Some recent trends in corrosion science and their application to conservation

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Abstract

Conservators and corrosion scientists face many of the same issues, and thus it is reasonable to assume that recent advances in corrosion science may also be of use in conservation. Of course, there are also significant differences – while quite active interventions are permissible in conserving infrastructure or industrial plant, they may not be permitted for cultural artefacts. Further, while the conservator must deal with a limited number of normally stationary objects, the corrosion scientist may have to deal with distributed infrastructure (pipelines, powerlines) or mobile infrastructure (fleets of aircraft).

In this paper, some recent trends in research (predominately carried out at CSIRO) are highlighted and, where possible, implications for conservation are discussed. Areas covered include meta-methodology, models of degradation and new sensors.

Résumé

Les conservateurs et les spécialistes de la corrosion rencontrent des problèmes identiques. Il est ainsi raisonnable de penser que les avancées récentes dans le cadre des recherches menées sur la corrosion peuvent également être utiles pour la conservation. Il y a bien sur des différences notables. Ainsi des interventions actives sont permises pour les infrastructures conservées ou pour les sites industriels mais elles ne peuvent être autorisées pour les artefacts. De plus, alors que les conservateurs s'intéressent à un nombre d'objets limités normalement stationnaires, les scientifiques du domaine de la corrosion doivent prendre en compte des infrastructures distribuées (canalisations, lignes électriques) ou mobiles (flottes d'avions).

Cet article présente quelques unes des pistes de recherches récentes dans le domaine de la corrosion (et plus particulièrement les recherches menées au CSIRO). Les domaines abordés concernent la méta-méthodologie, les modèles de dégradation et les nouveaux capteurs.

Keywords: corrosion, degradation, sensors , aerosol, deposition , transport

1. Introduction

One could regard corrosion science and conservation as sister sciences, or at least close cousins. Both disciplines are concerned with maintaining metal objects in as close to their original state as possible with minimum intervention. Further, both disciplines would agree that the intervention should not alter the function of the object. It is in the definition of "functions" that the fields tend to diverge – to the corrosion scientist "function" is purely utilitarian, while to the conservator many other values, often intangible, are associated with function.

Given this similarity of purpose of these fields, this paper will outline some recent trends in corrosion science and highlight areas that may be of relevance to conservators. However, the paper will not attempt to be exhaustive in mapping applications from corrosion science to conservation, rather it will provide examples that it is hoped can be expanded on by conservators. In discussing advances in corrosion science, one should not be restricted to the purely physical, for advances have occurred in our philosophical approach to the discipline. Advances that will be discussed in this paper include those relating to

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- Meta-methodology.
- Models of degradation.
- Sensors.

2. Meta-methodology

In this context, meta-methodology refers to the overall approach to a field. Until the 1990s, corrosion science was approached in a narrow reductionist manner. Two schools existed – one based on developing an electrochemical understanding of corrosion processes (Mansfeld, 1982; Fiaud, 1982; Stratmann, 1990; Stratmann & Streckel, 1990; Neufeld et al., 2002), and the other on empirical relationships between environmental parameters and corrosion rate (generally for atmospheric corrosion) (Guttman & Sereda, 1968; Atteraas & Haagenrud, 1982; Benarie & Lipfert, 1986). Although both made considerable progress, dialogue between the two groups was limited. By the late 1980s fundamental issues were constraining the application of either methodology.

Within the empirical approach to atmospheric corrosion, a number of very large research programs (Guttman & Sereda, 1968; Atteraas & Haagenrud, 1982; Benarie & Lipfert, 1986) had developed "dose" functions defining statistical relationships between climatic parameters and corrosion damage. Although these relationships were soundly based on large data sets, they suffered from a number of limitations. Firstly, as they defined statistical relationships between predefined variables, a relationship would not be identified if the variable was either constant or not included in the predefined variables. Further, these models defined statistical rather than causal relationships, and thus the statistical variable selected as significant may only have a correlation with the actual causal variable. This correlation may be determined by the environment and thus database specific. It is thus, perhaps not surprisingly, that dose functions derived in different countries or regions vary significantly (Jernberg et al 2004), and no consensus has been reached as to the "correct" dose function.

The electrochemical approach has developed accurate models to define the electrochemical processes occurring in immersed solutions (Mansfeld, 1982; Fiaud, 1982; Stratmann, 1990; Stratmann & Streckel, 1990). More recent work has allowed the development of an understanding of processes under thin moisture films (Neufeld et al., in press). However, these electrochemical models did not take account of the complex factors that control the formation of moisture films. Further, there is some uncertainty as to how the processes occurring under bulk solutions or thin films relate to processes that occur under cycles of micro-drop formation and evaporation that represent real service conditions.

In response to these limitations, a number of authors developed process-based models (Cole et al., 1999; Lyon et al., 1995; Graedel, 1998) that attempted to describe, on a more fundamental basis, the fundamental processes that control atmospheric corrosion. Graedel (1998) proposed the first model to systematically look at the chemical interactions across the range of interfaces that occur in the metal/oxide/solution/environment system. Graedel refers to his model as the "Gildes" model, where Gildes is an acronym for **G**as, **i**nterface, **l**iquid, **d**eposition layer, **e**lectrodic regime and **s**olid. Graedel applies the model to corrosion under moisture films on metal surfaces. However, while the Gildes model is a significant advance on previous models, at present its applications focus primarily on the liquid and the deposition regime. The current authors (Cole et al., 2003a; 2003b) considered it necessary to model more complex external environments than the Gildes model. In fact, processes controlling atmospheric corrosion on a range of scales, from macro through meso to local, micro and lastly micron, needed to be modelled. These scales are defined in line with EOTA (1997), so that macro refers to gross meteorological conditions (polar, subtropical etc.), meso refers to regions with dimensions up to 100 km, local is in the immediate vicinity of a building, while micro refers to the absolute proximity of a material surface. A diagram of such a model is given in Fig. 1.

