Metal Textile Composites and Improved Treatment Outcomes Through Application of In-Situ Corrosion Data

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Abstract

Before embarking on the conservation of the royal collection of the Thai court, housed in the Queen Sirikit Museum of Textiles, it was necessary to establish new methods of examination and assessment using replicas of the traditional court garments. The silver and copper alloys used in the construction of these highly decorated objects and the impact of accumulated sweat residues determined both the extent of corrosion and the nature of the decay products. Use was made of late 20th-century Khon dance costumes belonging to private Bangkok collectors in training exercises in which the critical evaluation of corrosion potential data, pH and chloride ion measurements was made. Specific forms of degradation varied and this, in turn, determined what treatment paths could be pursued with safety to the textile and comfort to the conservator. The sensitivity of the surface pH of textiles to the chloride concentration from sweat was very high. Comparison with data from less humid environments has quantified the impact of high temperature and relative humidity on the decay mechanism. The training program resulted in empowered conservators conducting in-situ measurements on composite textiles that placed the artefacts onto the decision-making tree.

Keywords

Queen Sirikit, textiles, metallic threads, sweat, corrosion, biodegradation, dithionite reduction, Khon dance

Introduction

The royal collection at the Queen Sirikit Museum of Textiles (QSMT) in Bangkok consists of approximately 5,000 textiles associated with the Queen and includes her personal clothing, textile collections and textiles arising from her 50-year SUPPORT Foundation involving rural crafts development. A program of rotating exhibitions about Her Majesty, the King and their textiles involves the full range of conservation activities – from the analysis of materials to the treatment of objects – on a continuing cycle. Many textiles from the 18th and 19th centuries are woven and embellished with metallic threads and adornments, which makes them metal-textile composites for which there are no standard operating procedures. The first training program in Thailand was held in 2016 at the QSMT to assess the treatment issues associated with metallic fabrics, since this type of object is common to the Thai court. Included here are the complex costumes of the traditional Khon dance, a narrative dance form in which dancers are literally sewn into the costumes for periods of up to 8 hours. Such composite textiles need great flexibility owing to the extreme movements performed by the dancers and show copper corrosion products associated with reactions with human sweat. The workshop was the first exposure of textile conservators in Thailand to decision-making based on a knowledge of the pH, chloride and metallic compositions of the objects. Data gained from in-situ measurements provided a matrix for determining which treatment methods were the best to pursue. Planning of the workshop took two years, during which the team leader (Brennan) built trust in the processes with the stakeholders.

There are specific challenges associated with the treatment of royal Thai textiles. The development of the conservation workshop had to consider that many of the young conservators had learned their skills on the job through traditional apprenticeships in the conservation department. Others had some engagement with a course from the CollAsia program (Brennan et al. 2014), but perhaps one of the most significant outcomes of this work was that the results and the pedagogical approach are directly transferable to textile collections throughout Southeast Asia and the Pacific Islands. While signifi-

