Mitigation of the effects of pollutant gases on susceptible objects

Susan Bradley*, James Parker, Philip Fletcher and Lorna Lee

Introduction

Out-gassing from the materials used in the display and storage of museum collections have been shown to cause the corrosion of metals and the formation of mixed salts on porous materials such as limestone, marble and low fired ceramics. The main defence against this is to screen all materials for use in new gallery and store developments and only use those which do not give off corrosive gases (Thickett and Lee 2004). However there are situations where materials which out-gas have to be accepted including the reuse of existing showcases and historic buildings where wooden showcases and structures are part of the building fabric. In a building which does not have a filtered air handling system the ambient reduced sulphur gases are always present and tarnishing of silver occurs. Here the investigation and use of activated carbon to reduce the concentrations of organic acids in the Kings library and the Medieval Gallery, and the experimental work on the use of zinc oxide to reduce the rate of tarnishing of silver are reported.

Activated Carbon

Since 1996 activated carbon has been used in old style wood showcases to reduce levels of organic acids and aldehydes. When first deployed passively in the Medieval Gallery in-case levels of acetic acid appeared to fall by 50%. Most recently activated carbon was deployed in an attempt to alleviate potential problems in the Kings library. Activated carbon has a high capacity for adsorption of acetic acid, a satisfactory adsorption for formic acid, but may not function for adsorption of acetaldehyde and formaldehyde (Anon 2004). For this reason the efficiency of activated carbon has been reviewed with respect to acetic acid alone.

The Kings Library

The Kings Library which is lined with wood book presses is the grandest room in the Museum (Figure 1). When the British Library moved to its new building at St Pancras in London the Kings Library was emptied of books and a plan for its redevelopment as a gallery on the enlightenment was established. Because the room has listed status the wood presses were to be used for display of objects. The acetic and formic acid levels in two of the presses were measured on three occasions during a one year period to provide data to ensure safe display conditions, see Table 1.

Date of monitoring	Acetic acid levels µg/m^3	
	Press 2 (South)	Press 141 (East)
2 - 17/8/2000	1216	502
30/11 – 14/12/2000	562	228
18/6 – 3/7/2001	705	282

Table 1 Acetic acid levels in presses in the Kings Library before redevelopment 2000 – 2001

The measurements showed the expected seasonal variation with higher acid levels present in summer. The difference in levels measured in the two presses was most likely due to poor sealing of the press doors affecting air exchange rates. Based on our experience of monitoring acid levels in showcases and observing the objects on display for signs of deterioration the acid levels would be safe for most of the objects proposed for display. However there were two classes of objects which raised concerns, leaded bronzes and shells. As a result an investigation was undertaken into the use of activated carbon to reduce the level of acetic acid in the presses.

The investigation was carried out by David Thicket and Kristy Short working in the presses prior to the redevelopment (Thickett and Short 2002). They selected four adjoining presses and set up the shelves in them to create four pairs of shelf spaces with each space the same size. Because there was a gap of only 5 and 10 mm between the shelf fronts and the closed glazed doors of the presses they speculated that each shelf space would act as an individual unit, and the level of acids could be controlled independently. Because the environmental monitoring campaign had indicated variability in the level of sealing of the press doors, for the duration of each experiment thin card was pushed into the door seals to mimic the expected level of sealing following redevelopment. The first stage of this work was to establish that the pairs of spaces had similar levels of acetic acid present. Having confirmed this activated carbon cloth was put on to one shelf in each pair to cover 100%, 50%, 25% and 16% of the shelf area and the acetic acid levels measured in each shelf space. The shelf space which had no carbon cloth present was used as a control. The levels of reduction in build up of acetic acid present are given in Table 2. Unfortunately the test in the pair with 50% coverage of activated carbon cloth was ruined by workmen removing the press door.

% Coverage of carbon cloth	Control shelf acetic acid ($\mu g/m^3$)	Test shelf acetic acid ($\mu g/m^3$)	Reduction against control
100	337	76 (at limit of detection)	79%
25	443	222	51%
16	370	239	35%

Table 2 Reduction in acetic acid build up by the use of activated carbon cloth

The experiments summarised here showed that activated carbon cloth could be used to reduce the build up of acetic acid in shelf spaces. However because the wood had to be exposed and could not be covered by fabric further tests were made to establish that activated carbon granules had the same effect. A tray with a perforated lid 650mm wide and 70mm deep which covered 18% of a shelf area was designed to hold the activated carbon. The maximum level of reduction expected from the use of the trays was around 35%. Greater deployment of activated carbon was not possible because of the large number of objects to be displayed on each shelf.

The Enlightenment exhibition opened in December 2003, Figure 2. Monitoring to establish the effectiveness of the activated carbon was undertaken between August and December 2004. Initially the strategy was to measure the acetic acid levels in shelf spaces with activated carbon present and to then remove the carbon tray and re-measure levels after one month. The results of this monitoring were inconclusive there being no significant difference between the pairs of readings in each shelf space. However the measurements may have been affected by the prevailing temperature and RH, see Table 3.

