

Report Colorbond Degradation Model

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EXECUTIVE SUMMARY

This report documents work carried out in order to develop and prove a model for predicting the lifetime of painted metal components, with a particular emphasis on Colorbond® due to its prominent use throughout Australia. This work continues on from previous developments reported in 2002-059-B No. 12 [1]. Extensions of work included the following research:

- (1) Experimental proving of the leaching of chromate inhibitors from Colorbond® materials.
- (2) Updated models for the accumulation of salts and the time of wetness for gutters, based upon field observations.
- (3) Electrochemical Impedance Spectroscopy investigations aimed at correlating the corrosion rates of weathered Colorbond® with those predicted by modeling.

1 INTRODUCTION

In the previous phase of this project a model was developed for predicting the lifetime of painted metal components, with a particular emphasis on Colorbond® due to its prominent use throughout Australia. [1] Colorbond® is a product of Bluescope steel and has been proven to have exceptional performance in most locations across Australia. Although there are different grades of Colorbond®, the most common make-up for guttering is steel sheet (low carbon steel) with a coating of zincalume AZ 150 (150 g m-2), which is overcoated on both sides with a 5 μ m chromate-containing epoxy primer. The one-sided product has a 20 μ m thick UV-resistant topcoat and a 5 μ m grey backing coat covering the primer (Bluescope Steel, 2005). Colorbond® gutters are assembled so that the backing coat forms the interior of the gutter and the coloured topcoat forms the outer gutter.

This document reports on experimental work to validate and refine the model for degradation of Colorbond®. This includes:

- (1) Experimental proving of the leaching of chromate inhibitors from Colorbond® materials.
- (2) Updated models for the accumulation of salts and the time of wetness for gutters, based upon field observations.
- (3) Electrochemical Impedance Spectroscopy investigations aimed at correlating the corrosion rates of weathered Colorbond® with those predicted by modeling.

2 THE LEACHING OF CORROSION INHIBITORS FROM COLORBOND®

The leaching of chromate inhibitor from Colorbond was studied as a function of the following: 1) topcoat or backcoat

- 2) type of defect (circular defect, scribe or edge)
- 3) the size of the defect.

Seven samples were prepared as detailed in Table 1. Each sample was exposed to 50 mL of aqueous solution at pH 2 (pH adjusted using HCl) for varying periods of time. The dissolution of chromate corrosion inhibitor pigments into the aqueous solution was monitored.

Sample	Exposed coating	Damage	Total area exposed to leaching solution (cm ²)	Exposed area of metal (cm ²)	Exposed area of primer (cm ²)
1	Topcoat	-	18.2	0	0
2	Backcoat	-	18.2	0	0
3	Edge	Eight 2 cm × 2cm	Topcoat =8 Edge =2.16	Steel =1.92 Zincalume =0.128	0.032
4	Topcoat	3 × 70 µm wide scribes	18.2	0.101	0.0144
5	Topcoat	10 × 100 μm diameter circular defects	18.2	7.85 × 10 ⁻³	0.314
6	Topcoat	4 × 500 µm diameter circular defects	18.2	7.85 × 10 ⁻³	0.628
7	Topcoat	1 x 2 mm diameter circular defect	18.2	0.0314	0.628

Table 1. Experimental details of leaching studies.

Figures 1 and 2 show the appearance of each of the samples after two leaching cycles and seven leaching cycles, respectively.

2.1 The action of chromate

Appendix B gives the details of the various solution concentrations measured over a 43-day period. Over the length of the test Colorbond specimens were exposed to aqueous solutions at pH 2. Cell 1 showed no detectable trace of soluble chromium suggesting that the topcoat provides an effective barrier against degradation over short time frames. Cell 2, which exposes the backcoat of Colorbond to pH 2 solution, showed a release of 0.025 mg/L (0.0005 mol/L) into solution over the first 24 hours. At neutral pH, Scholes et al. (2006) showed that 200 μ g/cm² of Cr could be released from a chromate inhibited primer over a 10-day period [2]. The amount released in the first 24 hours from the backing coat in the present study amounted to less than 0.07 μ g/cm². No chromium was detected in leaching for the remainder of the experiment.

