Management of sodium sulfate damage to polychrome stone and buildings

David Thickett* and Bethan Stanley
English Heritage
*david.thickett@english-heritage.org.uk

Abstract

English Heritage holds large collections of polychrome stone. Often the polychromy only remains as small fragments, loosely adhered to the stone surface with any original binders having converted to oxalate. The sixteenth century limestone Thetford Tomb fragments are amongst the most significant part of the collection. Salt analyses indicated very high concentrations of sodium sulfate present, (up to 1.5% by mass of the stone). Considering the very fragile nature of the remaining polychromy and the aggressive nature of this salt, strict preventive conservation is needed to ensure survival of the information. Theoretically, keeping the RH below the thenardite transition line (the RH is temperature dependant) should avoid any damaging salt transitions. Monitoring with acoustic emission in the storage environment, provided a direct tracing of salt transitions. When plotted against temperature, it became clear that transitions were occurring at between 3 and 7% lower RH than expected from theory. Tests with pure sodium sulfate powder coincided with the theoretical values. The most likely reason is the effect of the pore structure, particularly fine pores. The values are consistent for a single piece of stone and vary between pieces. A good correlation was observed between acoustic emission events and small pieces appearing on the imaging plate of a prototype particle deposition analyser. Loss of material from two interior building surfaces was monitored using a similar automated camera system. Inspection of the environmental data when material fell, shows similar depression of the RH below the theoretical values for sodium sulfate.

Keywords: Sodium sulfate, polychromy, acoustic emission, image analysis, preventive conservation

1. Introduction

English Heritage holds large collections of polychrome stone. Often the polychromy only remains as small fragments loosely adhered. Such material is extremely susceptible to salt damage and evidence of polychromy can easily be lost. Sodium sulfate is an extremely damaging salt and used in several salt crystallisation tests. It undergoes an over 300% expansion when converting from the anhydrite, thenardite to the decahydrate, mirabilite. The RH that this conversion occurs at is strongly temperature dependant. Controlling temperature and RH can prevent the damage. However, the exact parameters are needed to design effective control.

The sixteenth century limestone Thetford tomb fragments are amongst the most significant part of the collection. They formed the focus of a major recent historical research project. The tomb was destroyed during the English Reformation (1530s) and the small (less than 24 cm) pieces were exposed to the elements for almost half a century before acquisition into the National collection. In these circumstances it is highly likely...
that the original organic binder present with the pigment has converted to oxalate. This makes the pigment stone bond extremely weak.

Two techniques have been used to directly monitor salt transitions or material loss caused by them. Acoustic emission allows a direct measurement of certain phenomena. It has been used to monitor sodium sulfate transitions and stone decay. The data can be of sufficient time resolution to allow direct correlation with environmental data. Automated image analysis of a glass plate was used to monitor material falling from the carved surfaces of the pieces. Various other analytical techniques were used to determine the nature of the lost material.

2. Methods and Materials

Salt analyses were undertaken with 0.4 mm drilled samples from break surfaces. The first 2 mm of the sample from the surface was discarded and sampling continued for another 10 mm after that. The sample volume was over thirty times the maximum grain volume of the fine grained limestone determined by eye. The samples were dried at 110 °C and extracted with 18.2 MΩcm/cm water. The filtered solutions were analysed with a Dionex DX600 ion chromatograph with AS14A column and an eluent of 8mM sodium hydroxide and 1mM sodium bicarbonate for anions and CS12 column with 1mM sodium carbonate and 1mM sodium bicarbonate for cations. Mixed by grinding to obtain a composition close to the soluble extracts from the stone object with highest percentage of non sulfate and sodium ions (object number 78101879), hence referred to as impure sodium sulfate. Water was added to form a solution and this was dried at 60 °C in a Bakelite top. When dry the top and impure sodium sulfate was placed on top of a WD acoustic emission sensor. These were placed in an environmental chamber and the temperature set to 15, 20, 25 and 30 °C. At each temperature the RH was increased from 5% below the pure sodium sulfate transition RH at 0.2% intervals using glycerol solutions.

The temperature and RH was measured with a Rotronic Hygrolog logger. The RH at which significant acoustic emission occurred was taken to indicate the transition. Acoustic emission sensors were attached to the five pieces for twelve months in their storage environment. The temperature and RH was monitored beside each block with a Rotronic Hygrolog D logger with hygclip probe, calibrated with UK National Measurement Accreditation Service traceable standards. Triaxial shock loggers (MSR145) were attached to two pieces to assess shock events that could be detected with the sensors and, potentially mis-interpreted, as salt activity. Acoustic emission monitoring of wooden objects has been limited by large amounts of noise.