This framework has been developed into a full model, as describe in a number of papers by Cole and co-authors (Cole et al., 2003a; 2003b; 2002c; 2004a; Cole & Paterson, 2004; Cole et al., in press, a). Specific results of the model are relevant to the conservation of metallic objects and will be discussed later in the paper.

The holistic model has proved very successful in providing information where there is limited uncertainty in the failure path that leads to corrosion. By and large this is the case for buildings (or for exterior sculpture), but it is not for well-built and complex structures such as aircraft. In such cases, failure occurs as a result of a long and hard to predict fault tree. Under these circumstances, any deterministic models (including process-based models) are not meaningful. In these circumstances, most researchers will use sensor-based data, which has the advantage that it relates directly to the actual situation.

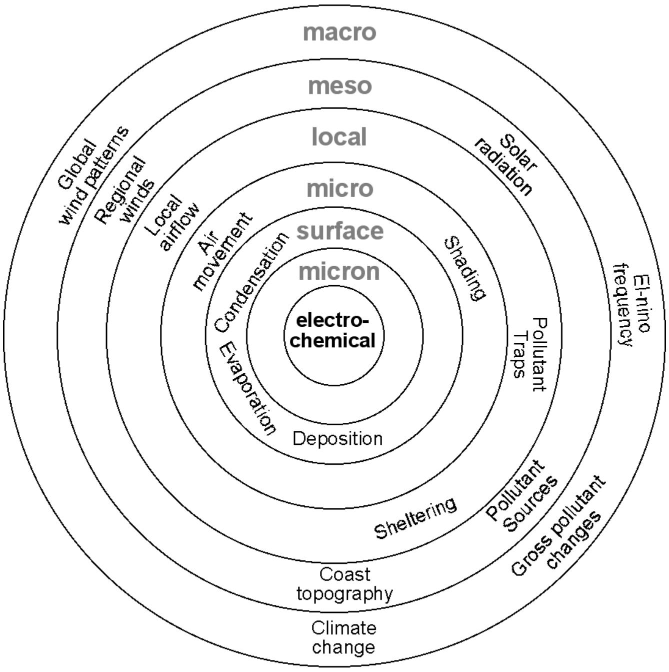

Fig. 1 Framework for a holistic model of corrosion.

The disadvantage is that standard statistical processing algorithms do not allow the inclusion of process understanding. Recently work at CSIRO is aimed at introducing into the statistical processing, operators that embed process knowledge and can be used to determine relationships between factors promoting damage (wetness, salinity etc.) and to measure damage. The same studies are also considering how arrays of agents (microchips linked to an array of climate and damage sensors) can be distributed throughout a complex object. This allows the agents to learn from each other and, in particular, it allows the relationships established from the most advanced damage zone to be used to predict damage progression at other points.

Thus, the recent history of corrosion science indicates a progression from reductionist models with a precise but limited technical focus, to holistic models that attempt to unite models across scales and disciplines, and then finally to a multi-agent approach that attempts to use learning to allow models to be developed directly from sensor data. A critical question is whether this experience is transferable into the field of conservation. The experience indicates that a reductionist approach at too fine a level can lead to misleading conclusions. The corollary in the context of conservation is that studies of the degradation of metallic objects need to extend past simple exposure analysis to a fuller understanding of pollutant sources, transport, deposition, and moisture layer formation and chemistry. In the example of black spots on brasses, discussed later in this paper, this implies an understanding of sources of sulfur species, the effect of indoor climatic conditions on their transport, and the chemistry that develops on surfaces as a response to deposition of sulfur species.

Sensors have frequently been used in the conservation of metallic cultural objects. The principal that progression of damage of an individual object can be assessed by reference to like objects (as in the CSIRO approach) has possibilities, but may be restricted by the requirement to minimise all damage to cultural objects.

3. Models of Degradation

The holistic model discussed above has deepened our understanding on a number of fronts, including:

- Deposition, retention and cleaning of pollutants from objects and, in particular, how the shape of objects influences these processes.
- The effect of marine aerosols on surfaces and different damage forms associated with sea salt relative to NaCl.
- Factors promoting wetness on metal surfaces.

3.1 Deposition, retention and cleaning of pollutants

In Australia, the main atmospheric pollutant is marine aerosols and thus an understanding of aerosol production is paramount. Marine aerosols are produced both in the open ocean and by breaking surf. Cole et al. (2003a) outlined the factors controlling aerosol production in both cases. In the open ocean, aerosols are produced by whitecaps of ocean waves. Whitecap production varies systematically with longitude and season, being at a maximum in low latitudes in July and at a maximum in high latitudes in December, and low all year round in tropical seas. Thus, tropical seas produce a relatively low volume of marine aerosol, resulting in decreased marine corrosion in near-equatorial regions. Salt production is also controlled by ocean effects such as local wind speed , beach slope, and fetch.

Factors controlling aerosol transport are also outlined in Cole et al. (2003a). Aerosol residence times are controlled by convection, gravity and aerosol scavenging by cloud drops, raindrops and physical objects on the ground (trees, buildings etc.). Thus, marine aerosol transport is likely to be higher in dry climates with low rainfall and low ground coverage, while it will be restricted in humid and high rainfall climates with forest cover. Aerosols produced by surf tend to be coarse (5–20 µm) and those produced by whitecaps are generally smaller (0.5–3 µm). Thus, surf-produced aerosol rapidly deposits (due to gravity), while ocean-produced aerosol may be transported considerable distances.