Chromate release from cut edges was more significant than from planar faces of Colorbond. Cell 3 contained an edge length of 64 cm. Assuming a 5 μ m thick primer, this equates to a primer area of 0.032 cm². In the first 24 hours the Cr release is estimated to be approximately 405 μ g/cm², a release that more closely matches the reported value of Scholes *et al.* [2]. The release over the first 24 hours was modeled against Fick's second law of diffusion [3], whereby a plot of log[dC/dt] (the concentration change over time) against log t gives a slope that represents the exponent of the inhibitor release. Fickian diffusion is represented by a slope equal to -0.5 (assuming a constant surface concentration of diffusing species) whilst anomalous diffusion is a collective term given to concentrations that do not change as t^{0.5}. Figure 3 shows that chromate is initially released from a cut edge with a slope of -0.85 = n-1, resulting in an exponent of t^{0.15}, indicating a rapid release of chromium. In contrast, strontium was found to release with an exponent of t^{0.55}, which is a close approximation of Fickian diffusion behaviour.





Figure 1. Photographs of the seven cells after two leaching cycles.

2

4

6















Figure 2. Photographs of the seven leaching cells after seven leaching cycles.



Figure 3. The leaching rate of chromium as a function of time from the cut edge of Colorbond XRW.

Figure 4 below shows that cell 7 (with a 2 mm diameter area of damage) produced a significant amount of soluble chromate after 5 minutes. A second sample taken after one hour showed no detectable chromium concentration. Cell 5 also showed some chromium in the initial sample but none thereafter. No soluble chromium was present on cell 6. Both cell 2 and cell 4 showed a gradual release of chromium for 5 to 24 hours, and thereafter no chromium was released into solution.



Figure 4. Leaching of chromate from paint films with various damage sites.

Cr(VI) species are known to have high aqueous solubility, however, Cr(III) species are likely to precipitate out of solution at more neutral pH's. Solubility of Cr(OH)₃ is reported to be 10^{-30.27} at 17 °C in 0.1 M KCI (Bjerrum et al., [4]). Despite the low solubility, the low pH should ensure that Cr species are able to exist in solution. pH measurements of the final solutions showed increases during the experimental lifetime, which can lead to the precipitation of Cr(III) oxides. For this reason the chromium levels appeared to be initially high (where the time of solution contact with the sample was short) and then decreased at longer experimental times, as the concentration of metal ions in solution increased, which leads to increased pH levels through hydrolysis.

Strontium and zinc concentrations, unlike most other species measured by ICP analysis appeared to be unaffected by an increase in pH. Therefore, the relationships existing between strontium and chromium concentrations in the measurements taken during the first 24 hours were extended to longer time periods in order to predict longer-term chromate concentrations. SrCrO₄ should ideally be dissolved to give a 1:1 ratio of Cr:Sr, however, as Figure 5 shows the initial release of chromium is significantly higher than for strontium. For the cut edge, the 1:1 ratio is obtained after longer leaching times, approximately greater than 300 hours.



(b)

Figure 5. (a) Concentrations of Strontium and Chromium during the first 48 hours of leaching from the cut-edge of Colorbond XRW in 50 mL aqueous solution at pH 2. (b) Cr:Sr ratio for leaching from the cut-edge over a longer time period.

Estimations for the rate of chromate leaching were obtained from strontium chromate leaching data, which showed consist changes in concentration as a function of time, as shown in Figure 6.



Figure 6. Leaching data for strontium and chromium from cell 5 (topcoat with pinhole defects) as a function of leaching time. Note that a return to zero concentration occurs when the pH 2 leaching solution is refreshed.

The rate of chromate depletion from a damaged topcoat (with pinholes according to Cell 5) and undamaged backcoat of Colorbond materials was determined for the first 24 hour period, after which it was estimated from the solution concentrations of strontium ions. The resultant dependence upon time is given in Figure 7.



Figure 7. Chromium concentrations removed from Colorbond after short time periods and those estimated from strontium ion concentration after longer time periods.

The original model assumed that chromate was depleted with a dependence of $t^{0.5}$. It is now believed that $t^{0.25}$ or $t^{0.35}$ are more realistic dependencies [2], and hence an updated calibration has been made.

