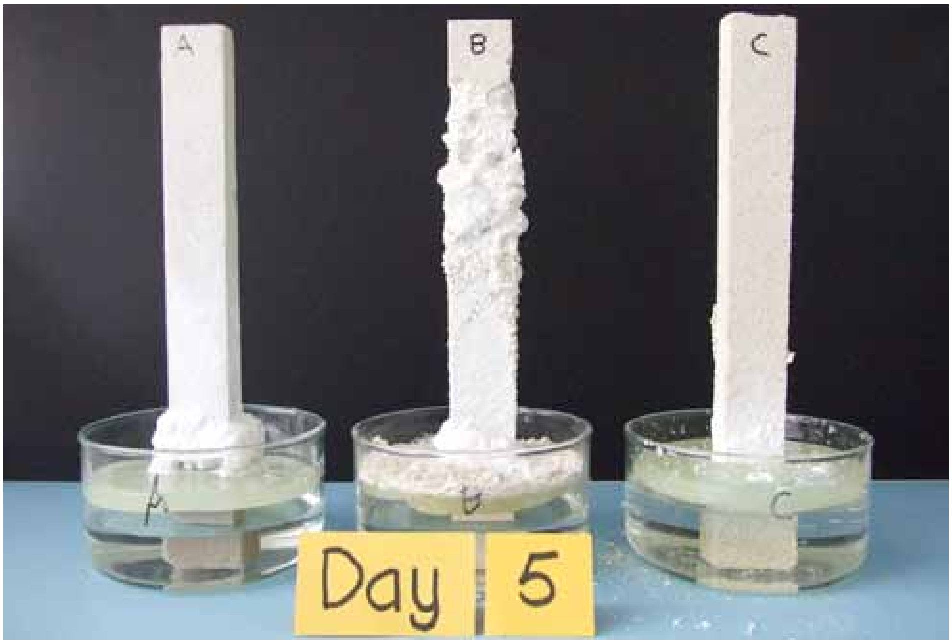

Figure 6. 120 hours after contact with the solution and the damage variations are now significant

Figure 7. 14 days after contact with the solution and the rupture modulus of the pores of sample B continues to be exceeded by the crystallising salts

Figure 9. The rate of capillary rise and subsequent evaporation of the solution where the inhibitor has been added is approximately half

Figure 8. There is extensive damage to sample B on all four sides

The Results

The results of the accelerated tests were spectacular. Figures 3–9 show the difference between the impacts of the saturated sodium sulphate solution on the two identical limestone samples.

Sample C is relatively undamaged. While some crystallisation occurred in sample C in the form of relatively harmless surface efflorescence on the sodium sulphate-laden porous ornamental stone.

The addition of ATMP in the form of Sodium Salt 2100 to the solution in container C at a concentration of 10^{-1} molar inhibited the growth of damaging sodium sulphate crystals within the material.

In this laboratory experiment the growth of damaging sub-efflorescence in the pore structure of sample C has been prevented. The addition of ATMP resulted in the crystallisation of what are essentially weaker crystallising salts. When crystallising, these organically modified salts are unable to generate sufficient expansive pressure in the stone's pore to exceed the rupture modulus of the material.

This experiment demonstrates the potential effectiveness of crystallisation inhibitors. However, it should be noted that it was done using sodium sulphate-free stone samples where the sodium sulphate solution and the crystallisation inhibitor were introduced to the stone at the same time.

While this research is not to be confused with techniques designed to prevent the initial entry of sodium sulphate or any other potentially damaging salts, it is clear from the significant reduction in the amount of salt-laden solution drawn into the limestone in sample C that the addition of crystallisation inhibitors to salt-laden solutions or to salt-free masonry members may be an effective preventative measure.

However, the work at UGR is very much focussed on dealing with the issue of conservation of stone *after* the presence of sodium sulphate within the stone has been established.

The Fellow was then given an opportunity to get an understanding of the importance of matching conservation solutions to the fabric being conserved. This exposed the Fellow to the work of Dr Encarnación Ruiz Agudo, a UGR graduate, currently working at the Institut für Mineralogie at Westfälischen Wilhelms-Universität in Münster, Germany.