Location	Date monitoring started	Activated carbon present?	Acetic acid (μg/m^3)	Mean RH (%)	Mean temperature (^{o}C)
Press 158 shelf 6	5 August 04	no	188 ? 65	61	19
	16 September 04	no	200 ? 29	49	20.8
Press 158 shelf 2	5 August 04	yes	188 ? 65	58	20.5
	16 September 04	no	165 ? 29	49	20.8
Press 34 shelf 4	5 August 04	yes	164 ? 65	54	22
	16 September 04	no	161 ? 29	48	21
Press 35 shelf 4	5 August 04	Yes	179 ? 65	58	22
	16 September 04	no	171 ? 29	48	21

Table 3 Monitoring acetic acid levels on press shelves with and without activated carbon present.

In a third monitoring round presses containing pairs of shelf spaces, one with and one without activated carbon present were selected to mimic the Thickett and Short investigation and overcome the temperature and RH effect, see Table 4. This monitoring was started on the 1 December 2004.

Press number	Shelf number	Activated carbon present?	Date carbon put in case or shelf	Acetic acid (μg/m^3)
148	3	yes	December 03	178 ? 24
	4	no		213 ? 24
143	3	Yes	December 03	155 ? 24
	4	no		153 ? 24
158	2	yes	September 04	161 ? 24
	6	no		243 ? 24
34	4	yes	September 04	166 ? 24
	3	No		166 ? 24
35	2	Yes	December 03	181 ? 24
	3	no		197 ? 24

Table 4 monitoring pairs of shelf spaces for acetic acid levels

In presses 34 and 143 there was no difference in the acetic acid levels in the pairs of shelf spaces. In presses 35, 148 and 158 there was a small difference with lower acetic acid levels in the spaces with activated carbon present. The levels were low compared to previous measurements made in the presses and a high air exchange rate was suspected. An attempt was made to measure the air exchange rate in press 148 using the carbon dioxide decay method. Unfortunately the press appeared to be so poorly sealed that the carbon dioxide had leaked away in a very short time, 10 minutes. More measurements are planned, but the logistics of carrying out these measurements whilst the gallery is open to the public precludes further work until the next annual closed period in January 2005 when maintenance work is carried out.

The Medieval Gallery

The showcases in the Medieval Gallery are made of wood. In 1997 because of concerns about the potential effect of out-gassing from the wood on enamel objects acetic acid levels were measured in two showcases and found to be greater than 2000$\mu g/m^3$. Several small trays of activated carbon granules were put into the case to reduce this level and measurements showed a reduction of 50% was achieved. The activated carbon remained in the case until August 2004 when monitoring to assess its effectiveness was carried out. With the trays of activated carbon in place the acetic acid level in the case was twice that when the trays were removed. The lower mean temperature at the time of the second measurements would have reduced the extent of out-gassing and hence the build up of acetic acid in the case. However these measurements suggest that the activated carbon was exhausted after 7 years of deployment.

Activated carbon samples from two showcases in the Medieval Gallery and from two press shelves in the Kings Library were extracted in water for 24 hours and the extracts analysed by ion chromatography. The results indicate a high level of adsorption of acetic acid on the activated carbon which had been deployed for seven years compared with that which had been deployed for one year, see Table 5. The surface area of the activated carbon trays and the showcase baseboards or press shelves, and the volume of the activated carbon 10mm deep in the trays, the showcases and press shelf spaces are also given.

Location	Years	Acetate (%w/w) extracted from activated carbon	Surface area of activated carbon trays (m^2)	Surface area of base (m^2)	% surface area covered	Volume (m^3) showcase
Medieval Gallery Case 5	7	3.03	0.0036	5.02	0.72	5.56
Medieval Gallery Case 4	7	4.7	0.0036	5.39	0.67	5.99
Kings library Press 34 shelf 4	1	0.023	0.052	0.28	18	0.12
Kings Library Press 35 shelf 2	1	0.037	0.052	0.28	18	0.17

Table 5 Exposure of activated carbon in the Medieval Gallery and Kings Library

Given the results of the investigation into mitigation of acetic acid levels in the presses in the Kings Library the surface area of activated carbon exposed in Cases 4 and 5 in the Medieval Gallery appear to be totally inadequate. However when first exposed the activated carbon did have an effect. Although the amount of water extractable acetate on the carbon cannot be used as a measure of the level of saturation, the indication from the comparison of the extracted levels of acetate in Table 5 is that the carbon must have stopped having any effect within a short time of deployment. Activated carbon has a high capacity for many common air borne substances and these substances are just as likely to be adsorbed as are organic acids. A regular regime of replacing the activated carbon is needed for it to be effective.

Adsorbents to control tarnishing of silver.