3 THE WEATHERING OF POLYMERS

Previous work by Martin and co-workers at the CSIRO accrued data on the solar irradiance, ultraviolet radiation and solar weathering performance of polymeric films Australia-wide [5]. The data from this work has been analysed and compared with climatic data from the Bureau of Meterology. Climatic variables considered were the average maximum daily temperature, average relative humidity (9am and 3pm) and average rainfall. Previous work by Bauer [6] demonstrated that solar irradiation data could be converted to a weathering index by considering the affects of daily temperature maximum's and relative humidity. Increases in temperature provide the polymer with energy, which increases the rate of photooxidation through an Arrenhius-type relationship with temperature. Relative humidity is known to influence the weathering of polymer and to promote photooxidation, however, it is not used in deriving the relationship between climatic conditions and the solar weathering index of Martin [5]. Rather, the increased rate of degradation in humid environments is dealt with elsewhere within the model in terms of the rate at which the corrosion inhibitor is consumed within a polymeric film.

Figure 8 shows the dependence of the solar weathering index on average maximum daily temperature, average relative humidity (9am and 3pm) and a combined variable of average maximum daily temperature^k/average relative humidity (T^k/RH, which has an optimised regression of 0.75 where k = 1.7).



Figure 8. Relationships between simple climatic parameters (average daily maximum temperature and average daily relative humidity [9am and 3pm]) and the solar weathering index of Martin [5].

4 IMPLEMENTATION OF MODEL

In the previous model the relative photooxidation rates with damage to colorbond was achieved through by matching the % failure data provided by Bauer [6] with the failure ratings of Colorbond provided by King et al. [7]. Failure of the topcoat and backing coats leads to an increased loss of chromate from the primer. The total loss of chromate, L_{total} (mol) was given as:

$$L_{total} = L_{Cl}(1+xt)(-0.0004*LAT^2+0.0003.LAT)$$
 mol ... Eqn(1)

where x = 0.8 for topcoat and 0.4 for backing coat, t = time in years, LAT = latitude in degrees.

In the current model the solar weathering index, W is given as:

$$W = \frac{\frac{(1.54 \frac{T_{av}}{RH_{av}} + 6.5)}{6.5}}{\dots \text{Eqn(2)}}$$

The value of *W* represents the rate of degradation of a painted sample due to irradiance from the sun and leads to a revised expression for the loss of chromate, which will be discussed below.

4.1 Influence of salt concentration on leaching rate

Chromate leaching has been shown to be a function of chloride concentration [8]. Chloride anions are able to associate with soluble chromate and encourage dissolution of pigments. Prosek and Thierry [8] found that 10 mmol L⁻¹ of NaCl increased chromate leaching by 30%. Also, by increasing the NaCl concentration to 100 mmol L⁻¹ had minimal additional impact. From previous work [1], the amount of chromate leached during a 3-hour period allowing for the influence of salt concentration was given as:

$$L_{Cl} = (L_t - L_{t-1})^* (1.2123[Cl]^{0.1544}) \qquad \dots \text{Eqn(3)}$$

In the present model new data from chromate leaching experiments at pH 2 have developed relationships that link the rate of chromate removal to the rate at which the underlying metal is removed.

Annual rainfall in Australia generally varies from less than 200 mm up to 1500 mm. The percentage time of wetness can vary from less than 10% to over 60%, and up to 100% if the coated metal is dirty, with for instance leaf litter. Chromate was previously assumed to leach according to Fick's second law (i.e. $t^{0.5}$ dependence), however, data from Figure 7 (above) indicates that leaching from Colorbond follows a dependence closer to $t^{0.25}$ or $t^{0.35}$. The solubility and rate of chromate removal is pH dependent, as demonstrated by Sinko [9]. From Sinko, strontium chromate (SrCrO₄) was shown to have a pH-dependent saturation solubility given by:

$$C_{sat} = -0.5 \times pH + 4.5 \qquad \dots \text{Eqn(4)}$$

Therefore, at pH 2 C_{sat} = 3162 mmol/L and at pH 6 C_{sat} = 31.62 mmol/L. The amount of chromate removed in the accelerated experiment can be approximated to be 100 times that at pH 6.