A GIS system has been developed (Cole et al., 2004a) to both define the concentration of marine aerosol at the shoreline arising from both surf- and ocean-produced aerosol, and then to estimate the transport of this aerosol to a given point inland. An Australia-wide map of airborne salinity has been derived and is presented in Fig. 2. The salinity map highlights the pronounced effect of both ocean state (as defined by whitecap activity) and climate factors in controlling airborne salinity in Australia. For instance, southern Australian coastal zones, where whitecap activity is high, have appreciably higher airborne salinity levels than Australia’s northern coast, where whitecap activity is low.

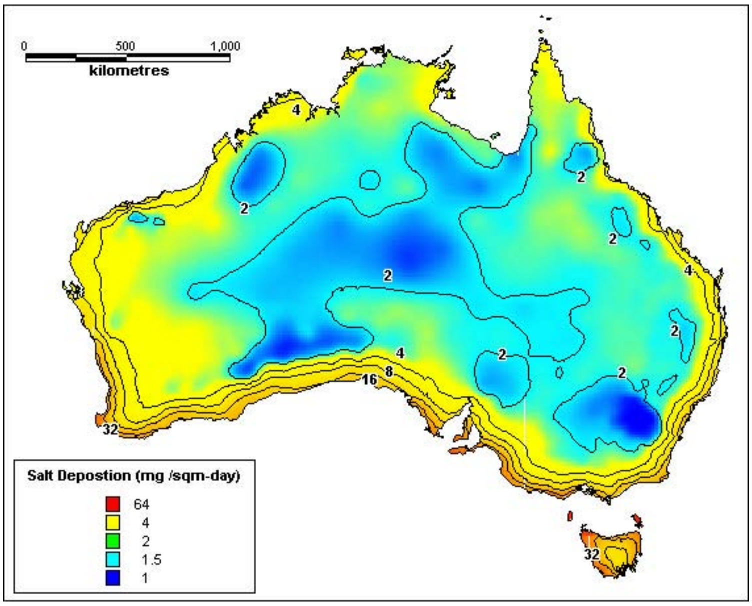

Fig. 2 Salinity map of Australia.

Marine aerosol deposition onto objects is primarily controlled by wind turbulence, and deposition onto an object is a function of turbulence intensity, wind speed, object shape and, to a lesser extent, aerosol size (Cole & Paterson, 2004). For marine aerosols of 0.1–10 µm, the deposition efficiency (as a function of size) is relatively constant, while the efficiency increases rapidly for aerosol sizes above 20 µm, so that the efficiency of 100 µm aerosol is roughly four times that of the 20 µm aerosol. The size and shape of objects are also important. The deposition on an exposed plate (at 45°) is likely to be more than that on an equivalently exposed salt candle. For complex forms such as dwellings, deposition efficiency will vary across a structure, with deposition being highest at the edges of a structure where turbulence is highest. Figure 3 presents the results of a computational fluid dynamics simulation in which particles impact on a simplified building of dimensions 10 m high and 20 m by 20 m in plan. In Fig. 3 the units are particles per square metre, given that 225 particles are released each square metre upstream of the building.

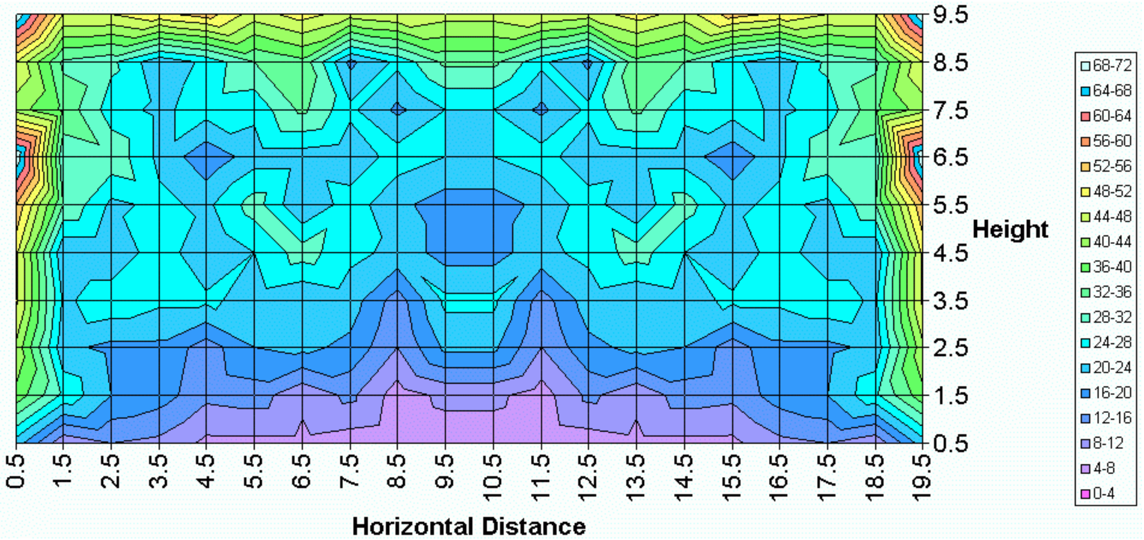

Fig. 3 Aerosol deposition on the front face of a high building (scale total (sum of all sizes) particles per m^2).