Further tests were undertaken with two pieces of stone (4.2 by 2.3 by 1.8 and 2.2 by 4.5 by 2.0 cm). The acoustic emission, T, RH (using a calibrated Meaco system) and impure sodium sulfate laden group of brick casemates at Fort Brockhurst, on the South coast of England. The prototype image analysis system was placed under a mortar joint exhibiting powdering and loss. Salts had been observed mainly to act at the mortar and not the brick surfaces. The T and RH were measured with a Meaco system. The casemates are dark when not in use. The increase in percentage coverage of the glass plate was measured with image analysis (Image J) every...
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2. Methods and Materials

Salt analyses were undertaken with 0.4 mm drilled samples from break surfaces. The first 2 mm of the sample from the surface was discarded and sampling continued for another 10 mm after that. The sample volume was over thirty times the maximum grain volume of the fine grained limestone determined by eye. The samples were dried at 110°C, and extracted with 18.2 MΩ cm water. The filtered solutions were analysed with a Dionex DX500 ion chromatograph with AS14A column and an eluent of 8mM sodium carbonate and 1mM sodium bicarbonate of the Caenstone. Staining with iodine vapour indicated no remaining organic material on the stone surface or in the interior (the blocks were cut).

A set of preliminary experiments were also undertaken to determine the effect of the other small concentrations of ions present on the acoustic emission detection of the hydration transition. Salts (sodium, calcium and potassium sulfate, sodium nitrate and chloride) were mixed by grinding to obtain a composition close to the soluble extracts from the stone object with highest percentage of non sulfate and sodium ions (object number 78101897), hence referred to as impure sodium sulfate. Water was added to form a solution and this was dried at 60°C in a Bakelite top. When dry the top and impure sodium sulfate was placed on top of a WD acoustic emission sensor. These were placed in an environmental chamber and the temperature set to 15, 20, 25 and 30°C. At each temperature the RH was increased from 5% below the pure sodium sulfate transition RH to 0.2% intervals using glycerol solutions.

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A second set of monitoring was carried out with a sodium sulfate laden group of brick casemates at Fort Brockhurst, on the South coast of England. The prototype image analysis system was placed under a mortar joint exhibiting powdering and loss. Salts had been observed mainly to act at the mortar and not the brick surfaces. The T and RH were measured with a Meaco system. The casemates are dark when not in use. The increase in percentage coverage of the glass plate was measured with image analysis (Image J) every
3. Results

The salt analyses for the Thetford polychrome stone are shown in Table 1. Errors are in the order of 3% of the calculated value. The errors were calculated from the reproducibility of multiple standard injections on the ion chromatograph, the calibration graph, and the stated error in the measuring balance and measuring pipettes used to prepare the solutions. The major anion is sulfate, which makes up over 97% of the anions present. The levels are very high, over 1.2% by mass of the stone. Sodium is the predominant cation, making up over 88% of the cations present.

The temperature and RH recorded when acoustic emission events were observed, are shown in Figure 1. The mirabilite to thenardite transition for pure sodium sulfate (pure) is marked on the figure. Figure 1 also shows three of the four points determined for the impure sodium sulfate (labelled impure). They are coincident within the experimental parameters (1% RH). The fourth, higher temperature point was not plotted, to allow better reading of the graph. It also was coincident with the pure transition value.

Acoustic emission is occurring a few percent RH below the theoretical transition line in all instances. The stated accuracy for the probes is 0.03ºC and 0.8% RH. All RH values were within 1% during the three point calibrations. The RH is plotted to one decimal place. The digital output from the probe gives a much higher precision but was not used with no way to check the calibration to that level of accuracy. The traceable standards are only valid to one decimal place. The depression value.

Two reasons for this observed RH depression were postulated. Slow ingress of RH and T into the stone, could retard the transition behind the prevailing ambient conditions. The presence of fine porosity could reduce the critical RH of the transition through the Kelvin effect. This has been postulated for sodium sulfate, but this is the first experimental evidence. Examination of the T/RH traces before the observed transitions indicated a large proportion, over 25% where if this was due to a lag in heating or RH transmission, then the transition would have been expected to be observed higher than the theoretical values, due to the environmental data around those instances.

The monitoring experiments at Fort Brockhurst and Rangers House showed powder falling from the mortar and plaster, coinciding with 4% and 6% RH below the thenardite to mirabilite transition line.

4. Discussion and Conclusions

It has been shown that the hydration transitions of sodium sulfate in some porous matrices can be lowered by several percent RH from the expected equilibrium values. This has also been shown to relate to the amount of loss observed. Care needs to be exercised when interpreting both acoustic emission and material loss data. Several other phenomena can cause acoustic emission, and its use for monitoring wooden objects has been impacted by significant noise. Ca-
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reful control of the environment reduced this in these three instances. When salt expansion occurs, loss of material may not be instantaneous and lose, hardly bonded material is often observed, on surfaces. This could fall at a later date. Small numbers of events were detected with acoustic emission and no powder loss and two instances of powder loss with no acoustic emission due to large shock events. However, the overall excellent correlation between the two sets of results gives a reasonable degree of confidence, that the events detected fit the interpretation presented.