Dr Ruiz Agudo's research in the field of crystallisation inhibitors was applied to rock samples extracted from Santa Pudia's quarries in Escúzar, Granada. Stone from these quarries was used in the construction of renaissance buildings in Granada including the Monastery of San Jerónimo.

Following initial salt crystallisation tests of Santa Pudia-sourced stone in laboratory conditions, Dr Ruiz Agudo then prepared a method for the conservation treatment of in situ ornamental stone materials. She then applied the new conservation treatment in pilot areas on the Monastery of San Jerónimo where significant problems existed due to salt crystallisation.

The International Experience

San Jerónimo was therefore chosen by Professor Rodriguez-Navarro as the best site for the Fellow to learn about assessing substrate and prevailing salt types so that the most suitable, site-specific crystallisation inhibitors may be trialled and applied. Application can only take place after ‘spot’ testing has been carried out. Many months or even years may elapse before tests results are assessable.

Visit to the Monastery of San Jerónimo

The Ministry of Culture nominated the monastery for World Heritage listing in April 2007. In submitting the nomination the following description of the Monastery was provided:

> This building may very well be the first example of classicism in the city of Granada. This was perhaps due to the initial participation of two Italian masters in its construction, Francisco and Jacobo Florentin ‘El Indaco’ who commenced building in 1525, and that of the master architect Diego de Siloé who took over in 1528 following the death of Jacobo. The church was first conceived by María Manrique, with the authorisation of Charles V, as a pantheon for her deceased husband Gonzalo Fernández de Córdoba, ‘El Gran Capitán’, possibly the most famous military personality in the history of Spain and veritable revolutionary of war art. Granada built this fabulous church in honour of a man who instilled terror in the hearts of Turks and French but who was idolised by his soldiers and admired by his enemies. Initially of Gothic style, it was the cross-vault, transept and main altar which marked the beginning of classicism in architectural design (pilasters, coffered vaults, medallions, figures, fleurons, monsters).[5]

The fact that the government of Andalucía approved in situ testing of new conservation methods, is testament to the esteem in which Dr Ruiz-Agudo, Professor Rodriguez-Navarro and Professor Sebastián-Pardo, and their colleagues at the Department of Mineralogy and Petrology, UGR, are held.

Figure 10. The Monastery of San Jerónimo

[5] www.unesco.org (Application Reference No 5136)

The International Experience

Many of the masonry surfaces at the monastery have experienced significant and, in some places, irreparable damage as a result of salts crystallising in the fabric of the building. Unfortunately, much of the damage is in the fresco work.

Figure 11. The altar in the Monastery of San Jerónimo. The pilot area studied is to the right of the central stairs.

Figure 12. One of the frescos in the monastery

Figure 13. Dr Ruiz Agudo is seen working at the pilot site

Figure 14. The Fellow is carrying out the non-destructive collection of presenting surface salts for analysis back at the laboratory

In Figure 13 Dr Ruiz Agudo is seen working at the pilot site. Unfortunately, the fresco that once covered this wall has been almost completely delaminated as a result of the mechanical pressure exerted by the crystallising salts. This pressure has exceeded the rupture modulus of the pores of the render, thereby resulting in render failure. Only a minute portion at the bottom left-hand corner of the original work remains.

In Figure 14, the Fellow is carrying out the non-destructive collection of presenting surface salts for analysis back at the laboratory. The analysis of these samples is essential before any attempt is made to use organic additives to modify the crystallisation location and processes of any salts contained within masonry in service.

Figure 15. A view of the rear of the monastery showing the results of poor housekeeping and maintenance practices

The International Experience

Figure 16. An example of penetrating damp

Figure 17. The orange grove that was subsequently planted on the raised garden and watered daily

The International Experience

As a result of a combination of building methodologies, poorly thought through changes to ground levels, inappropriate treatment of both surface and ground water, and perhaps inattention to good maintenance practices, the monastery has hosted all three versions of damp: rising damp, falling damp and penetrating damp.

