6 INVESTIGATION INTO ROLE OF INERT DUSTS IN CORROSION AND CORROSION MITIGATION IN AN AGGRESSIVE MARITIME ENVIRONEMENT

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ABSTRACT

Monitoring the corrosion rates of steel in the Secret Wartime Tunnels under Dover Castle has shown great differences between tunnels with similar environments. The corrosion rate differences could not be rationalised by differences in RH, anion deposition rates or gaseous pollution concentrations and appeared to correlate with dust deposition rates. Time of wetness measured with grid type sensors was greatest in the most corrosive tunnels and the critical wetting RH was lowered in these locations. Laboratory experiments confirmed that the critical wetting RH could be lowered by the presence of inert dust on a metal surface. Corrosion rates of mild steel coupons loaded with salt and inert dust particles were determined at 5% intervals. These increased dramatically above the measured critical wetting RHs. A number of mitigation strategies have been tested in the Secret Wartime Tunnels, with a commercial corrosion inhibiting spray proving to be the most suited to that extremely corrosive environment and the collection displayed within it.

KEYWORDS

Environmental monitoring, steel and copper alloys, corrosion, mitigation.

INTRODUCTION

Dover Castle on the south east coast of England has the longest recorded history of any in Britain. Three brick-lined casemate tunnels were excavated under the famous white cliffs to house troops during the Napoleonic Wars. These tunnels housed Rear Admiral Ramsey's headquarters for the evacuation from Dunkirk during World War II. The tunnels are partially presented as they would have been during that period. The presentation includes large amounts of historic steel cabinet type telecommunications equipment in the Repeater Station and Equipment Room, see **Figure 1**. The Telephone Exchange contains twelve QB10 telephone exchanges. These three rooms contain very large amounts of steel casing, copper wiring and brass fittings. The porous nature of the chalk and close proximity to the sea give rise to an extremely aggressive atmosphere inside the tunnels towards steel and copper alloys. The historic original natural ventilation system for the tunnels was supplemented, for their use as a headquarters, with the addition of sets of fans and filters at the cliff face in each casemate. Mild steel trunking, is used to distribute the air down the length of the casemate. The fans for the central casemate run twenty four hours a day, whilst those for the two outer casemates only run when the site is closed overnight. After a serious outbreak

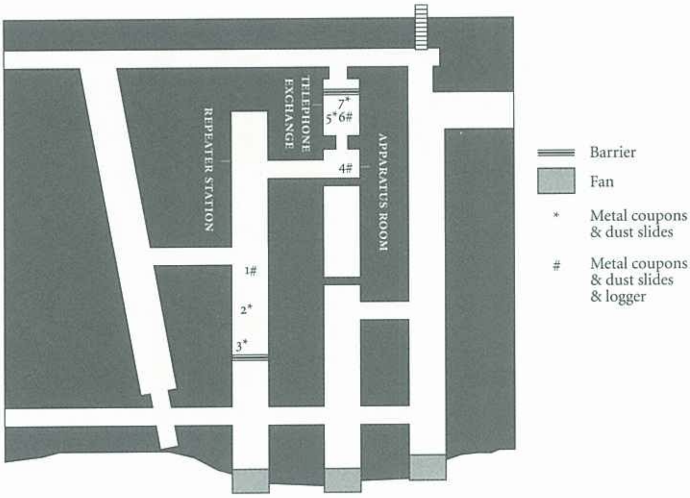

Fig. 1 Monitoring Locations.

of mould in 2002 additional free standing fans and some background heating was introduced in vulnerable areas. The very large visitor numbers attracted to the tunnels, in excess of 200,000 in 2004, caused large amounts of dust to be deposited on surfaces despite chest high open wooden barriers restricting access into many of the collection spaces. An environmental assessment of the tunnels has been carried out for the collections on display. This work reports that part of the assessment for metals.

A number of experiments were undertaken to determine the likely success of several mitigation approaches including; using solid barriers instead of the open wooden ones to reduce dust deposition, different types of fabric covers to cover stored material or block the back of equipment to reduce corrosive dust ingress and the use of protective coatings for the metals including Renaissance Wax and Shield and their reversibility.