A knowledge of airborne salinity and its deposition is of course relevant to the preservation of metal objects exposed in the open. The mapping work defined in Fig. 2 provides an indication of environmental severity in a given geographical location. For example, where salinity is greater than 8 mg/m^2.day, moderate atmospheric corrosion (of course the extent of the corrosion rate depends on the material) is probable. However, preventative maintenance, primarily regular washing, would be sufficient to protect most metal work (with the exception of uncoated iron or steel). Where salinity is greater than 32 mg/m^2.day, severe corrosion is possible for some metals and more active protective measures such as coatings may be required.

Local effects may, however, change these effects. Key effects relate to roughness and turbulence. Surface features, trees, buildings etc., scavenge salt from the atmosphere, depleting aerosol concentration to roughly the height of the object. Thus, a structure in a landscape with significant features of greater height than itself will have a reduced salt load compared to the same structure in an open area. This can of course be used to advantage in landscaping, as trees may be planted to reduce salt loads on structures that are upwind from marine breezes. Structures that rise above the surrounding landscape may show a maximum in salt deposition (and thus possibly corrosion) just above the height of surrounding objects. The second major effect is that of turbulence. This can, of course, lead to differential deposition on an object (as in Fig. 2) and thus additional attention during maintenance should be given to edges on objects. However, turbulence may also affect objects placed on structures. For example, “gargoyles” placed on medieval churches are at a position of high turbulence and thus will suffer from increased pollutant and aerosol deposition. In a more modern context, care should be taken when placing structures near or around sculptures or other openly exposed pieces, to ensure that they do not produce heightened turbulence on the cultural object. This may be negated to some extent due to moisture effects, where increased turbulence will promote drying and lead to decreased corrosion rates, which is especially important when hygroscopic salts are present on a surface.

3.2 Modes of deposition and resulting oxide products

Previously, we discussed the fact that aerosol size depended on its source (surf or whitecaps), but as marine aerosols are hygroscopic, their size also depends on ambient relative humidity (RH). Further, when an aerosol first breaks free of a wave it has seawater composition and then gradually equilibrates (and thus decreases in size). Thus, marine aerosols may take four forms (Cole et al., 2004b) – non-equilibrium near-ocean aerosol (size range 6–300 µm), wet aerosol (3–150 µm), partially wet aerosol (1–60 µm) and dry aerosol (<1–20 µm) – depending on time of flight and ambient RH. These size ranges are based on aerosol mass or volume; mean sizes based on the number or the surface area of aerosols are much smaller. When these aerosols are deposited on a metal surface, a number of characteristic surface "forms" result from the surface aerosol reaction (Cole et al., in press, a). These forms differ in the extent of retained salts, degree of surface alteration and in the formation of corrosion nodules. For example, when a wet aerosol impacts on an aluminium surface (limited initial reactivity), a cluster of deposited salt crystals are formed. These crystals have compositions of either NaCl, MgCl or $CaSO_4$, indicating that the original seawater solutions have segregated. In contrast, if the same aerosol impacts on a galvanised steel surface, there will be strong oxide growth on the surface (predominately simonkolleite and gordaite), with the retention of a NaCl crystal on this oxide layer. Interestingly, rather than the clean crystal edges that are observed for the NaCl crystal formation on aluminium, the NaCl crystal on galvanised steel appears to blend into the underlying oxide. Further oxide formation tends to be favoured at the grain boundaries and triple points on the galvanised surface (see Fig. 4).

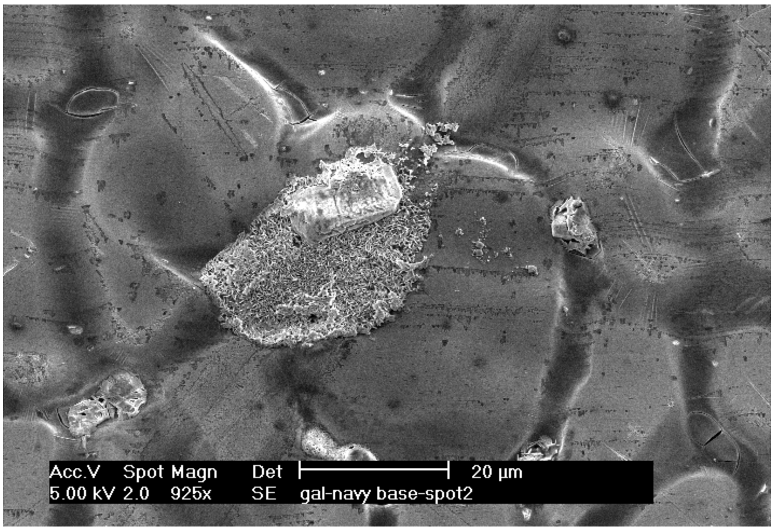

Fig. 4 SEM micrograph showing increased activity between salts and a galvanised steel surface at grain boundaries and triple points.

Recent work by Cole et al. (submitted) investigated the phases that form when microlitre saline drops were placed on zinc. This study demonstrated the variety of corrosion products that may form, and highlighted the importance of mixed cation products in a situation where Na and Mg concentrations are orders of magnitude higher than the Zn concentration generated by anodic activity. The study also highlighted that when dealing with microlitre droplets, processes within the droplet (anodic and cathodic activity, mass transport and diffusion) can dramatically alter droplet chemistry and lead to corrosion products that would not be expected from the initial conditions.