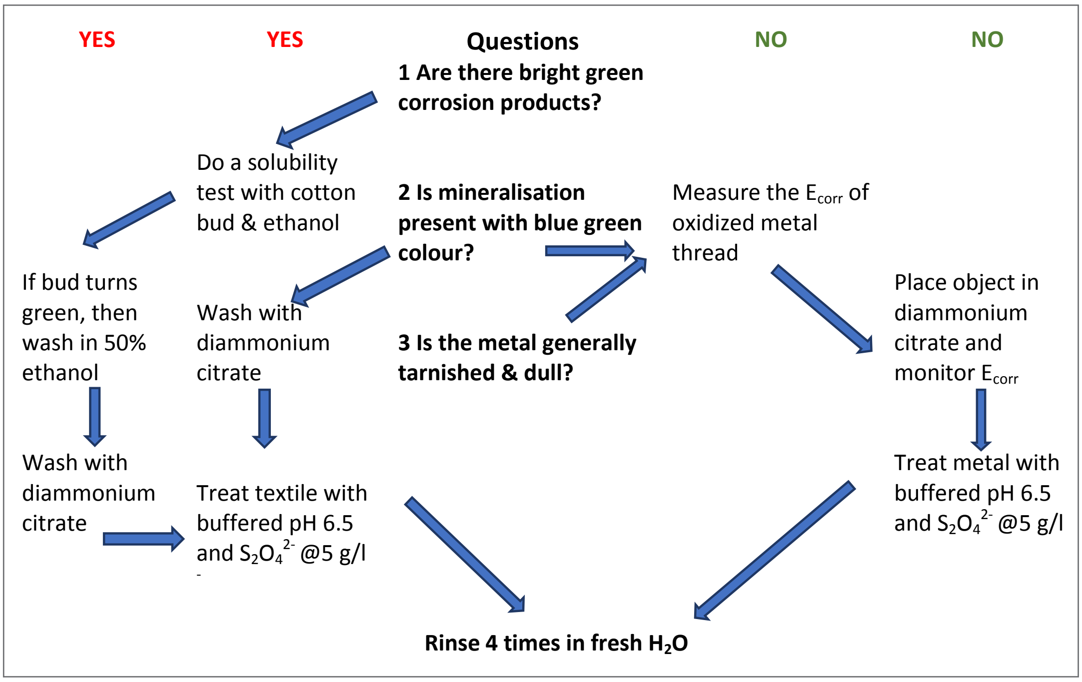

Figure 1. Decision-making tree for treatment of composite textiles

cant inroads into the challenges of stabilising textile collections in Singapore have been made (Janaway and Cunningham 1995), this has been a long-term process involving many millions of dollars. The *raison d'être* of the workshop was to use the experience at the QSMT as the launch pad for an Asia-wide approach to understanding the decay and conservation needs of composite metallic textiles. The workshop empowered the conservators to become more able to achieve good collection outcomes when negotiating with curatorial managers who understand the practices. By approaching collection items in terms of their significance, their conservation needs and the specific nature of the decay of the metallic elements, it was possible to demonstrate that even the most difficult and problematic items could be managed through a decision-making tree (Figure 1). This approach removed a lot of stress from the individual conservator by developing appropriate treatment options. Additionally, the project sought to build the confidence and leadership skills of the local team which should open pathways to additional training, including their own implementation of workshops in regional and rural collection centres in Thailand.

Collection samples

Given the experimental nature of the workshop, the historic textiles belonging to the Royal Court could not be directly used due to their high cultural value and rarity. Protocol demands that only proven approaches to textile conservation are acceptable for any Royal items. Thus, textiles from private collections were sourced for the workshop since they exhibited a wide range of deterioration issues. The fabrics were mainly cotton, silk and some woollen materials. The owners were happy to have their items tested, assessed and treated as part of the workshop outcomes. These textiles included typical netted robes called 'sua khrui', with heavy metallic thread brocades typical of the late1800s and 1900s royal costumes, and long lengths of cloth worn as hip wrappers by the court and in dance traditions called 'pha nung', as well as many dance costume components such as collars, arm bands, belts, leggings and jewellery (Salim 2015) (Figures 2 and 3). New approaches were needed to develop treatment protocols for Royal metallic textiles – which are rarely worn and often highly corroded – and dance costumes – which are heavily used, poorly stored and heavily corroded.

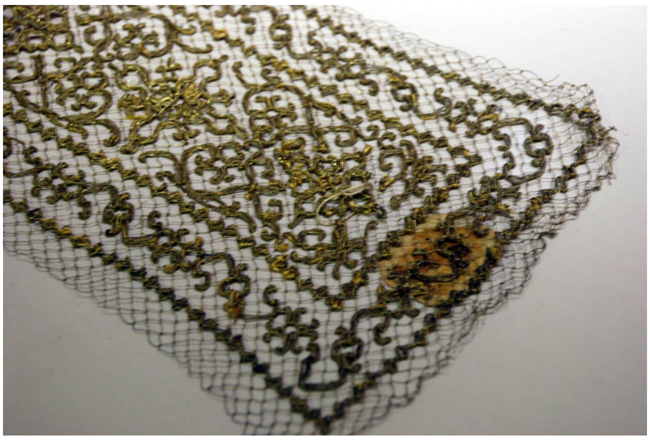

Figure 2. Stained Thai 19th-century textile embellished with gilded Indian silver alloy thread

