Chloride, Dust and RH, Risks in Coastal and Inland Areas

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Sea salt aerosol is a significant cause of metal corrosion in coastal regions. The synergistic effects of the salt, dust particles and relative humidity are important in understanding the corrosion process and risk. This relationship has been investigated at 2 coastal English Heritage sites.

Dover Castle on the South East Coast of England holds a collection of important wartime telecommunications equipment, displayed in a series of chalk tunnels. The environment in the tunnels is very aggressive towards metals with high relative humidities and salt from their close proximity to the sea. The tunnels have an historic forced ventilation system with air intakes on the cliff face. The efficiency of the filters against sea salt aerosol was determined by exposing Whatman's filter papers in the ducting, extracting the filters and analysing the extracts for chloride with ion chromatography. This showed extremely little chloride egressing the filters. Other potential salt sources are from efflorescence on the ceilings and from redistribution by visitor circulation. The dust and anion deposition rate and corrosion rates were measured by exposing glass slides and steel coupons. The glass slides were analysed with microscopy and image analysis (Howell et al 2003), extracted and then analysed with ion chromatography. The corrosion rate was determined by stripping the corrosion products from the steel coupons after exposure (ASTM 1999) and calculating the weight loss. Both dust deposition and corrosion rate were significantly reduced when the ventilation system was in operation. In one tunnel the system runs continuously, in another two it only runs overnight. The chloride to sulphate ratio was significantly lower than that of sea water and sea salt aerosol, confirming that some process other than direct deposition was the source of the salt in the tunnels. Metal corrosion rate is strongly influenced by time of wetness. Monitoring with grid type wetness sensors determined surface water on surfaces for 10% of the time in the tunnel with the ventilation running continuously and 25% of the time in one of the other tunnels. The critical relative humidity for the contaminated surface was determined by taking the RH when the sensor resistance dropped, indicating the presence of surface water, (the sensors were attached to loggers also recording air temperature and RH). Since this process occurred a number of times an average value

RH determined. The critical RH of a clean sensor was 81%, this dropped to 78% with the crystabolite sand on the surface, 63% with salt mixture and 54% with both on the surface. This demonstrates the synergistic effect of salt and inert particles on a surface, similar to that reported for sulphur dioxide gas (Vernon 1934). Tyvek covers are used to protect equipment not visible from the tour route against dust. Monitoring showed the RH to be on average 10% higher under the covers, and time of wetness, to be significantly greater also, illustrating the increased corrosion potential under such covers in these conditions. Improved housekeeping and a commercial corrosion inhibitor (Shield) have been found effective at retarding ferrous corrosion in the aggressive tunnel environment.

Porchester Castle on the south coast of England has a small site display presenting archaeology discovered at the castle. This includes three showcases of archaeological iron. Deployment of glass slides showed that the cases were allowing ingress of both dust and between 41 and 124 $\mu g/m^2$/day of chloride. Since the amount of salt aerosol is a function of sea conditions, wind speed and direction, it would be expected to vary considerably. In order to confirm the representative nature of these figures, samples of the display fabrics; which had remained in situ since the display opened were taken. These were extracted and analysed for chloride, giving results between 31 and 75µg of chloride. The results followed the same pattern as the glass slide deposition measurements.   When assessing the risk the deposited chloride poses, it is necessary to take into account the chloride already present in the objects. The display is of archaeology from the site and its maritime location would be expected to give high chloride levels, higher than the not inconsiderable ones normally associated with archaeological iron (Watkins). The chloride in archaeological iron is thought to be mainly in the form of the mineral akaganeite. The amount of akaganeite in a nail excavated very close to one of the objects displayed in a case of interest was determined by sectioning and thermomagnetometry (Thickett 2005a). The chloride concentration in the object was estimated at 0.2% by weight from this value and the measured chloride concentration of samples of the akaganeite from this object. Over the twenty five years of display the deposition from salt aerosol is less than 10% of this value, although a higher figure may be expected for flat, thin objects with a greater surface area to volume ratio. Whilst some workers have ascertained that akaganeite is stable and will not release chloride from its structure, analysis from objects and experimental work by the author has discovered a conversion to geothite with release of chloride at moderate RH levels (Stahl 2003, Thickett 2005b). Whilst this is a chloride cycle, it is not that postulated to be occurring in archaeological iron tarnish, along with sulphide. Similar results were obtained from tarnish formed on silver over a period of up to 35 years (Thickett 2005c). Chloride deposition rates between 36 and 139 µg/m^2/day were measured in showcases in the Museum of London, and chloride deposition as an aerosol cannot be ignored if the tarnishing of silver is to be controlled. Showcases can significantly reduce dust ingress. A positive correlation between air exchange rate and higher dust and chloride deposition rates and silver tarnish rates has been established. However, reducing the air exchange rate of certain types of showcases below 1 day^{-1} is expensive and the fitting of low flow rate pumps with appropriate filters to deliver clean air to the case can be a more cost effective solution. Ideally the pump should deliver just enough air to overcome the showcases air exchange rate, taking into account that the instantaneous air exchange rate can be much larger than the average air exchange rate measured with tracer gas or pressure difference methods.

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