The implications of these observations to the conservation of metallic objects are both direct and indirect. The study of course provides direct evidence for mechanisms of zinc corrosion in marine environments. It also reinforces that when considering objects exposed to marine conditions, consideration must be given to the size range of aerosols and to the chemistry of marine aerosol. Misleading results can be made if marine exposures are approximated with immersion or NaCl only exposure. The unique dynamics of droplets are relevant not only to marine locations, but to all cases were corrosion is promoted by localised wetting or deposition of rain aerosol or hygroscopic particulates. Droplets with volumes in submicrolitres can undergo significant changes in chemistry unlike corrosion in immersed situations, and the chemical changes can either enhance or restrict corrosion.

3.3 Wetting and surface temperature

The presence of a moisture layer is a prime requirement in the corrosion of metals in almost all circumstances. As a first approximation, a surface will wet when the surface relative humidity (RH_s) is greater than the deliquescence RH of any contaminating salts. RH_s can be calculated from the ambient air RH and the surface temperature of the metal. Work by Cole et al. (in press, b) has validated this approach. The surface temperature of an exposed metal can be derived by considering both undercooling to the night sky and daytime solar heating. For undercooling, the rate of heat transfer between the surface of any object and the sky through radiation is given by:

$$Q/A = \varepsilon\sigma(T_{sky}{}^4 - T^4) = h_r(T_a - T)$$

where Q is the heat flow rate (in watts), A is the surface area facing the sky, ε is emissivity, σ is the Stefan–Boltzmann constant (= 5.6697×10^{-8} W m^{-2} K^{-4}), T_{sky} is the mean temperature of the sky, T is the temperature of the surface of the object, h_r is radiation heat transfer coefficient, and T_a is the local air temperature.

However, estimation of surface temperatures also needs to take into account the effect of convection (air above object) and conduction (within the object), and thus wind speed becomes an important limiting factor. Clouds also tend to reduce undercooling (due to reflection of radiation from the earth). Change in the surface temperature of an object in the morning depends on the change in local air temperature, direct and diffuse solar radiation on the object, and heat loss from evaporation. Further, if the surface is wet (e.g. from condensation) a number of other factors apply. Firstly, the effect of evaporation and condensation on heat transfer to the surface must be considered. Secondly, emissivity of water ($\varepsilon = 0.96$) rather than of galvanised metal ($\varepsilon = 0.12$) is used in calculating the radiative heat losses. Thus, undercooling will be significantly reduced by the presence of a condensation layer. After sunrise, the rise in the plate temperature will also be significantly reduced by the cooling effects of evaporation from the surface. Taking all these factors into account, an accurate estimation of surface temperature can be derived (Cole et al., 2004b, p.22). The implications of these results will be considered along with that of moisture layer formation and chemistry in the next section.

3.4 Moisture layer chemistry and pollutants

In considering the effect of pollutants on surfaces, as with marine aerosols, it is vital to consider transport and deposition processes (Seinfeld & Pandis, 1997). Deposition onto a surface may, in principle, be wet deposition (facilitated by rain) or dry deposition (deposition by gases or by particles). A number of transport processes are common to both gases and particles – aerodynamic transport through the atmospheric surface layer to a thin layer of stagnant air adjacent to the surface, molecular or Brownian transport across this thin layer, and finally uptake by the surface. The uptake by the surface is very significantly affected by any surface moisture. The surface absorption of gaseous species is controlled by the normalised reactivity. Gaseous species can also be absorbed in moisture droplets, either in the air or on surfaces:

$$A(g) \Leftrightarrow A(aq) \qquad [1]$$

$$\text{where } [A(aq)] = H_A\, p_A \qquad [2]$$

where p_A is the partial pressure of A in the gas phase (atm), $[A(aq)]$ is the aqueous phase concentration of A (mol L^{-1}), and H_A is Henry's law coefficient. Table 1 presents the effective H_A and normalised reactivity values for various gas species. The effective H_A in Table 1 differs from that represented in Eq. [2], in that it takes into account reactions of the aqueous species.

Where H_A is high and the normalised reactivity is low (e.g. sulfur dioxide), then deposition will be primarily through absorption into a moisture droplet (be it a wet aerosol or a surface moisture film). Where H_A is low and the normalised reactivity is high (ozone), direct gaseous absorption will dominate.

As indicated above, the uptake of gaseous species into moisture layers may be significantly affected by aqueous reactions. For example, the uptake of SO_2 in aqueous solutions is governed by the following equations (Seinfeld & Pandis, 1997):

Table 1. Relevant properties of gases for dry deposition calculations (extracted from Seinfeld & Pandis (1997)).

Species	H_A* (M atm^{-1}) at 298 K	Normalised reactivity
Ozone	1×10^{-2}	1
Nitrogen dioxide	1×10^{-2}	0.1
H_2S	0.12	—
Ammonia	2×10^{4}	0
Sulfur dioxide	1×10^{5}	0
Hydrogen peroxide	1×10^{5}	1
NO_3	2.1×10^{5}	—
Hydrochloric acid	2.05×10^{6}	0

* Effective H_A assuming a pH of 6.5.

$$SO_2.H_2O \leftrightarrow H^+ + HSO_3^- \qquad [3]$$

$$\text{while } HSO_3^- \leftrightarrow H^+ + SO_3^{2-} \qquad [4]$$

The balance of HSO_3^- versus SO_3^{2-} depends on pH, with the former dominating at pH values of 2.5–7, and the latter above this. A major aqueous reaction of importance is the oxidation of SO_3^{2-} or other forms of S(IV) to SO_4^{2-} or other forms of S(VI). This may occur via a variety of mechanisms, including reactions with O_3, H_2O_2 and O_2 (catalysed by Mn (II), Fe (III) and NO_2):

$$S(IV) + 0.5\, O_2 \overset{Mn^{2+},Fe^{3+}}{=>} S(VI) \qquad [5]$$

for example, where S(IV) may be HSO_3^- or SO_3^{2-} and S(VI) is HSO_4^{2-} or SO_4^{2-}.