Figure 3. Owner of a Burmese jacket (centre) watching Rinske Car and Julia Brennan treating the object

Study methods

The workshop was structured into theoretical and practical lectures on the nature of metal alloys used for decorative purposes and how they can be identified without access to modern expensive instrumentation such as x-ray fluorescence (XRF) and Fourier transform infrared spectroscopy (FTIR). The program covered the sensitivity of alloys to corrosive elements found in tropical climates, which included issues of the high relative humidity, high temperatures and persistent low levels of hydrogen sulfide emanating from nearby drains and canals in Bangkok. All these factors accelerate corrosion of metals. The loaned textiles provided excellent samples of how metal decay processes can also impact on the rates of deterioration of the associated textiles. Training presentations were interspersed with hands-on testing and cleaning procedures that illustrated the technical sessions, thus consolidating learning. Treatments included the use of chelating agents to remove the corrosion products from the metal surfaces which obscured the structural details of the textiles. Optical examination under 20× hand lenses and a binocular microscope proved to be sufficient to characterise the degradation of the silver-copper alloys. In the characterisation steps it was important to use only methods that are inherently available in low-funded regional conservation centres.

The training workshops involved combinations of discussions about the nature of metals and what can be gleaned from the nature of the different corrosion products. Simple spot tests for solubility of blue-green copper corrosion spews, using ethanol-soaked swabs, clearly demonstrated the difference between organic copper complexes and inorganic corrosion products which are only soluble in acidic or chelating solutions. The textile conservators integrated their topics of the traditional weaves of village-based looms versus machine-assisted woven fabrics and how natural silk fibres have a different response to relative humidity than those of cotton, flax and hemp. The textile discussions included how the metallic threads were made and then woven into the fabrics to create the lustrous and highly valued garments. Gradually, there was a significant change in the approach by the local conservators who, emboldened by their own practical measurements and trained in the interpretation of the analysis of the results, began to see the strategic advantages of knowing much more about the nature of the collections on which they were working. Prior to the workshop, traditional responses to the artefacts took the least interventive approach possible, since this appeared to pose the least risk. Another important aspect of the training was to develop cheap methods of analysis, as expensive analytical equipment is currently not feasible for the QSMT conservation lab.

Corrosion potential measurements

The first essential step for the local conservators was gaining confidence in taking direct measurement of the corrosion voltages of the textile alloys. The reference electrode was a silver chloride (Ag/AgCl, 3 M KCl) and a platinum working electrode connected to a digital multimeter, with the reference plugged into the common terminal. Corrosion potential measurements have previously been used to determine alloy contents on a wide range of artefacts (Degrigny et al. 2011) and were made by inserting the platinum wire electrode (2 mm o.d.) through a section of a domestic sponge rubber cloth to touch the metallic elements and establish electrical contact. The sponge was wetted with carbonated mineral water (Perrier, France), which acts as a mildly alkaline electrolyte. The 'sponge method' is remarkably effective at enabling corrosion measurements to be done on embroidered threads and attached bells, sequins, etc., without wetting the textile or leaving any tell-tale tide line, which could occur from partial immersion. Calibration voltages were developed using assayed jewellery items and other known alloys belonging to the training team and from personal jewellery. Thus, the characteristic corrosion potentials (E_{corr}) of white gold, 18 ct. and 9 ct. gold alloys, sterling silver, sterling silver with 2% zinc, metallic copper and brass voltages were all recorded (Table 1). These measurements were reproducible within

± 2 mV by touching the platinum electrode at new contact points on the same object. Measurements of the surface and solution pH were made using a Thermo Instruments flat surface electrode connected to a Thermo Star A121 portable pH meter. Measurements of chloride ion activity (Merck QuanTab test strips) established that many objects would need desalination to remove the sweat and to rid the textiles of acidity associated with the biodeterioration of the fabrics.