MONITORING

The temperature and relative humidity was continuously monitored over three years in four locations within the tunnels using Smartreader SR002 data-loggers, including the Telephone Exchange, Equipment Room and Repeater Station. The locations are marked on **Figure 1**. Point 5 was inside the back of a QB10 telephone exchange and point 6 ontop of that exchange. **Figure 2** shows the temperatures and RHs in the Telephone Exchange for a years period 2003/4. All of the spaces are generally damp and show strong seasonal effects with June through September showing the highest RHs. The Telephone Exchange experiences lower RHs and this shows the beneficial

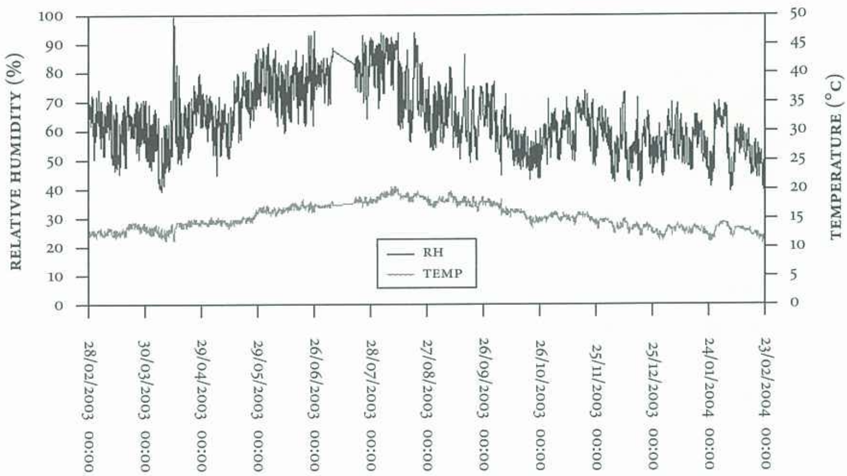

Fig. 2 Years RH Telephone Exchange.

effect of keeping the fan running throughout the day. **Table 1** shows the RH data collated at 10% intervals. The Repeater Station has the highest RHs; the Telephone Exchange is lower, with the Apparatus Room sitting between the two. The time of wetness defined by ISO 9223 is that time when the RH is above 80% and the temperature above 0° C, ie the sum of the last two bins (ISO 9223). For a years period the time of wetnesses are shown in **Table 1**, below. For two separate, one month periods, temperature and RH were monitored at three locations in the Repeater Station and Telephone Exchange to give an idea of the distribution throughout the rooms. This showed that the Repeater Station had a very large RH differential across it with the back generally experiencing 10–15% higher RHs than the front.

Surface wetness was also monitored for eighteen months in the Telephone Exchange and Repeater Station using gold grid type sensors, (Starlog Model 6524) with 0.45 mm grid spacing. Their resistance was recorded using the spare resistance channel on the SR002 loggers. The sensors have a very high resistance when dry and this drops when the surface is wet. Since the RH was also continuously recorded then a critical RH could be determined. This is when the surface changes from being dry to being wet, taken at the point when the resistance dropped below 1,000,000, 500,000, 200,000 or 100,000Ω. Norberg has reported on the uncertainty in the actual resistance that corresponds to wetting of a surface and recommended that such calculations be determined at several resistance values to confirm their robustness (Norberg 1993). Very little difference was observed in the critical RHs from using the different resistance values, confirming the utility of the measurement and value at

200,000Ω are quoted. A large number of wetting events were observed in all locations and the values quoted. The critical RHs for the three spaces were determined as; 50.19 + 1.25% in the Repeater Station (198 wetting events), 55.99 + 1.27% in the Equipment Room (121 wetting events) and 53.34 + 1.32% in the Telephone Exchange (64 wetting events). Although the nominal tolerance of the RH sensors on the SR002 dataloggers is + 2.5%, calibration checks with the three loggers in 50, 55 and 60% RH atmospheres above glycerol solutions showed the logger sensors reading within 0.5% of each other. The critical RH figures quoted are calculated statistics and hence quoted to a much greater degree of accuracy than the RH measurements from which they are derived. The times of wetness calculated when the resistance was below 200,000Ω are shown in **Table 1**.