Figure 16 provides an example of penetrating damp as a result of a change in ground levels and land use that took place well after the original construction was completed. The ground behind the wall at this point of the building was raised by as much as four metres over the centuries. A grove of orange trees was subsequently planted on the raised garden and the trees are watered daily.

The excess water, as well as occasional surface water percolates through the ground bringing a variety of destructive salts with it. When the moisture reaches the surface of this recently rendered wall, the moisture evaporates, the salts remain and continue to concentrate as new salts arrive. This concentration and crystallisation process will lead to the mechanical breakdown of the plaster.

Analysing the Samples

On return to the University with the samples collected at the monastery Professor Rodriguez-Navarro took the Fellow through UGR's preferred method for analysing samples of this size and nature.

In the nuclear testing and analysis laboratory the Fellow was introduced to Professor J D Martín-Ramos, a colleague of Professor Rodriguez-Navarro's in the Department of Mineralogy and Petrology at UGR.

Figure 18. Two vials of the salt samples collected at the Monastery of San Jerónimo and the slide used to hold the samples in position during the analysis process

The International Experience

Professor Martín-Ramos is a pioneer in X-ray diffraction and is responsible for the simplification of the hitherto cumbersome and often time-consuming processes associated with the analysis of crystal samples.

X-ray diffraction is a method for studying microscopic crystal form and structure. It involves the scattering of X rays by the atoms of a crystal with the diffraction pattern showing the structure of the crystal. The resultant patterns are known as diffractograms. Normally, these diffractograms would be compared visually to patterns of known origin in order to establish a match. The more complex the compound: the more complex and time consuming the analysis.

Figure 19. The Fellow and Professor Rodriguez-Navarro prepare to analyse the sample

In 2004 Professor Martín-Ramos developed XPowder, a software package for Powder X-ray diffraction analysis.[6] His XPowder software is able to carry out automatic acquisition, evaluation, and identification of crystal samples based on a comprehensive database of known and confirmed X-ray Diffraction (XRD) diffractograms. Results are delivered in minutes instead of hours or days. The program is now commercially available and is used by academic, industrial and law enforcement organisations.

Conventional Powder (XRD) was applied to determine the bulk mineralogical composition of the samples. As the samples were already in powder form they did not require further preparation. A thin layer of the crystal samples was set on a special slide holder and placed in to the X-ray diffractor.

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[6] www.xpowder.com, 2004 (GR 1001/04. ISBN 84-609-1497-6)

The XPowder software that drives the XRD machine was started and in 15 minutes the database search was complete. The sample was confirmed to be primarily magnesium sulphate ($MgSO_4$) with a small amount of gypsum ($CaSO_4 2H_2O$) also present.

Establishing the presence of the gypsum in the sample, even in a small quantity, is critical in the preparation of a contextualised organic crystallisation inhibitor for this site.

It is vital that no assumptions about the site are made. Failure to take into account the presence of another material could have a dramatic and possibly deleterious effect on any results achieved. These may include discolouration, localised staining and in some cases undesirable changes to the previous crystallisation locations and processes of the treatment area.

Meeting with Dr María Teresa González-Muñoz

In addition to the field trial being carried out on the use of crystallisation inhibitors at the Monastery of San Jerónimo, the University of Granada has also being carrying out a field trial at the same site on the potential for the conservation of ornamental stone by *Myxococcus xanthus*-induced carbonate biomineralisation. This field trial relates directly to the paper published in 2003 by Professor Carlos Rodriguez-Navarro, Professor Manuel Rodriguez-Gallego, Professor Koutar ben Chekroun and Professor María Teresa González-Muñoz.

Professor Rodriguez-Navarro introduced the Fellow to Professor María Teresa González-Muñoz and went to examine the site of UGR’s first field trials at the Monastery of San Jerónimo. The timing of the visit could not have been better as the attempt at consolidation of in situ ornamental stone had commenced only six weeks previously and this was to be the first observation of results.