Table 1. Corrosion potentials of metal objects for reference and with composite Thai textiles

Object	$E_{corr.}$ volt vs. Ag/AgCl	Object	$E_{corr.}$ volt vs. Ag/AgCl
white gold earring	0.262	silver Roman coin ring	0.119
white gold ring	0.210	rose gold ring	0.095
cleaned gold ring	0.182	Khon plated brass sequins	0.050
sulfided Ag sheet	0.161	Thai brass	0.034
18 ct. gold ring	0.154	Thai soutache threads	-0.040
Sterling Ag 2% Zn	0.145	Thai Indian Ag	-0.089

Results

Acidity and sweat

The decision-making tree (Figure 1) was used in group discussions with the team at QSMT and this approach enabled the treatment of both acidity and sweat as one issue. There are specific deterioration problems associated with residual sweat which adversely affect both the textiles and the metals. Confidence-building exercises involved pairs of QSMT staff working since their natural shyness inhibited individual responses. During the training workshop it was demonstrated that without the prior removal of copper corrosion products before reductive consolidation unsightly bright pink metallic copper can be deposited on the surfaces. An example of the 'invisible copper' problem was demonstrated by following the gradual increase by 60 mV in the positive direction in the E_{corr} values of 18-carat gold rings in diammonium citrate. Although there was no apparent corrosion problem, the corrosion potential increased from 0.044 to 0.104 volts vs. Ag/AgCl over 15 minutes as the diammonium citrate complexed the 'invisible' layer of cuprite. The conservators were amazed at the power that had been given to them with just a couple of electrodes.

By the end of the program the conservators at the QSMT had their tables of E_{corr} values and the correlation of the values with known compositions as discussed above (Table 1). They rapidly developed the confidence to identify methods to remove copper corrosion products and to bring about safe and cost-efficient treatments which also removed chloride ions and the acidic bacterial metabolites. During the last two days of the workshop, the conservation staff reported the results of their tests on the amount of salt (as measured by the chloride test strips) and the surface pH of the textiles. When all the results were tabulated, it became apparent that there was a direct causal link between the amount of sweat (as indicated by the chloride strips) and the observed acidity of the textiles, with most of the data coming from the Khon costumes (Figure 5).

Bacteria degrade fabrics in the ambient conditions of high relative humidity and temperature in Bangkok, with a mean annual relative humidity (RH) of 76.0 ± 2.8% and temperatures of 28.4 ± 1.9°C. The apparent sensitivity of the rates of deterioration on water activity was indicated by comparison with data from the much drier climate in Western Australia, which had corresponding values of RH of 51.8 ± 10.0% and temperature of 20.7 ± 5.7°C (Figure 4). The correlations between the pH and chloride were tested using linear regression analyses in Excel. The square of the correlation coefficient, R^2 values, provides a guide as to the statistical validity of the fit to the equation. For the Thai Khon costumes, the R^2 value for the correlation between pH and chloride ion (ppm) was high at 0.98 and Equation 1 describes this relationship.

$$pH_{Khon} = 5.73 - 0.0007\,[Cl] \qquad (1)$$

The slope of the pH vs. ppm [Cl] means that for every 1,000 ppm or gram of chloride in the textile, the pH will fall by 0.7 units, or there will be a five-fold increase in the concentration of hydrogen ions. The high degree of correlation reported in Equation 1 is seen through the small error of ± 0.05 in the pH intercept value (less than 1%) and an error of ± 0.00004 or 6% in the slope. This is one of the first reported direct relationships between the amount of sweat in textiles and the surface pH for tropical textiles. Similar data had been collected from a mid-19th-century *pretiosa* (precious) mitre from the Benedictine community in New Norcia, Western Australia (MacLeod and Car 2016). The regression analysis for the mitre (R^2 0.99) showed that the pH decreased by 0.3 pH per gram of chloride ions, i.e. the acidity of the textiles increased by a factor of two times per gram of chloride, as shown in Equation 2. The R^2 value of 0.99 for the regression for the mitre resulted in only very small errors in the intercept (5.69 ± 0.04) and the slope (0.00030 ± 0.00003) for Equation 2.