4.2 Degradation of damaged (with pinholes) Colorbond topcoats

Several calculations are required to estimate the longevity of roofs. The approach here is to estimate the amount of chromate removed in one year. The rate of loss of chromate, zinc and aluminium species has been estimated under laboratory conditions. Therefore, the amount lost in subsequent years can then be estimated and matched with the rates of zinc and aluminium loss given the amount of removed chromate. This model is not expected to hold where there is more significant damage to the topcoat (i.e. scuffing and scratching).

1. The average annual maximum temperature and average annual relative humidity are used to calculate the solar weathering factor, based upon the work of Martin [5], where:

$$W = \frac{1.54 \frac{T_{av}^{(1)}}{RH_{av}} + 6.5}{6.5} \qquad \dots \text{ Eqn(5)}$$

The weathering factor alters the rate at which chromate is leached during wet conditions. A value of W=1 exists where the average maximum temperature = 0 °C. The weathering factor for Australia largely varies between 1.1 in cooler climates (Melbourne) up to 3.1 for warmer climates (Longreach). A value of W=1 is also used for internal surfaces, such as the interior of downpipes where exposure to solar radiation can be ignored.

2. Chromate loss occurs during the periods where the surface is deemed to be wet. These wet periods are obtained from the current holistic model [11] as time-of-wetness (TOW). The chromate loss during the first year is calculated as:

$$Cr_{1yr} = [(1.1 \times (1 + (TOW/100))^{0.25W/6.5}) \times 1.2123 \times [Cl_{av}]^{0.1544}]$$
 ... Eqn(6)

Where $[Cl_{av}]$ is the average salinity (mg/m².day) measured over a 1 yr (or longer period). The chromate loss has the units of nmol/cm².

3. The loss of chromate for each subsequent year is given as:

$$Cr_t = Cr_{1yr} \times t^{0.25W}$$
 where time (t) is in years. ... Eqn(7)

4. The loss of zincalume from the topcoat is calculated by the following equation:

$$AlZn_{loss(\mu m)} = \left[\left(Cr_t \times 0.0643 \right) + \left(Cr_t \times 0.3 \right) \right] \times \frac{\left(0.00045 [Cl_{av}] \right) + 0.02255}{0.182075} \qquad \dots \text{Eqn(8)}$$

Where $(Cr_t \times 0.0643)$ accounts for the loss of zinc, $(Cr_t \times 0.3)$ accounts for the loss of aluminium and the remainder of the equation is the scaling factor that links the rate of zincalume loss from laboratory tests in 0.01 M chloride to the daily average salinity in the field (mg/m².day). Figure 9 below demonstrates the correlation between strontium chromate removal and that of the underlying zincalume and steel.



Figure 9. Correlations between the concentration (in mol L-1) of strontium released into solution and those of zincalume and steel in aqueous solution acidified to pH 2 using HCI.

The onset of white rust can be estimated where ZnAl losses exceed 2 μ m. The onset of red rust is achieved when a loss in ZnAl thickness of 15 μ m has been reached.

4.2 Degradation of undamaged Colorbond backcoats

The application of the weathering factor is essentially the same for the backcoat as for the topcoat but with its own relationships for chromate and zincalume loss.

The governing equation relating to chromate removal from a backcoat is:

$$Cr_{1yr} = [(1.65 \times (1 + (TOW/100))^{0.33W/6.5}) \times 1.2123 \times [Cl_{av}]^{0.1544}] \qquad \dots \text{Eqn(9)}$$

This again is the chromate loss for one year (Cr_{1yr}).

- 5. The loss of chromate for each subsequent year is given as: $Cr_t = Cr_{1yr} \times t^{0.35W}$ where time (t) is in years. ... Eqn(10)
- 6. The loss of zincalume from the backcoat is calculated by the following equation:

$$AlZn_{loss(\mu m)} = \left[(Cr_t \times 0.417) + (Cr_t \times 1.066) \right] \times \frac{(0.00045[Cl_{av}]) + 0.02255}{0.182075} \qquad \dots \text{Eqn(11)}$$

Where $Cr_t \times 0.417$ accounts for the loss of zinc, $Cr_t \times 1.066$ accounts for the loss of aluminium and the remainder of the equation is the scaling factor that links the rate of zincalume loss from laboratory tests in 0.01 M chloride to the daily average salinity in the field (mg/m².day).