This research work and field trial is a result of a 13-year partnership between UGR’s Department of Mineralogy and Petrology, and the Department of Microbiology. Many attempts have been made to repair or consolidate stone that has been subjected to the expansionary forces of crystallising salts. Many attempts have been unsuccessful, largely because of the incompatibility between the stone or material treated and the nature of the material applied in the treatment. In many cases attempts at consolidation have proven to be counterproductive and in some cases have accelerated the deterioration processes.

UGR’s researchers use a common soil bacterium called *Myxococcus xanthus* to consolidate and rebuild in situ the original stone in historically significant listed buildings. The UGR team nurture the naturally occurring microorganism by feeding it a broth that encourages it to grow. The broth is sprayed repeatedly on to the surface of the stone and drawn in by capillary action. During the growth phase the microorganism produces calcium-carbonate cement, which consolidates and protects the material being treated.

UGR research has shown that the newly formed carbonate reduces the water permeability of the stone while maintaining its transpiration properties, thereby allowing gas exchange. It also promotes a greater cementing of the mineral particles that make up the stone making it more resistant than the original. These processes occur without altering the colour of the stone and without plugging its natural pores.

The International Experience

Noteworthy results have been achieved by Rodriguez-Navarro et al. (2003) treating calcarenite with cultures of *Myxococcus xanthus*. In this instance the original porosity of the stone was 28 per cent and that of the treated stone 26 per cent, with almost no alteration of the mean pore size distribution. With regard to stone consolidation, after the use of different culture media, treated and untreated samples exposed to five 5-minute cycles of ultrasonic treatment showed that the untreated stone lost more than 0.9 per cent of its weight while the samples treated with *Myxococcus xanthus* in one of the media had less than 0.4 per cent loss with another below 0.6 per cent.

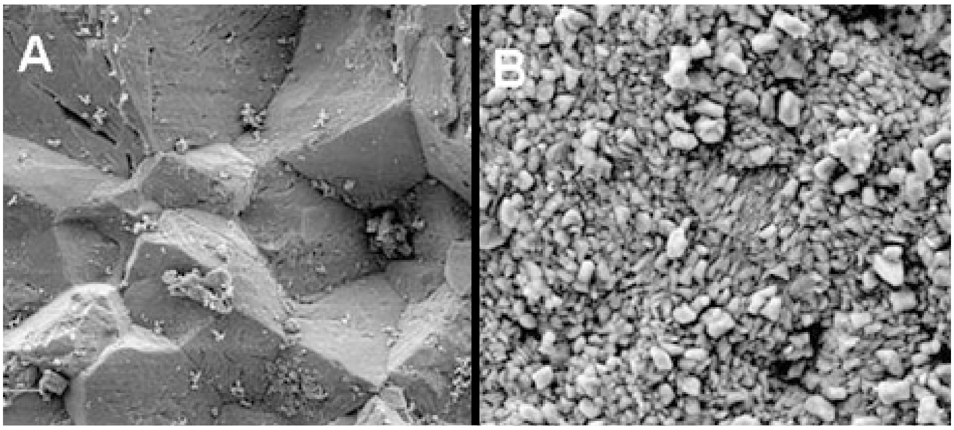

Figure 20. Shown here are two samples of Macael marble. One is untreated and the other treated following the protocols described for calcarenite in the work of Rodíguez-Navarro et al. (2003). The newly formed calcite crystals are very compact and grow epitaxially on the substrate.

The field trial focused on the two major masonry units at the base of the jambs of the doorway to the chapel. The bases of both stones are in direct contact with the tiled surface of the cloister. The cloister would have been mopped daily by the monks and more recently by the nuns. A damp proof course of any description has not been incorporated into the structure (or may have been and has been bridged by subsequent increases of corridor levels).

Figure 21. The two major masonry units at the base of the jambs of the doorway to the chapel

The moisture from the daily mopping and any salts it contained would have come into contact with the base of the stone and been drawn inwards and upwards by capillary action. The moisture then evaporated and the salts remained to concentrate and crystallise. This process would have been repeated at least daily for almost 500 years. The crystallisation and dissolution of the crystals upon further wetting would have been relentless and the expanding force of the salt crystals has then exceeded the rupture modulus of the pore, breaking grain from grain, leading to a complete failure of the stone.