$$pH_{\text{front of mitre}} = 5.69 - 0.0003\,[Cl] \qquad (2)$$

The pH of the Khon and of the exterior of the mitre at zero chloride were the same (i.e. the intercepts of Equations 1 and 2 are within experimental errors), which indicates that similar chemical processes had been used in the manufacture of the silk into the textile yarn. It is likely that the underlying reason why the slope of the Thai Khon (Equation 1) was 2.3 times that of the New Norcia silk mitre is the greater availability of moisture and the warmer temperatures of Bangkok, which make for easier microbiological reproduction rates. An opportunity to test this hypothesis occurred during a visit from New Zealand to Perth in the form of an unwashed red cotton dress shirt which had been carried in luggage for four days. The slope of the pH vs. chloride of the shirt after four days was the same slope as the Khon textiles (Equation 1), but the pH of the intercept was essentially neutral, at pH 7.70. After two months in a sealed polyethylene container, containing a beaker of saturated NaCl, the areas previously measured were reassessed. The intercept value of pH had fallen from 7.7 to 6.1, indicating increased biodegradation, but the sensitivity to chloride had decreased to -0.0004 pH/ppm. During the two months in the plastic container, the mean RH of 70.3 ± 2.3% and temperature of 25.3 ± 2.4°C equates to a mean vapour pressure of 17.0 ± 0.6 mm of Hg (mercury). Using mean temperature and relative humidity data for Bangkok, the mean vapour pressure of water was 16.8 ± 2.7, which is the same as the red shirt data, while the New Norcia mean vapour pressure was 9.8 ± 1.8 mm Hg. Work on rock art sites in the Napier Ranges, in the Kimberley region of Western Australia, has shown that in the wet season, the mean pH fell from 7.8 ± 0.8 to 6.4 ± 0.9 due to increased bacterial counts (MacLeod and Haydock 2008).

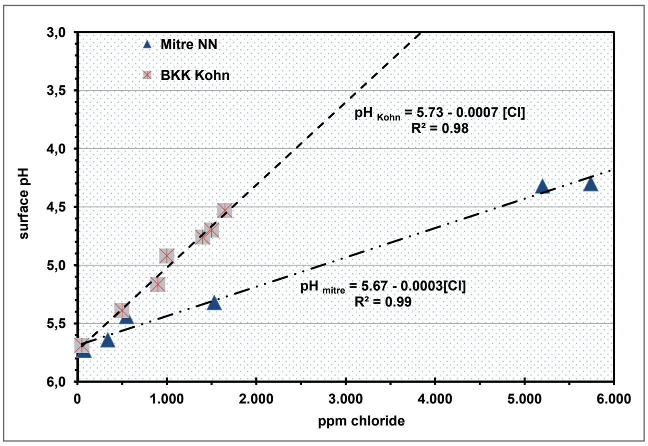

Figure 4. Plot of the relationship between the chloride concentration and the pH of textiles in Bangkok and rural Western Australia

Figure 5. Detail of Burmese jacket before conservation

Removal of copper corrosion from corroded silver alloys

Many of the silver embellishments showed a proliferation of the characteristic blue-green hue of copper (II) corrosion products. Organic copper salts from sweat corrosion are readily removed with methylated spirits, followed by cleaning using neutral pH (6.5 ± 0.1) solutions of diammonium citrate to complex and thereby remove any 'invisible' copper materials prior to the final dithionite treatment. The effectiveness of such washing procedures was demonstrated by placing aluminium foil (commercial cooking grade) into the rinsing solution overnight. Copper which had been removed from corroded silver decorations cemented out on the aluminium foil to give a dull grey-pink deposit and regenerated the complexing solution in the process so that it could be used again, while the contaminated aluminium foil could be simply discarded.