Location	Time of Wetness (hrs)	
	Surface Wetness Sensor	ISO 9223
Telephone Exchange	4258	2277
Apparatus Room	4091	2041
Repeater Station	6382	3054

Table 1 Time of Wetness by Surface Wetness Sensors and ISO9223.

Dust deposition rates were measured by exposing glass slides for four week periods in each quarter. The locations within the tunnels are shown in **Figure 1**. The percentage area coverage of the dust was determined by image analysis (Howell 2002). The particle size distribution for each dust sample was also determined. Results from June, the month with the highest visitor numbers during which dust measurements were taken, are shown in **Figure 3**. The right hand casemate has the highest dust deposition levels. This is at the beginning of the tour route and when the visitors disturb and generate the most dust (Lloyd *et al* 2002). The Telephone Exchange consistently had the lowest dust deposition levels, probably due to the ventilation in this casemate running continuously. There was no statistically significant decrease in dust deposition away from the tour route, the distances on the labels of **Figure 3** are from the barriers demarking the tour route. This is a different behaviour to that which has been observed for several historic houses (Lloyd *et al* 2002). The difference may be due to the high level of ventilation required for the tunnels or the relatively high visitor density compared to the previous studies.

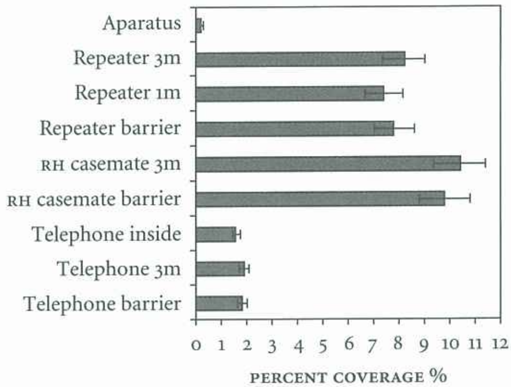

Fig. 3 Deposited dust.

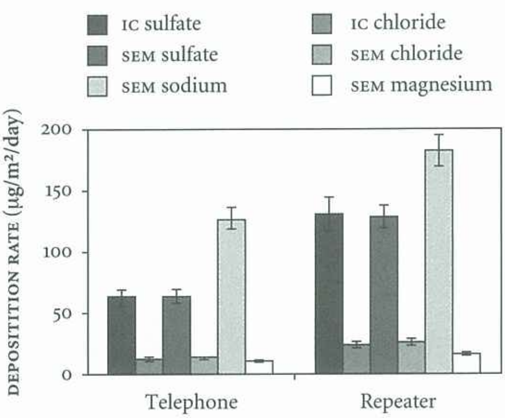

Fig. 4 Anions.

Anion deposition rates were determined by extracting the surfaces of the glass slides with 18.2MΩ water after dust analysis. The extracts were analysed with Ion Chromatography, Dionex DX600, AS14A column with 18mM sodium hydrogen carbonate and 8mM sodium carbonate eluent. The concentrations of anions in the extract were used to calculate the anion deposition rates onto the glass slide surfaces. Four adhesive samplers were also deployed based on adhesive carbon pads (SPI 0507-BA) on aluminium discs. These were exposed adjacent to four of the glass slide samplers. The surfaces were analysed with Scanning Electron Microscopy (SEM) with Energy Dispersive analysis, Joel 740 with Oxford Link analyser. Analyses were calculated from the averages of twelve 1 mm squares on each surface. Both Ion Chromatography and SEM analyses results are shown in **Figure 4**. The two sets of results were very consistent. Surprisingly sulphate was the major anion, with relatively little chloride detected. The relative amounts of both anions and cations differed between the three locations.

