

Management of sodium sulfate damage to polychrome stone and buildings

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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.^{1, 2} 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.³ 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.⁴ The tomb was destroyed during the English Reformation (1530s) and the small (less than 24cm) 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 transitions⁵ and stone decay.⁶ 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 0.4mm drilled samples from break surfaces. The first 2 mm of the sample from the surface was discarded and sampling continued for another 10mm 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 18.2MOhm/cm water. The filtered solutions were analysed with a Dionex DX600 ion chromatograph with; AS14A column and an eluent of 8mM sodium carbonate and 1mM sodium bicarbonate for anions and CS12 column with a 1mM methane sulfonic acid eluent of for cations. The solution ion concentrations were converted to percentages by mass based on the dry mass of stone.

Five pieces were analysed with acoustic emission. Initially, the performance of two instruments was compared. A Physical Acoustics Pocket AE system was used with WD sensors (1-1000kHz, non resonant) with and without Slyglide couplant. A Hanwell Woodwatch was also assessed with the supplied sensor (1-

1000kHz, 150kHz resonant), clamped to the stone and with couplant present as well. Test blocks (6cm by 6cm by 6cm) of Caenstone impregnated to give approximately 1 and 0.2% sodium sulfate by weight, were exposed to increasing RH. The RH was generated in a polycarbonate chamber with a commercial Rh generatore, (Preservatech MiniOne unit). Slyglide couplant gel was found to be required to achieve sufficient sensitivity for the Woodwatch sensors with the 0.2% sulfate blocks. The Woodwatch system generated signals for the 1% sulfate blocks, but this was not deemed sensitive enough. Two cycles with the 0.2% sulfate blocks generated loss from their surfaces. More of the Woodwatch units were available to the project, although the use of couplant is not ideal. Removal of the couplant was investigated. Acetone was found to remove all visible residues of the Slyglide from 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 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.⁷

Object number	Ion concentration (% mass/mass of dry stone)					
	chloride	nitrate	sulfate	sodium	potassium	calcium
78101879	0.022	0.020	1.354	0.485	0.004	0.054
78101845	0.015	0.014	1.335	0.478	0.001	0.043
78101881	0.008	0.009	1.251	0.449	0.002	0.046
78101843	0.008	0.009	1.247	0.448	0.000	0.032
78101880	0.012	0.011	1.224	0.433	0.003	0.041

Table 1: Ion concentrations extracted from drillings of Thetford Tomb limestone

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 hygriclip 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.⁸

Further tests were undertaken with two pieces of stone (4.2 by 2.3 by 1.8 and 2.2 by 4.5 by 2.0cm). The acoustic emission, T, RH (using a calibrated Meaco system with Rotronic hydroclip probes) and vibration were monitored. Each stone was placed above a prototype image analysis system, such that any material lost, fell onto a glass plate. A digital camera was focused through magnification onto the plate and recorded images with a circumferential LED lighting system every 30 minutes. The side LED lighting and camera/magnification combination were

found to reliably detect particles down to 3µm diameter.⁹ The system works well in dark or very low light surroundings. This was facilitated by running the experiments in closed cupboards. Any fall of material onto the plate was determined by subtracting sequential JPEG images using Image J software. A particle appearing in the difference image was assumed to have been lost, in the 30 minute time interval from the stone surface. The position of the particles lost from the polychrome stone and falling onto the glass plate was noted. They were collected with a chemically sharpened needle under magnification every 3 months and analysed with a Renishaw System 1000 Ramascope confocal Raman system, 632.8 nm laser, Nicolet Inspect FTIR microscope and Eagle III XRF system.

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 join 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

30 minutes. Readings were discarded for 72 hours after the room had been accessed due to dust raised and deposited. Previous experiments had shown over 99.9% of the small amount of dust settled in this period. No activities took place during the monitoring period that would raise large amounts of dust.

A basement store room in Rangers House, London was losing plaster from several areas of the walls. Salt analysis, extracted both from the losses and from drillings indicated sodium sulfate was the predominant salt present in the wall and in one area this made up over 99% of the soluble ions detected. The automated image analysis system was placed below an area on an internal wall' to capture loss and the room temperature and RH measured with a calibrated Meaco system. Access to the store was restricted for the monitoring period, so that re-depositing dust did not cause significant interference.