According to Hoffman and Calvert (1985), the reaction rate is given by:

$$1.2 \times 10^6\, [Fe(III)][S(IV)] \qquad [6]$$

The sulfate that forms from the oxidation of S(IV) may exist as SO_4^{2-} or HSO_4^- (H_2SO_4 dissociates to HSO_4^- under pH ranges likely for droplets in the atmosphere or on surfaces). The balance is governed by:

$$HSO_4^- \Leftrightarrow H^+ + SO_4^{2-} \qquad [7]$$

However, the absorption of ammonia into moisture films will tend to reduce the acidity produced by SO_2 absorption through the following equations.):

$$NH_3 + H_2O \Leftrightarrow NH_3.H_2O \qquad [8]$$

$$NH_3.H_2O \Leftrightarrow NH_4^+ + OH^- \qquad [9]$$

In Fig. 5, the ion concentration in a droplet exposed to conditions of CO_2 at 400 ppm, SO_2 from 20, 40, 75, 150 and 300 ppb, and NH_3 at 20 ppb, is given (Cole, 2000). This examination of pollutant deposition and aqueous chemistry has a number of implications to the conservation of metallic objects. Clearly in the case of metallic objects located in the open, the implications are direct. In this case the major implication is that a knowledge of the gaseous SO_x may not give a reliable measure of corrosivity. Deposition rates, which will depend highly on both rain and RH, and oxidants and catalysts (such as O_3, H_2O_2 and Mn (II), Fe (III) and NO_2), and any alkali precursors (e.g. ammonia), will control the pH of resulting moisture films or drops.

In an interior environment, the possible deposition pathways for pollutants will be highly dependent on RH and on any hygroscopic particulates or aerosols. If RH is low and in the absence of hygroscopic species then only direct gaseous deposition is possible. However, if the RH exceeds the deliquescent RH (DRH) of particulates in the air or on metal surfaces, then pollutant deposition will be enhanced by the absorption of gaseous species into the aqueous phases that form when the particulates wet. The DRH of some common salts is given in Table 2.

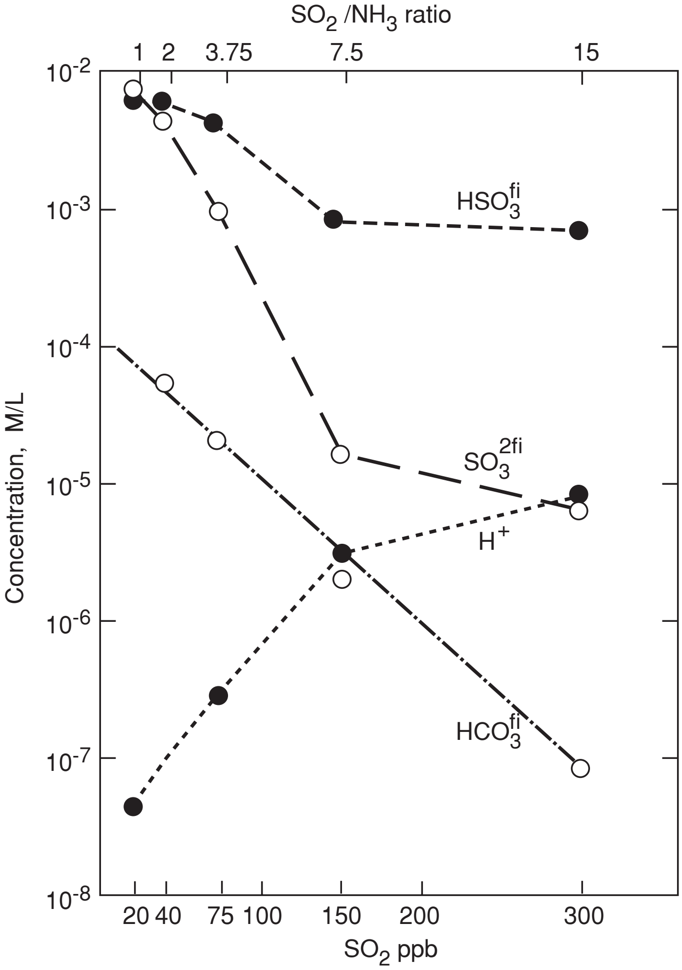

Fig. 5. Ion concentration as a function of gaseous SO_2 concentration and SO_2/NH_3 ratio (from Cole (2000)).

Table 2. DRH for common aerosols (at 20°C) (from Seinfeld & Pandis (1997)).

Salt	DRH (%)
Na_2SO4	84.2
NH_4Cl	80.0
$(NH_4)_2SO_4$	79.9
NaCl	75.3
$NaNO_3$	74.3
$(NH_4)_3H(SO_4)_2$	69.0
NH_4NO_3	61.8
NaHSO4	52.0
$(NH_4)HSO_4$	40.0
MgCl	35.0

An example where these factors may be in play is in the black spots on brass. It is observed that such black spots are favoured by the presence of high RH and hygroscopic dust particles (Weichert et al., 2004). Further,

SO_2 is readily absorbed into the aqueous phase (as indicated by its high H_A). Thus, under these condition, acidic sulfide and sulfate containing moisture phases are likely to form. The reaction of moist aerosols or surface droplets of such a composition with bronzes could well lead to spotting, although the corrosion products likely to form would be chalcanthite $CuSO_45H_2O$, antlerite $Cu_3SO_4(OH)_4$ and brochantite $Cu_4SO_4(OH)_6$, rather than covellite (CuS).