Figure 10 below demonstrates the correlation between strontium chromate removal and that of the underlying zincalume and steel.



Figure 10. Correlations between the concentration of strontium released into solution and those of zincalume and steel in aqueous solution acidified to pH 2 using HCI.

4.3 Application of model to other painted metal building products

The model presented for the degradation of Colorbond guttering may be extended to other building components including downpipes, roof sheeting and ridge capping. In order to do this the average salinity, $[Cl_{av}]$ and average time-of-wetness (TOW) for each component need to be predicted. Weathering factors calculated for gutters apply to all other predictions excluding the internals of downpipes.

Modelling of Colorbond downpipes

- estimate TOW and [Clav] as per deposition models
- estimate chromate leaching rate and subsequent loss of zincalume using equations 5-8 (external) and 9-11 (internal). The weathering factor, W reduced to a value of 1 for the internal section of the downpipe.

Modelling of Colorbond roof sheeting and ridge capping.

- estimate TOW and [Clav] as per deposition models
 - estimate chromate leaching rate and subsequent loss of zincalume using equations 5-8 (external).

5 MODELS FOR THE ACCUMULATION OF SALTS AND THE TIME OF WETNESS IN GUTTERS (re-worked)

The environmental conditions inside a gutter can vary significantly from those of openly exposed surfaces. The prime causes of these variations during roof surveys have been observed to be: (i) the presence of dirt or leaf litter in the gutter, or (ii) incorrectly installed or damaged gutters that retain pools of moisture.

For modeling purposes the time-of-wetness (TOW) experienced by gutters is assumed to be the same as an openly exposed roof only if it is clean and well-drained (i.e. the gutter is wet when the roof is wet). Work by Ganther et al. showed that dirty gutters on the other hand have been shown to take up to ten days to dry once they have been wet [10]. For modeling purposes a dirty or water-retaining gutter is assumed to be wet unless the relative humidity (RH) is less than the critical humidity (defined by the types of salts present) for greater than 240 hours. Please refer to the work of Cole et al. [11] for rules concerning the critical relative humidity.

The accumulation of salt in gutters is modeled by assuming that all salt entering the gutters has its origins from the roof. As figure 10 demonstrates, the amount of salt being deposited onto a roof (mg/m^2) can be translated to a salt concentration within the gutter with knowledge of the volume of moisture runoff (mm) and the collection length of the gutter (L). The width of the gutter is assumed to be 0.1 m.



Figure 11. The relationship between roof area and gutter area. Roof area = L/0.1 (or 10 × L) times the gutter area.

Therefore, the following inputs must be specified for the calculation of TOW and salt concentration within gutters:

- 1. Clean and well-drained gutter
- 2. Dirty or water-retaining gutter
- 3. Input roof collection length (m).

Details of the implemented model for the calculation of TOW and salinity are contained in Table 2.

NEW IMPLEMENTATION
At the <u><i>i</i>+1</u> th <u>3-hour interval</u> if rain cleaning occurs then
NEW IMPLEMENTATION At the <u>i+1th 3-hour interval</u> if rain cleaning occurs then Salt deposition is given by the Holistic model as follows: $D_{i+I} = \phi + (\psi^* D_i)$ Salinity loss is calculated as follows: $Sal_{loss} = D_{i+I} - D_i$ Salinity increment is calculated as follows: $\Delta Cl = SAL_{loss} * L * 10$ Rain depth in gutter is calculated as follows: $R_g = Rain * L * 10$ Fraction of SAL remaining is calculated as follows: $SAL_{fraction} = 1 - \left(\frac{R_g - R_g timiz}{R_g} \right) \qquad R_g > R_g timiz}$
$R_{g}^{iimit} = \begin{cases} 1 & clean \& well drained gutter \\ 5 & dirty or water retaining gutter \end{cases}$ NOTE: if there is no rain cleaning occurs then $SAL_{fraction} = 1$

Table 2. A comparison of old and new implementations for the calculation of salt concentration and time-of-wetness in gutters.