In common with many other museums the British Museum is not fully air conditioned. As a result the reduced sulphur gases hydrogen sulphide and carbonyl sulphide are present in the ambient air in galleries and showcases, Table 6. Hence even though no materials which emit reduced sulphur gases have been used in the construction of showcases since the 1980s silver objects tarnish whilst on display.

Location	Hydrogen sulphide (ppt)	Carbonyl sulphide (ppt)
External	232 ? 37	596 ? 98
Gallery 70	248? 50	622? 46
Gallery 70, Case 30 Silver objects	122? 24	523? 89
Gallery 70, case 17 Glass objects	164? 27	497? 62

Table 6 Typical reduced sulphur gas levels in galleries and showcases

In 1996 Lorna Lee reported on an investigation of activated carbon (as Charcoal Cloth) and Puraspec catalysts manufactured by ICI katalco composed of zinc oxide bonded with a cement to control the rate of silver tarnish formation (Lee 1996, Bradley In press). In this work the effectiveness of the adsorbents was evaluated in an array of bottles containing the adsorbents and silver test coupons, through which ambient air was pumped (Figure3a and 3b).

The experiment continued until the control coupon in a jar with no adsorbent present started to visibly tarnish. The degree of alteration of the coupons was determined by X-ray Photoelectron Spectroscopy (XPS), see Table 7.

Sample	Elements present (Atomic %)		
	Ag3d	S2p as S^{2-}	S2p as SO_4^{2-}
Clean, unexposed	46.5 Ag(0)	1.0	nd
Control in lab	27.4 Ag(I)	2.4	nd
Control in container	40.4 Ag(0) Ag(I)	3.1	4.2
Puraspec 5040	40.6 Ag(0)	1.6	1.1
Puraspec 2040	22.2 Ag(0)	1.3	tr
Charcoal cloth	20.0 Ag(0)	1.1	nd

Table 7 Laboratory evaluation of tarnish inhibitors. Results of XPS analysis expressed as atomic weight %

Following this investigation a gallery trial was conducted in two showcases containing silver in gallery 70. Puraspec 2040 was deployed passively in one case and the second case was used as a control. Silver coupons were again used to monitor the effectiveness of the adsorbent. In this trial the silver coupon in the control case was found to have a lower level of sulphur contamination than that in the showcase with the Puraspec 2040 present. The size, shape and air exchange rate of the cases were substantially different with the control case being a rectangular wall case and the test case being an L shaped free standing case, much larger and with many more joins in the glass, allowing more leakage of gallery air into the case. From this and other experiments it seemed reasonable to deduce that an active rather than a passive removal of reduced sulphur gases would be more effective in reducing silver tarnish.

A new form of Puraspec, Puraspec 2030, was introduced in a second gallery trial In addition to zinc oxide Puraspec 2030 contains aluminium oxide and a copper compound. The aluminium oxide converts carbonyl sulphide to hydrogen sulphide which is subsequently adsorbed by the zinc oxide. The copper compound is present as an indicator and should turn black due to formation of copper sulphide when the catalyst is exhausted.

In this second trial air was pumped into a showcase through a filter bed of Puraspec 2030 and activated carbon cloth, maintaining a positive pressure. A small pump system consisting of a filter bed containing Puraspec 2030 and activated carbon cloth was constructed and fitted to a showcase containing silver in gallery 70, Figure 4a and b. A second silver case was used as a control. Silver coupons were exposed in the gallery and both showcases and a clean unexposed coupon was used as a second control. After 60 days exposure the silver coupons were analysed by XPS, Table 8.

Location	Ratio atomic% element/atomic% silver	
	S2p as S^{2-}	S2p as SO_4^{2-}
Clean unexposed	tr	tr
Showcase Silver + pump	0.009	0.017
Showcase Silver	0.018	0.028
Gallery 70	0.318	0.057

Table8 Gallery trial of filter pump. Results of XPS analysis expressed as ratios of atomic %

These results showed that the most effective method of reducing the rate of silver tarnishing was a positive pressure system. As a result of this investigation and a long term trial of the filter pump a bid has now been made for filter pumps to be installed under all of the showcases where silver is displayed.

Conclusions

Passive deployment is the easiest way of introducing adsorbent materials into showcases, but for this to be effective there has to be a high surface area present, particularly in a large volume space. Activated carbon has a high surface area and at the levels of pollutant gases in the Museum should have a long lifetime, but the indications are that it should be replaced regularly to maintain any effect, probably every two years. Active filtration is a more effective way of deploying adsorbents in showcases, but this is not always possible.

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Figures 1 2 and 3a

Figure 1 Wood book presses lining the Kings Library

Figure 2 The Kings Library after opening of the Enlightenment exhibition

Figure 3a Experimental apparatus for evaluating adsorbents for reduced sulphur gases.

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Figures 3b, 4a and b

Figure 3b Detail of jar. The adsorbents are at the bottom of each jar and the silver test coupon is suspended from the top. The air is pumped to the bottom of each jar.

Figure 4a Showcase for filter pump trial.

Figure 4b Filter pump for removing reduced sulphur gases