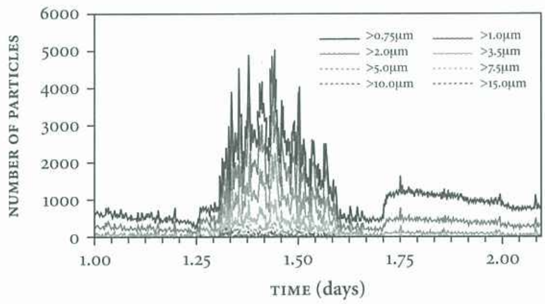

Fig. 5 Airborne dust in Repeater Station.

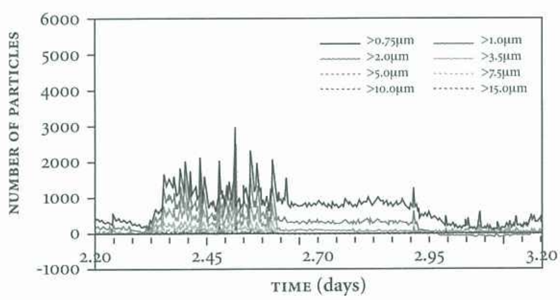

Fig. 6 Airborne dust in Telephone Exchange.

The airborne dust fractions were determined with a Grimm Portable Dust Monitor Version 1.100 particle size analyser over five days, with the sampler in the Repeater Station for three days and the Telephone Exchange for the remaining two days. The sampler gives results in eight particle diameter bands. A twenty four hour period for the Repeater Station is shown in **Figure 5** and for the Telephone Exchange in **Figure 6**. The visitors are conducted through the tunnels in groups. Each group of visitors causes a distinct peak in dust concentrations. Again the Telephone Exchange has much lower levels. Examination of the tour group sizes for the two days graphed in **Figures 5** and **6**, showed that they were all within 25% of each other and overall the daily totals differed by less than 10%. Integrating the areas under the peaks, and assuming an average density for the dust from the weight gain of the incorporated filter over the sampling period, indicated that the mass of suspended dust in the Telephone Exchange was approximately a third of that in the Repeater Station. This was in good agreement with the deposited dust rates. The finer fractions of the dust, less than 3.5 μm equivalent spherical diameter, act in a different manner to the courser fractions. These finer particles are re-suspended when the ventilation system starts up at approximately 6pm, (1.70 on **Figure 5**). In the Repeater Station these fine fractions of the dust remain suspended until the following morning, with only a slight drop off in concentration overnight. The behaviour in the continuously ventilated Telephone Exchange is different. The fine fractions remain suspended after the last tour has departed, but settle much more rapidly and have mainly settled by midnight (3.0 on **Figure 6**).

Concentrations of pollutant gases; sulfur dioxide, nitrogen dioxide, hydrogen chloride and ozone were measured by exposing diffusion tubes for a four week period in September 2005 in the Telephone Exchange and externally. Results are shown in **Table 2.**

	Pollutant concentration (ppm)			
	sulfur dioxide	nitrogen dioxide	hydrogen chloride	ozone
External	3.23 + 0.23	8.65 + 0.61	0.96 + 0.07	12.83 + 0.90
Telephone Exchange	0.45 + 0.03	7.82 + 0.69	0.37 + 0.03	2.81 + 0.20

Table 2 Polluant Gas Concentrations.

The filtration system for the tunnels is designed for particulates only and contains no chemical filtration. The gases with high deposition velocities on calcite, sulfur dioxide and ozone are significantly reduced inside the tunnels, whilst nitrogen dioxide which has a much lower deposition velocity is only slightly reduced (Blades *et al* 2002). The levels detected do not present a significant risk of corrosion towards mild steel (Oesch 1996). Exposing steel for 12 months to 90% RH atmospheres with 0.5ppm sulfur dioxide, 10ppm nitrogen dioxide and 16ppm ozone caused under 0.05mg/m^2 corrosion (Oesch 1996). Similar exposure experiments with copper have shown a very low corrosion rate at these concentrations (Oesch and Faller 1997).