3.5 Surface cleaning

Experimental studies have indicated that surface cleaning of deposited salts by wind and condensation drip-off is of limited efficiency, and that surface cleaning by rain is the predominate mechanism of surface cleaning (Cole et al., 2004c). Surface cleaning occurs when raindrops run off the surface, collecting surface salts that are in their path. Run-off occurs when a raindrop on a surface has grown through coalescence to a critical size. When the slope of the surface is θ (0° for horizontal and 90° for vertical) and the maximum contact angle between the water and the surface is ϕ (the minimum contact angle is here assumed to be zero), then the maximum volume of a drop that can be retained on the surface V_{max} is calculated from (all dimensions are in mm):

$$A_{\max} = 7.49\,(1-\cos(\phi))/\sin(\theta)$$

$$h_{\max} = 1.2(1-\cos(\phi))^{0.8}(1+0.5/\sin(1.06\theta))$$

$$V_{\max} = \frac{8}{3\pi}\frac{A_{\max}^2}{h_{\max}}$$

Figure 6 presents the volume of a raindrop required for run-off against the contact angle. Figure 6 indicates that the more wettable a surface (the lower the maximum contact angle ϕ), the lower the drop volume before instability. Thus, more wettable surfaces will clean in lighter rain than less wettable surfaces.

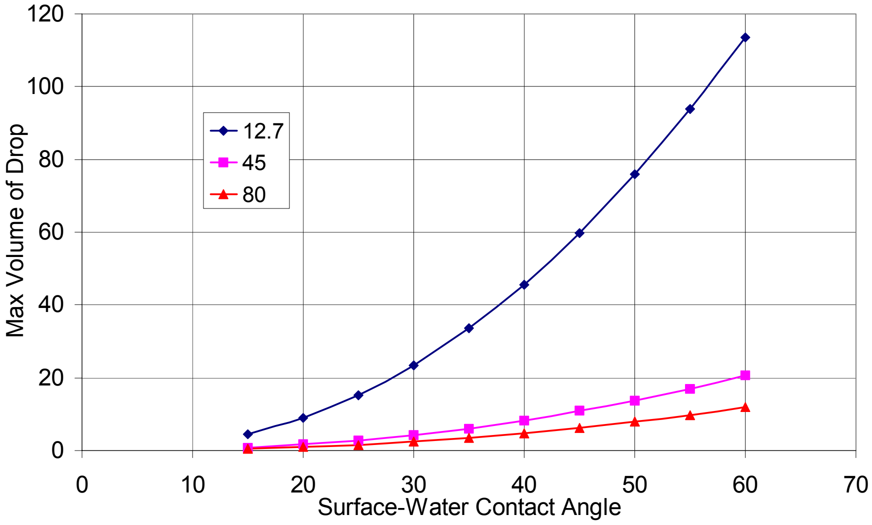

Fig. 6. Droplet run-off from a surface as a function of the surface-water contact angle ϕ for three surface slopes of θ = 12.7, 45 and 80.

The results of these studies are most relevant to cultural objects exposed in the open. The results indicated that below a given amount of rain, the rain will be retained on the surface and may promote salt concentration rather than cleaning. If rain is in excess of this critical value, wash-off will occur and the surface will be cleaned. The volume of rain deposited in a "shower" shows a relationship to latitude, and thus the average volume of rain per shower is significantly lower in Hobart relative to Cairns. Thus, maintenance practices in Hobart should not rely on cleaning by rain, despite the relatively high rainfall is this city. A second effect relates to the wettability of a surface. As indicated in Fig. 5, the higher the surface contact angle, the greater the maximum volume of a drop before run-off, and thus the greater the volume of rain before wash-off. Thus, surface treatments that reduce wettability will also reduce the effectiveness of rain washing.

3.6 Oxide properties

The ability of passivation films of varying chemistry to protect zinc was investigated by Muster and Cole (2004) and Muster et al. (2004). Passivation films replicating those produced during atmospheric corrosion (zinc oxide, zinc hydroxychloride, zinc hydroxysulfate and zinc hydroxycarbonate) were formed as precipitates from aqueous solution, and as surface films on zinc metal powder and rolled zinc sheet. The protective nature of oxides was evaluated in terms of stability (solubility) in chloride environments, surface charge and porosity. Microelectrophoresis measurements performed on precipitated oxides as a function of pH showed that oxides containing a majority of zinc hydroxycarbonate and zinc hydroxysulfate compounds possessed a negative surface charge below pH 6, whilst zinc oxide-hydroxide and zinc hydroxychloride surface films possessed iso-electric points higher than pH 8. The ability of chloride species to pass through a bed of 3 μm diameter zinc powder was found to increase for surfaces possessing hydroxycarbonate and hydroxysulfate surface species, suggesting that negatively charged surfaces can aid in the repulsion of chloride ions. Electrochemical analysis of the open-circuit potential as a function of time at a fixed pH of 6.5 showed that the chemical composition of passive films on zinc plates influenced the ability of chloride ions to access anodic sites for periods of approximately one hour. The ability of metals to wet was also shown to vary with the chemistry of its surface oxide. Contact angle determinations using liquid penetration and Wilhelmy balance techniques were able to systematically rank the oxides in order of their wetting properties. In addition, data from wet perimeter measurements on passivated zinc plates suggested that zinc hydroxychloride and zinc hydroxysulfate films possess a greater porosity than zinc oxide-hydroxide and zinc hydroxycarbonate films.