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 graph¹⁰ 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

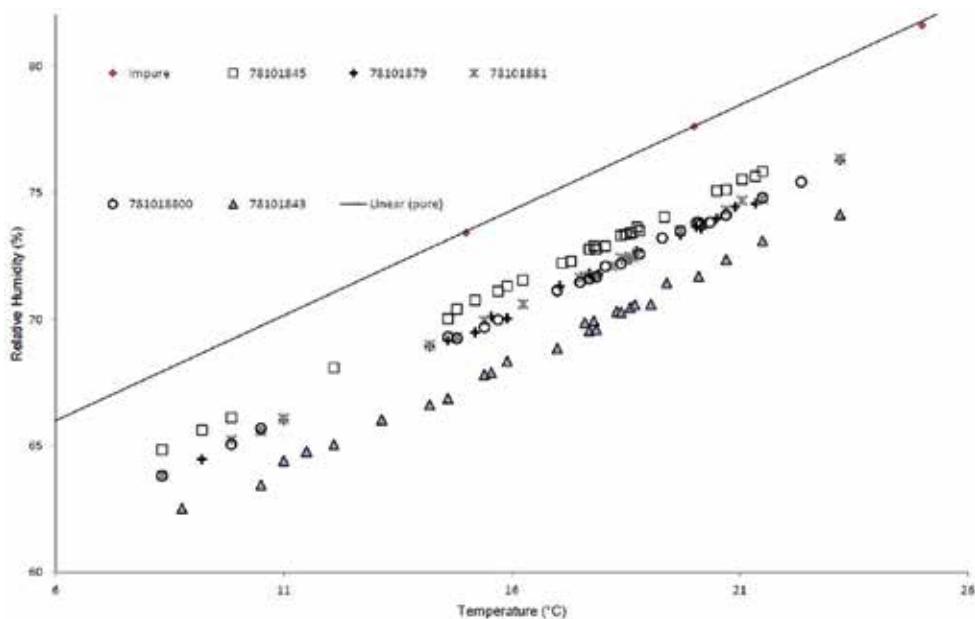


Figure 1: Temperature and RH values at which acoustic emission was observed.

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 0.03°C and 0.8%. 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 give 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 is consistent for a particular piece of stone. Fragment 78101843 showed a value of approximately 6%. Fragments; 78101879, 78101881 and 781018800 showed approximately 4% and 78101845 showed 3%. The store in which the monitoring took place had temperatures mainly between 15 and 24°C during the 7 month measurement period. Lower temperatures were experienced in the last 60 days.

The number of particles lost from stone 78101843 are shown in *Figure 2*.

Powder was observed falling from the objects, generally coincidentally with acoustic emission events detected (within the same 30 minute measurement slot). Three instances were observed with acoustic emission, but no powder detected, generally with lower numbers of acoustic emission events detected. Two instances of powder were observed with no acoustic emission. Examination of the vibration logger data indicated high shock levels coincident with two events. This was probably caused by unusual activity related to transferring files in the library above the room used for the experiments. Similar data was produced with 78101879. The Raman and FTIR microscope analysis showed approximately 30%

of the powder samples were pigments (hematite, carbon black, calcite), over 62% of the powder samples were sodium sulfate anhydrite (the phase information being lost due to the time delay before analysis) and the remainder, limestone powder. The Thetford limestone included approximately 2% iron, which XRF distinguished from calcite used as a pigment, that had no detectable iron present.

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.¹¹ This has been postulated for sodium sulfate, but this is the first experimental evidence.¹² 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.⁸ Ca-

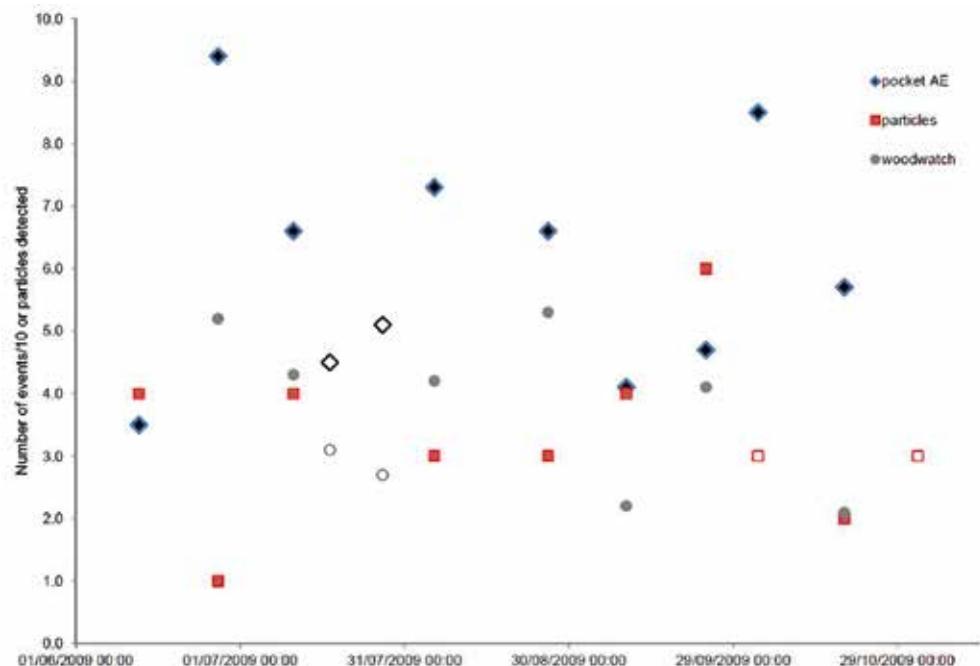


Figure 2: Acoustic emission and particle loss observed from polychrome limestone fragment 78101843