The corrosion rates for mild steel and copper were measured by exposing coupons in the rooms. The coupons were abraded with 1200 grade silicon carbide paper and degreased with acetone and then weighed. Copper and steel coupons were exposed for twelve months in seven locations. After exposure, coupons were analysed with Fourier Transform Infra-Red Spectroscopy using Diffuse Reflectance (DRIFTS), Perkin Elmer 16PC. The amount of each of the major corrosion products was estimated from DRIFTS spectra run of commercially purchased high purity standards. This method has the advantage of not requiring the coupon to be disturbed for analysis, but it is relatively insensitive to magnetite, which will almost certainly be present. The coupons were reweighed and the corrosion removed with cathodic stripping with a Uniscan PG580 potentiostat in 0.1% sodium hydroxide solution (ASTM G1 E5). Copper was found to corrode at a very slow rate, less than 0.02g/m² in all locations. The mild steel results are shown in **Table 3**.

Location	Corrosion Loss (g/m²)	Corrosion type
7 Telephone Exchange at barrier	0.099 + 0.007	95% Goethite, 5% Lepidocrite
5 Telephone Exchange 3m in	0.106 + 0.009	90% Goethite, 10% Lepidocrite
6 Telephone Exchange inside unit	0.085 + 0.009	95% Goethite, 5% Lepidocrite
3 Repeater Station at barrier	0.928 + 0.102	80% Goethite, 20% Lepidocrite
2 Repeater Station 1m in	0.874 + 0.984	80% Goethite, 20% Lepidocrite
1 Repeater Station 3m in	0.934 + 0.784	75% Goethite, 25% Lepidocrite
4 Apparatus Room	0.057 + 0.007	95% Goethite, 5% Lepidocrite

Table 3 Corrosion Results.

The coupons have corroded much more rapidly in the Repeater Station than the Telephone Exchange. The main corrosion product is Goethite in all cases, with variable amounts of lepidocrite detected, more in the Repeater Station. The chloride containing Akaganeite has been reported in many coastal locations, its absence in this case is due to the efficient particulate filtration on the ventilation system. Santana Rodriguez *et al* reported on a chloride deposition threshold of 14-16 mg/m²/day for the formation of Akaganeite, which contains approximately 6% chloride in its structure (Santana Rodriguez *et al* 2002, Stahl *et al* 2003). The chloride deposition rates measured in this work are well below the proposed threshold. Considering both the chloride and sulphate deposition rates, Corvo *et al* proposed a numerical model for mild steel corrosion rates (Corvo *et al* 1995). Taking the figures measured at Dover, their model

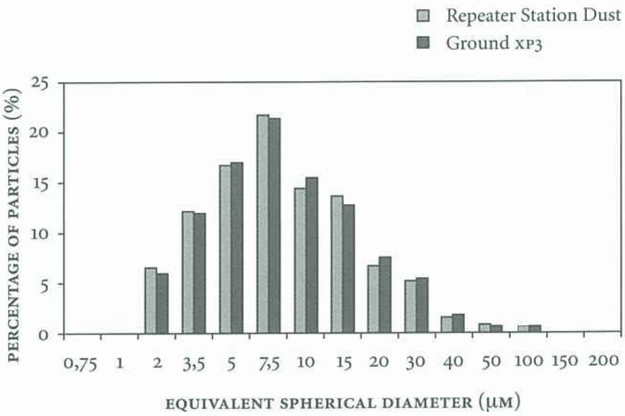

Fig. 7 Particle Sise Distributions.

would predict corrosion rates under 0.035 g/m² for the Telephone Exchange and under 0.315 g/m² for the Repeater Station, somewhat under those measured.