The International Experience

Figure 22. Professor María Teresa González-Muñoz and Professor Rodriguez-Navarro measure and record the results of UGR's first Myxococcus xanthus field trials

It was a privilege for the Fellow to be present when the researchers came to check their work for the first time. Only half of each stone had been treated with the broth and the results were incredible. Although the testing was done using electronic instruments even a simple rubbing of the treated and untreated areas showed the remarkable recovery of the stone in a matter of weeks.

Figure 23. Hands-on experience for the Fellow at the Myxococcus xanthus field trial evaluation

The International Experience

The surface of the treated area appeared to have been glued together using invisible glue. The glue is actually newly precipitated calcium carbonate that does not affect the transpiration properties of the stone, block its pores or change its colour.

On the end of the Fellow’s second week in Granada a documentary production team from Euronews television arrived at the UGR Department of Mineralogy and Petrology to meet with Professor Rodriguez-Navarro and his colleagues to learn about their work in crystallisation inhibitors and *xanthus*-induced carbonate biomineralisation.

Figure 24. Professor Rodriguez-Navarro talks to Euronews about UGR’s research and development work in the field of heritage conservation and the Fellow talks to Euronews about the impacts of salinity in Australia.

In preliminary discussions during the previous week, Professor Rodriguez-Navarro had informed Euronews that he was hosting a visiting ISS Institute Fellow from Australia. In response to their request for comment on the program the Fellow participated in the segment. The resulting four-minute piece titled ‘A Future for the Past’ was subsequently shown on the Euronews ‘Terra Viva’ program six weeks later. A transcript of the Euronews segment is provided in Attachment 1.

Knowledge Transfer: Applying the Outcomes

The University of Granada has undertaken innovative research into the development of affordable solutions aimed at reducing and eliminating salinity-related deterioration of masonry in built cultural heritage. Their research is directly transferable to the Australian situation where salinity-related threats to our built cultural heritage continue to increase.

This Fellowship has resulted in the establishment of a significant international relationship and important skills and knowledge have been gained. It is vital that the skills and knowledge obtained by the Fellow be shared with those best placed to recognise and appreciate their value and to advise on how best to act on the opportunities presented.

Transferring the skills and knowledge learned through the Fellowship has already commenced. At the Urban Salt Conference to be held in Sydney in June 2010 the Fellow will give a presentation titled 'The Use of Crystallisation Inhibitors to Minimise and Ultimately Control Salinity – Induced Deterioration of In-Situ Masonry'.

Skills gained through the Fellowship will also be disseminated through the NSW Department of Environment, Climate Change and Water (DECC&W), Building in a Saline Environment Awareness course presented to builders, engineers, architects and local government surveyors.

Information sharing meetings are also being planned for late 2010 at the Institute for Environmental Research, Australian Nuclear Science and Technology Organisation.

Recommendations

Government

Government at all levels should take every opportunity to begin to trial the methods developed and tested by the European SALTCONTROL partners and, where appropriate, apply them to salinity-impacted heritage building stock.

Recommendation: That relevant Australian, State, Territory and Local Government departments and agencies take note of the outcomes of the EU SALTCONTROL project and initiate testing and implementation programs utilising the knowledge on salinity control and alleviation flowing from this project for application to Australia's heritage building stock.

Industry

Recommendation: That industry investigates the potential of using the techniques described in this report for improving conservation outcomes for heritage building stock.

Education

Recommendation: That the findings detailed in this report be incorporated into the following courses and units:

Course:	Certificate III Stonemasonry (Monumental/Installation) (BCF30600)
Relevant Unit:	Renovate and restore stone work (BCG3050A)
Course:	Certificate, Diploma, Master of Heritage Conservation (Sydney University)
Relevant Units:	History and Theory of Conservation (ARCH9074) Conservation Methods and Practice (ARCH9028)

ISS Institute

Recommendation: That the ISS Institute continues to seek international opportunities to develop the skills required for organic solutions to the conservation of the built cultural environment.