This effect has important ramifications for designing environments to control such phenomena. Display of some of the Thetford pieces was achieved in a dehumidified showcase, controlling the RH below 60% RH using a Miniclimate unit. This value was determined by the research presented and knowledge of the minimum temperature likely to be encountered. Without the research, a value of 70% would probably have been used, reducing the conditioning load, but potentially allowing further damage to occur. The showcase was designed with a flat dark metal panel below the polychrome objects on display so any loss would be readily visible. This was examined every two years with magnification and any suspect particles analysed, as described previously. No pigment or limestone particles were detected during eight years on display. Depending on the situation, it is often not possible to achieve sufficient environmental control to totally stop an effect and the result is often expressed in a calculation of number of transitions. With the often complex environments in heritage buildings, even small changes in parameters can affect the number of transitions observed. Figure 3 shows the number of events where the transition line was crossed from the thenardite, into the mirabilite region at English Heritage sites with polychrome stone. For each location, four values are shown, those calculated from the equilibrium line and those, 3, 4 and 6% below.

In some instances, (Beeston store 4% and St Augustines Abbey 6%), the number of transitions increases dramatically, due to the nature of the environment. It was proposed to move the Thetford material from its existing store to a newly created store. The existing store environment was assessed using damage functions developed from this work and compared to the anticipated new store environment.

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Conservation of marble artifacts by phosphate treatments: influence of gypsum contamination

Enrico Sassoni1*, Gabriela Graziani1, Elisa Franzoni1 and George W. Scherer2
1 Dept. of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, Italy
2 Dept. of Civil and Environmental Engineering (CEE), Princeton University, USA
*enrico.sassoni2@unibo.it

Abstract

The use of ammonium phosphate solutions has proven to be very promising for protection and conservation of marble. However, all the studies carried out so far have been performed on uncontaminated marble. Unfortunately, this is rarely the case in the field, because marble artifacts exposed outdoors are often affected by sulfation, i.e. formation of a gypsum crust on the surface. Because gypsum is much more soluble than calcite, the outcome of the ammonium phosphate treatment is expected to be sensibly altered by the presence of gypsum. Therefore, in this study the nature and morphology of the new calcium phosphate phases formed by reacting gypsum with aqueous solutions of diammonium hydrogen phosphate (DAP) were investigated. In particular, the effect of DAP concentration, ethanol addition (aimed at reducing gypsum solubility), and pH were explored. The result is that phase formation can be controlled by suitably tuning the above mentioned parameters. Phases with low solubility (such as tricalcium phosphate and hydroxyapatite) can be obtained by increasing the ethanol concentration, the DAP concentration or the pH. However, their formation is associated with diffused cracking, likely because of excessive growth of the new phases. Among the investigated formulations, treatment with a 0.1 M DAP solution with 30 vol% ethanol at pH=8 seems to be the most suitable one, as it leads to formation of brushite (about 30 times less soluble than gypsum), without cracking, so that a reduction in gypsum solubility in rain is expected.

Keywords: marble, gypsum, black crusts, hydroxyapatite, protection

1. Introduction

Aqueous solutions of diammonium hydrogen phosphate (DAP, (NH4)2HPO4) have proven highly promising for protection and consolidation of marble.1-4 Thanks to the reaction between the phosphate solution (also containing a calcium source) and the substrate, new calcium phosphate (CaP) phases are formed1. These new phases are able to improve marble resistance to dissolution in rain (thanks to their lower solubility than calcite)2 and marble cohesion (thanks to their bonding action at grain boundaries).1-4 Ideally, the new calcium phosphate should be hydroxyapatite (HAP, Ca10(PO4)6(OH)2), which is the least soluble CaP phase in aqueous solutions at pH > 4.5, 6 However, depending on the reaction conditions (e.g., pH or addition of external calcium sources), different CaP phases may form in aqueous solutions at pH > 4.1, 2, 3 However, depending on the reaction conditions (e.g., pH or addition of external calcium sources), different CaP phases may form alongside HAP, such as octacalcium phosphate (OCP, Ca10(HPO4)6·5H2O), β-tricalcium phosphate (β-TCP, β-Ca3(PO4)2), brushite (CaHPO4·2H2O), monocalcium phosphate monohydrate (MCPM, Ca(HPO4)2·H2O) and monocalcium phosphate anhydrous (MCPA, Ca(HPO4)2). These phases have sensibly different solubility in water1, hence the exact nature of the new CaP phases is fundamental for success of the treatment.