EXPERIMENTAL

The differences in steel corrosion rate between the Repeater Station, Apparatus Room and Telephone Exchange cannot be explained by the differences in RH or anion deposition rates determined. The greater time of wetness and lower critical RH seem to be related to the amounts of dust deposited. In order to investigate this relationship between inert dust and steel corrosion a series of experiments were undertaken. Surface wetness sensors (in duplicate) and mild steel coupons (in triplicate) were loaded with salt mixtures and inert dust from crystabolite sand. The experiments are shown in **Table 3**. Solutions were made up to resemble the ion deposition measured in the Repeater Station by mixing sodium chloride, sodium sulphate, magnesium chloride and magnesium sulphate. The sensors and steel coupons were dipped into the solutions and shaken to remove excess solution and then allowed to air dry in a desiccator. Inert crystabolite sand was produced by grinding Hepworths XP3 sand in a rotary mill. Experiments determined that 2 hours dry grinding with a loading of 10% sand to alumina media gave a particle size distribution approximating that of the dust deposited in the Repeater Station. **Figure 7** shows the averaged particle size distribution of four sets of measurements of dust deposited at point 2 and the distribution for the ground XP3 sand. The distribution is presented in the same particle size bands as the results from the Grimm particle counter for ease of comparison. The combination of the magnification and image analysis parameters used in these measurements means that they are insensitive to dust with an equivalent spherical diameter less than 2μm. The ground sand was applied to the surfaces by brushing through a 120μm sieve, to remove large particles.

Surface Wetness Sensor	Clean	Salt	Dust	Salt and dust	RH interval wetness observed (%)	Critical RH (%)
1	✓				85	81
2	✓				85	81
3		✓			80	78
4		✓			80	78
5			✓		65	63
6			✓		65	63
7				✓	55	54
8				✓	55	54

Table 4 Surface Wetness Sensor Experiments with Salt and Dust Contaminated Surfaces.

Humidity chambers were conditioned to 50, 55, 60, 65, 70, 75, 80, 85 and 90% RH, with glycerol solutions (Grover and Nicol 1940). The surface wetness sensors attached to a SR007 logger were placed in each chamber sequentially from 50% up for two days each to allow equilibration and the RH at which surface moisture was detected is recorded in **Table 4**.

The surface wetness sensors were then placed in a Perspex drying chamber with the door opening covered with Tyvek. This material is an excellent dust barrier, but allows some water vapour to permeate into the chamber. The room containing the chamber had a very fluctuating RH and the chamber RH underwent significant fluctuations between 35 and 85% which were measured with a SR002 logger. The critical RH for each surface wetness sensor was calculated as before and these are included in **Table 1**.

The steel coupons were placed in the humidity chambers for 120 days. After exposure the coupons were cathodically stripped in sodium hydroxide and the loss of weight determined. The weight losses are shown in **Figure 8**. Each set of coupons showed a critical RH where the corrosion rate increased dramatically. These critical RHs were in good agreement with RH levels at which surface moisture was detected with the surface moisture sensors. The salt loaded surface critical RH is also in good agreement with similar work previously reported by Evans for mild steel loaded with sea water (Evans 1981).

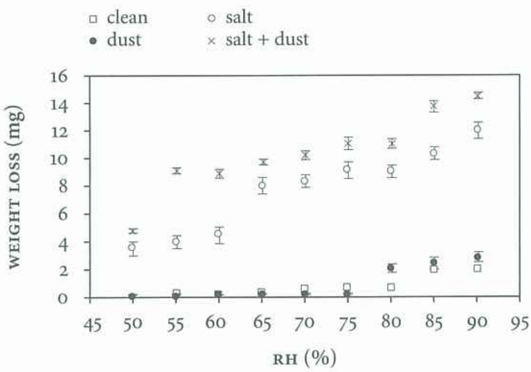

Fig. 8 Corrosion of Mild Steel Coupons.

MITIGATION

A number of methods of mitigating the corrosion risks in the Dover Tunnels were investigated.

Water percolating through the chalk leads to wet highly porous walls surrounding the tunnels. A series of tests were run with the ventilation off and on in the tunnels. The RH was significantly lowered with the ventilation system running. Results from the deposited and air borne dust monitoring also indicate that the ventilation has a significant beneficial effect on dust.

Work in historic houses has shown that 1.5m high barriers can significantly reduce dust deposition which, in that situation, originates mainly from the visitors themselves (Lloyd *et al* 2002). The spaces containing collections in Dover Tunnels all have open wooden barriers. The effect of converting these to solid barriers was investigated by blocking off the barriers in one room with polyethylene sheet. Two series of four week dust measurements were undertaken, one set before the polyethylene was added and one after. No significant reduction in deposition rate was observed with the polyethylene in place.