These results have direct implications to cultural objects coated with or composed of zinc or zinc alloys. However, the work also demonstrates the relationship between iso-electric points and chloride diffusion in controlling corrosion, which will affect a wider range of materials and may indicate methods of developing protective coatings or films.

4. Sensors

There are several electrochemical approaches used to sense corrosion processes, including linear polarisation resistance (LPR), electrical resistance (ER), electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN). In addition, corrosive processes are dependent upon environmental conditions and can therefore be monitored using microclimate probes to measure such things as temperature, pH, gas concentrations, RH, time of wetness (TOW), solution conductivity and chloride concentration. Other methods fall into the domain of non-destructive testing and include techniques based upon optical (i.e. CCD and optical fibre), ultrasound/acoustic, electromagnetic (i.e. eddy current) and electromechanical effects (Agarwala & Ahmed, 2000).

LPR and ER are well-developed approaches for corrosion sensing, and have the ability to provide an estimate of the actual corrosion rate of the sensing element, therefore making it somewhat simpler to create "sensed-to-actual" damage relationships. In addition, both LPR and ER sensing devices utilise degrading electrodes that replicate the material of interest. Another approach is the use of galvanic couples (i.e. Zn-Cu, Zn-Cd or Al-Cu) to detect the bridging of electrodes by moisture/electrolyte. Galvanic approaches require calibration to enable the detected current fluxes to be related to degradation rates of the material of interest. Galvanic sensors are often used merely as TOW sensors (ASTM, 1989). ER methods appear to be the most suitable electrochemical probes for in-service monitoring where the presence of electrolyte films is infrequent. In addition, the accuracy of LPR sensors also requires a continuous evaluation of the ionic exchange properties at the metal–solution interface. Solution resistances in thin electrolyte films must also be characterised for LPR (Klassen & Roberge, 2003). EIS is particularly useful for studying the degradation of organic films. One EIS approach utilises a conductive paint electrode to test for changes in the performance of painted metals (Davis & Dacres, 1999). EN is a technique that measures temporal fluctuations of current or potential to sense changes in the kinetics of electrochemical processes. EN measurements are non-destructive, however data is often difficult to interpret. Wain et al. (1996) have reported on the use of EN for the evaluation of coatings on museum artefacts.

In terms of corrosion sensors, the most exciting progressions are likely to be made in the areas of semiconductor devices, fibre-optic sensors and microelectromechanical sensors (MEMS). Semiconductor devices based on Silicon technology are already developed to detect changes in electromagnetic radiation, mechanical damage, magnetic fields, temperature and humidity (Middelhoek & Hoogerwerf, 1990). Some advancement in the area of chemical sensing has been made based upon field-effect transistor (FET) devices. Ion-sensitive FET (ISFET) devices exist for gases (CO, O_2, CO_2, NH_3), and simple ions such as protons (pH), sodium, potassium and chloride have been constructed. FET devices are also well developed as temperature and RH sensors (Kelly & Owen, 1990). Both *intrinsic* and *extrinsic* fibre-optic sensors show promise to detect physical strains in materials through deformation of the fibre. However, extrinsic fibre-optic sensors have the ability to detect the concentrations of chemical species in solution volumes too small for traditional ion-selective electrodes. A typical set-up for such a system would involve an optical fibre in contact with an electrolyte containing ionophores enclosed by an ion-selective membrane. A system has been developed to sense Cu ion concentrations down to 10^{-7} M using a cell volume of 200 nl. One of the main advantages of fibre-optic sensors is their immunity to corrosive processes. Their small size also allows them to be incorporated into or onto structures with minimal side effects (Lee, 2003). MEMS devices are generally based upon the piezoelectric effect, thus converting mechanical to electrical energy and vice versa. There are several MEMS systems developed to detect physical changes such as pressure, strain or acceleration (Galea et al., 2001). One particularly exciting adaptation of MEMS is to utilise piezoelectric materials to emit and detect ultrasound waves. Ultrasound wave techniques have the ability to detect localised defects based upon variations in wave propagation. One of the key advantages of MEMS is their small size and their ability to be incorporated into arrays on surfaces. MEMS devices may also be designed to function as gas sensors. Also, it is possible to utilise SAW devices that exhibit chemically selective thin films. The adsorption of chemical species onto SAW devices alters the transmission of acoustic waves.

Each of the techniques above is applicable to monitoring the condition of cultural objects. The selection of the particular system will depend on practical considerations, cost and the exact need. For example, if very early indication of conditions that may give rise to damage is required, FET or ISFET devices may be appropriate, or if a small amount of damage can be tolerated, LPR, ER or galvanic sensors would provide a more direct reading.

5. Conclusions

This paper has reviewed progress in corrosion science in the areas of meta-methodology, models of degradation and sensors for studying corrosion. It has been highlighted that the following advances have been made in the last decade:

- Meta-methodology – the modelling of corrosion has moved from a narrow reductionist process to a holistic approach, and then onto a sensor-based learning approach.
- Models of degradation – the new holistic models of degradation include an understanding of pollutant sources, transport and deposition, the nature and chemistry of any moisture layers formed on the surfaces, and the properties of oxides that develop on a surface.
- Sensors – a wide range of sensors, including linear polarisation resistance, electrical resistance, electrochemical impedance spectroscopy, electrochemical noise and galvanic couples, have been developed. Others including field-effect transistor devices, ion-sensitive devices, fibre-optic sensors and microelectromechanical sensors are in the late stages of development.

The implications of these developments for the conservation of metallic objects and structures are indicated.

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