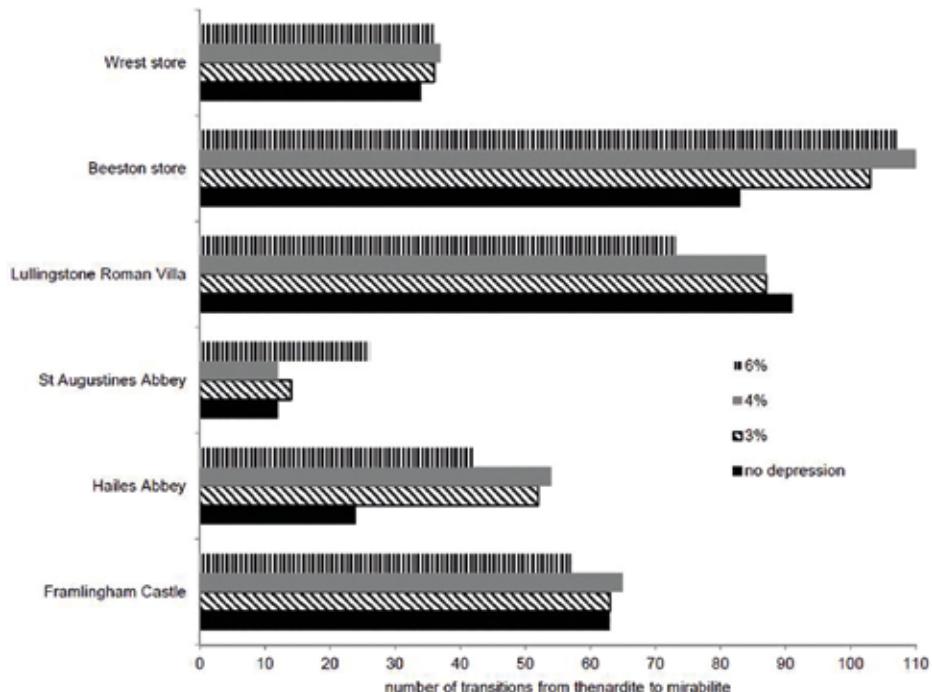


Figure 3: Number of thenardite to mirabilite transitions calculated from environmental data of English Heritage locations with polychrome stone.

reful control of the environment reduced this in these three instances. When salt expansion occurs, loss of material may not be instantaneous and loose, 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 Miniclima 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.¹³

References

- ¹ RILEM, Essais recommandees pour l'alkalisation des pierres et evaluer l'efficacite des methodes de traitement, Materiaux et Constructions (17-75), 1980, 216-220.
- ² Lazzarini, L. and Laurenzi-Tabasso, M., Il Restauro della Pietra, Cedam, Padua 1986.
- ³ Bionda, D., Modelling indoor climate and salt behaviour in historical buildings, PhD Thesis, Swiss Federal Institute of Technology, Zurich, 2006.
- ⁴ Lindley, P.G., Representing Re-Reformation: Reconstructing Renaissance Monuments, <http://representingreformation.net/> accessed 25 May 2017
- ⁵ Grossi, C.M., Esbert, Rosa Maria, Suarez del Rio, L.M., Montoto, Modesto, Laurenzo-Tabasso, M., Acoustic emission monitoring to study sodium sulphate crystallization in monumental porous carbonate stones, Studies in Conservation, (42), 1997, 115-125.
- ⁶ Esbert, R.M, Grossi, C., Suarez del Rio, L.M., Calleja, L., Ordaz, J. and Montoto,

M., Acoustic emission generated in treated stones during loading. In Sixth International Congress on Deterioration and Conservation of Stone Proceedings, ed J.Ciabach, Turon, 1988, 403-410.

⁷ Miner C.S. and Dalton N.N., Glycerol, Reinhold, New York, 1953.

⁸ Jakieła, Sławomir, J. Bratasz, Ł. and Koźłowski, R., Acoustic Emission for Tracing the Evolution of Damage in Wooden Objects, Studies in Conservation (52-1), 2007, 101-109.

⁹ Bowden, D. and Brimblecombe, P., Monitoring dust at Ickworth House with the dust-bug, Views, (42), (2005), 25-27.

¹⁰ ISO11095 Linear calibration using reference materials, 1996.

¹¹ Camuffo, D., Microclimate for cultural heritage, Elsevier, Amsterdam, 1998.

¹² Charola, A. E., and Weber. J. The hydration-dehydration mechanism of sodium sulphate. In Seventh International Congress on the Deterioration and Conservation of Stone, Laboratorio Nacional de Engenharia Civil, Lisbon, 1992., 581-590.

¹³ Xavier-Rowe, A., Newman C., Stanley B., Thickett D., and Pereira Pardo L. A new beginning for English Heritage's archaeological and architectural stored collections. In ICOM-CC 17th Triennial Conference Preprints, Melbourne, ed. J. Bridgland, International Council of Museums, Paris, 2014, art. 1517, 10 pp. (ISBN 978-92-9012-410-8).