Recommendation: That the ISS Institute seeks funding support from relevant government departments and agencies to provide further ISS Institute Fellowship opportunities that will enhance the Australian skill base in the use of organic solutions in the field of conservation of Australia's heritage building stock.

Further Reading

Conservation of Ornamental Stone by Myxococcus xanthus-Induced Carbonate Biomineralization, Carlos Rodriguez-Navarro, Manuel Rodriguez-Gallego, Koutar Ben Chekroun, and María Teresa González-Muñoz, Departamento de Mineralogía y Petrología, Departamento de Microbiología, Universidad de Granada, Fuentenueva s/n, 18002 Granada, Spain

Applied and Environmental Microbiology, April 2003, pp. 2182–2193, Vol. 69, No. 40099-2240/03/$08.00+0 DOI: 10.1128/AEM.69.4.2182-2193.2003, Copyright © 2003, American Society for Microbiology. All Rights Reserved. The American Society for Microbiology at http://aem.asm.org/cgi/content/abstract/69/4/2182

Attachments

Attachment 1

Transcript of 'Terra Viva: a Future for the Past'—Euronews, 31 August 2008

Weathering the effects of salt erosion. Historical buildings are constantly exposed to a fast changing environment. Where once the main threat came from smoke stacks and car exhausts, climate change has brought a more subtle risk: salt weathering. This problem has always existed, but is fast getting worse, especially around the Mediterranean. Spain's University of Granada is studying cutting edge methods to limit it.

Professor Carlos Rodriguez Navarro of the University of Granada told euronews:

"This area is more and more arid: there's more and more salt accumulation. There's the problem of over-exploitation of aquifers and more salt is getting into the structures of historical buildings. If we add to all this unsuitable restoration materials, that attract even more salts, we have a kind of a time bomb against our architectural heritage."

He added: "We think this phenomenon has got worse because of climate change. It's a kind of desertification on a small scale."

At the San Jerónimo Monastery, the University of Granada is studying the effects of salt decay and new experimental ways of preserving historical buildings. Bio-conservation is one example: by enhancing the development of local bacteria, a kind of bio-cement makes the stone more resistant.

"Here we have a clear example of salt weathering. In the lower part, salt has crystallised in a way that little by little has eroded the limestone. The stone surface that should be here doesn't exist any more," said Professor Rodriguez Navarro.

In a laboratory not far from the monastery Professor Navarro and his team simulate and accelerate the effects of salt weathering on different materials. As part of the European programme "Saltcontrol" they work on salt inhibitors with astonishing results:

"As we cannot eliminate this problem, we have to live with it, we try to minimise it. Here we put a compound, a polyacrylate, that inhibits the growth of salt crystals and blocks the damaging effect of salts. The salts are still there but they cannot generate pressure within the pores, so they cannot damage stones," explained Professor Rodriguez Navarro.

Inside the Church of San Jerónimo, several mural paintings and decorations are now lost forever because of the salt.

Researchers have found a very simple way of stopping the attack.

Applying a polyacrylate, usually used as a cement smoother, makes salts form as a harmless effervescence and the erosion stops.

Scientists expect the effects of salt weathering to spread to central and northern Europe. In Australia, salt decay has become an economic and social challenge.

Eoin O'Caoimh from the Environmental Department in the Australian state of New South Wales explained: "Salt weathering is a major problem. Private home owners have major problems, the mechanical pressure of salts as they cristallise have caused houses to fall down within 15 to 20 years. Every year our problem is getting bigger and I guess these problems are going to extend here into Europe. It's like we're maybe 30-40 years ahead of you."

The goal in Granada is to develop new ways of protecting Europe's architectural jewels, and also our homes, from subtle threats linked to climate change..

The video of the segment can be found at: http://www.euronews.net/2009/08/31/terra-viva-a-future-for-the-past/