Much of the equipment in both the Repeater Room and Telephone Exchange is open backed, allowing ready ingress of dust as shown by the monitoring results inside the QB10 exchange shown in **Figure** 3. A number of fabrics were investigated to determine their suitability to block these open backs stopping dust ingress. However the high potential for mould growth in the tunnels, means that it is important that the RH does not rise inside the fabric backing. The fabrics tested were Tyvek, Gortex and Permatex. The back of the Repeater Station was used for temporary storage for a series of teleprinters. These were covered with Tyvek and the covering was replaced with either Gortex or Permatex for the trials. The trials took place from June to October, the period of highest RH in the Repeater Station. Hanwell Humbug II data loggers were placed under each cover along with surface wetness sensors attached to a SR007 datalogger. Gortex increased the RH underneath it and the time of wetness. Tyvek and permatex behaved similarly and both caused a slight increase in RH and time of wetness.

Because of the very aggressive conditions within the tunnels much of the metalwork was treated with a propriety corrosion inhibiting spray Shield. The effectiveness of this treatment was compared to Renaissance Wax, the most common surface treatment used for open display in historic houses. Mild steel and copper coupons were surface cleaned, as described previously, and then treated with Shield or Renaissance Wax. The coupons were exposed in the same seven locations as the untreated coupons for twelve months. After exposure the coupons were cathodically stripped as before. The percentage reduction in corrosion compared to the untreated coupons was calculated. Shield gave an average of 99.0% reduction in corrosion rate in the Repeater Station and 98.1% in the Telephone Exchange, whilst Renaissance Wax gave only 31.6% and 30.7% in the same locations. Shield was first applied to equipment four years ago. One of the small units was removed and transported to Birkbeck College, London. A flat surface was analysed with Reflection Absorption on a Durascope on a Perkin Elmer 2000 FTIR. This produced a good spectrum of the 2μm coating. The surface was cleaned with white spirit and reanalysed. This showed that the Shield had been fully removed (estimated detection limit is 0.01μm) from the surface and was still reversible after four years. There are however some ethical concerns with Shield. Residues of oils have been found on some of the equipment and the use of Shield and its removal with white spirit is likely to interfere with these. In this extremely aggressive environment, the very high corrosion rate of the steel requires mitigation and Shield, whilst interfering with original residues provides the least interventive approach yet considered.

CONCLUSIONS

Inert dusts have been shown to lower the critical RH for wetting a metal surface, increase the actual time of wetness and increase significantly the corrosion rate of mild steel. This is an analogue to Vernon's findings that inert particles increase the corrosion rate of iron in atmospheres polluted with sulphur dioxide (Vernon 1935). The critical RH in the presence of these dusts and deposited ions at Dover was found to be between 50 and 56%. This is very significantly lower than the 80% taken as a standard for wetting in ISO 9223.

Ventilation of the tunnels has been found to be very beneficial both in lowering the RH and dust deposition rates. It is also essential in this instance due to the high propensity for mould growth in the tunnels. Solid barriers were found to be relatively ineffective against dust deposition and the deposition rate did not fall off exponentially as determined in historic houses. This indicates that the mechanisms of dust generation and transport are very different in this situation. Tyvek and Permatex were found to be suitable as a cover fabric. Further testing is required to determine the reduction in ventilation, as this is of real concern at this site due to mould growth. Shield was found to be a very effective corrosion inhibitor in this extremely aggressive location.

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BIOGRAPHIC NOTE

David Thickett worked for two years in ceramics research before entering conservation science. He joined the British Museum in 1990 working on the deterioration and conservation of stone, metal and glass artifacts and preventive conservation. He currently works in the Collections Management Team at English Heritage as senior conservation scientist with responsibilities for the research program and preventive conservation. Current research interests include light management, archaeological iron and silver tarnish mitigation on open display.