Removal of silver tarnish using neutral dithionite solutions

The efficacy of using weak solutions (0.1 wt%) of sodium dithionite in the neutral pH buffered solutions to remove silver sulfide corrosion products has recently been reported (MacLeod and Car 2014). The treatment for a richly decorated silver and silk jacquard-woven Burmese frock coat was meant to replicate the successful work done on the cope. However, it was determined that the dithionite had partially oxidized to sodium sulfite in the damp storage conditions of the supplying chemical merchant. Although sulfite is a reducing agent, it is not nearly as effective on silver sulfide as the dithionite. This problem presented real challenges as fresh sodium dithionite would take four weeks for delivery. This issue was managed by a ten-fold increase in the concentration of the reducing chemical (Figure 6). This approach demonstrated that if the underlying chemistry of the treatments is understood, it is possible to make adjustments on the spot. An important issue is that when purchasing reactive chemicals, such as reducing or oxidizing agents for a workshop, it might be prudent to pre-ship materials by sea from a known supplier six to ten months in advance, rather than relying on local suppliers. Having been alerted to such issues, trainees can do necessary tests on local chemicals to ascertain their purity and freshness.

Figure 6. Upper section of Burmese jacket following neutral dithionite treatment

Conclusion

The success of the workshop was measured by the engagement of the local conservators with the practical exercises and through their participation in all the learning experiences. One of the keys to the success of this training was the critical ratio of three students per trainer, especially important with a non-scientifically trained group. At the beginning of the program, the standard Thai conservation approach was only to use known methods; if a new object and set of conditions presented itself, then an alternative item would be selected for the exhibition, despite it having less engagement potential with a visitor. Through the process of using pH, chloride and E_{corr} measurements, which were combined with detailed textile condition analyses, the conservation team learned how to develop a decision-making tree. This process increased the confidence of the participants and resulted in greatly improved outcomes. Through a combination of skills of presenters all of the complex processes were able to be explained in a culturally sensitive context. The cultural and operational liaison, including program adjustments as needed, solved many issues. Staff at the Queen Sirikit Museum of Textiles became empowered and they were much more confident in asking questions and defending their proposed treatment programs in front of their colleagues and teachers.

This workshop on developing skills in managing composite metal and textile objects was designed for non-scientifically trained conservators. Amongst the challenges were the language differences and the strict guidelines around royal textiles. Future workshops will be able to develop from the established foundations. It was good that the textile conservator from the USA had many years of experience at the museum and had seen it grow from conceptual plans to the realities of a functioning organisation. Analytical skills developed daily in rapid response, once study materials were fully comprehended. The presentations, which were provided in advance to the attendees, were a very important preparation tool. Although the partial oxidation of dithionite to sulfite resulted in much slower kinetics, it demonstrated ways in which conservation problems can be managed, and so the desired outcome of treating the Burmese dress coat was achieved.

An unexpected bonus of the documentation on the pH and salt levels in the composite metal-textile objects was finding the direct link between increasing chloride levels and the falling pH, which quantified tropical decay mechanisms. The pH on the Khon costumes was found to be much more sensitive than on sweat stained textiles from temperate environments in Western Australia. It is likely that a combination of Bangkok's higher temperatures and relative humidity leads to a much higher absolute humidity that encourages bacterial reproduction and greater rates of chemical reactions involving the depolymerisation of the natural polymers found in the textiles. This data on the rates of biodeterioration in different climates has provided an insight into the specific effects of storage in tropical climates compared with temperate areas. However, it should be noted that the

Thai textiles were cotton with some woollen elements, the New Zealand shirt was cotton, whereas the New Norcia mitre was silk. Plans for a sequential workshop devoted to analysing storage conditions and providing sustainable and tailored solutions for the storage of metallic textiles in tropical climates are already in discussion.

Consolidation of the learning outcomes may also be achieved through engagement with academic and technical staff from a local university who have the necessary expertise to advise the conservators on practical scientific problems. The installation of temperature and relative humidity dataloggers in a number of locations would provide much needed information to assist the trainers in their tasks. Assessment of the microenvironment of the storage conditions for private collections as well as the QSMT royal collections would provide the necessary data for checking on the universality of the impact of perspiration leading to biodeterioration of the textiles and corrosion of the metallic embellishments in tropical climates.

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