An example of the performance of the model is given by the calculated data for Brookfield State School in Queensland (152.913, -27.495). Figure 12 shows the data inputs of rainfall, chloride loss (from the roof), the surface state (old model) and accumulated chloride (cum_Cl using old model).



Figure 12. Estimations of the accumulation of salt in gutters at Brookfield State School calculated from rainfall runoff and accumulation using the old model.



Figures 13 and 14 show the revised chloride accumulation for clean and dirty gutters, respectively.

Figure 13. Accumulated chloride in a clean gutter over a one year period predicted using the revised methodology and assuming a collection length of 5m.



Figure 14. Accumulated chloride in a dirty gutter over a one year period predicted using the revised methodology and assuming a collection length of 5m.

There is a large different in the levels of accumulated salt in gutters. The old model has an average accumulated salt concentration of 10.7 mg/m^2 whilst the new model

calculates an average of 1.15 mg/m² for clean and well-drained gutters and 11.46 mg/m² for dirty gutters. The lower salt levels are likely to increase the working life of gutters. However, the presence of dirt in gutters and incorrectly installed gutters keeps them wet for longer periods of time. Typically open roofs can dry within 30 minute periods whilst dirty gutters have been shown to stay wet for over 10 days, even though the relative humidity can remain below a critical level in which salts are able to wet. For a dirty gutter at Brookfield state school it was estimated that it stayed wet for 354 days per year.

The levels of decreased chloride predicted using the new methodology have been observed experimentally, where a series of samples were taken from dirty gutters and analysed for their chloride content (Table 3). Here a fixed mass (100 g) of dried leaf/dirt matter or free tree matter was mixed with 500 ml of high purity water and allowed to incubate in a shallow tray for approximately 30 days. After this time the samples were filtered and the filtrate analysed using inductively couple plasma (ICP) atomic emission spectrometry (AES). Table 3 demonstrates that the amount of chloride ions available in a gutter is significantly reduced (in comparison to leaf matter) for most of the specimens tested. This indicates that chloride ions readily get washed from gutters due to a more consistent contact with aqueous solution and greater dilution due to increased thicknesses in water layers.

Table 3. Analytical analysis of aqueous solutions obtained from (i) leaf matter in dirty gutters and (ii) solutions prepared from identical amounts of tree matter only. Further experimental detail is given in the text.

Specimen	(ppm)
Willow Myrtle (gutter)	30
Willow Myrtle (tree only)	190
Liquid Amber 1 (gutter)	53
Liquid Amber 1 (tree only)	190
Liquid Amber 2 (gutter)	85
Liquid Amber 2 (tree only)	210
Golden Ash (gutter)	120
Golden Ash (tree only)	213
Eucalypt (gutter)	120
Eucalypt (tree only)	80
Conifer (gutter)	5
Conifer (tree only)	418

6 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) OF COLORBOND®

6.1 Introduction to EIS

The impedance describes the frequency-dependent relationship between voltage and current. It is comprised of real imaginary parts.

$$Z(w) = Z_{\rm Re} - jZ_{\rm Im} \qquad \dots Eqn(12)$$

where Z_{Re} is real, for example the resistance, R, and Z_{Im} is imaginary = reactance (X_C) = 1/ ω C.

The magnitude of |Z| is given by:

$$|Z|^2 = Z_{\text{Re}}^2 + Z_{\text{Im}}^2$$
 ... Eqn(13)

The phase angle (ϕ) is given by:

$$\tan\phi = Z_{\rm Im} / Z_{\rm Re} \qquad \dots {\rm Eqn}(14)$$

For pure resistance, $\phi = 0$, for pure capacitance $\phi = \pi/2$.

The total impedance of a corroding metal is given as:

$$Z_{\text{total}} = Z_{\text{metal-film}} + Z_{\text{film}} + Z_{\text{film-solution}}.$$
 ... Eqn(15)

As these elements are connected in series the largest impedance will dominate (MacDonald and McKubre, 1987). Dipolar properties are measured at high frequencies, bulk properties at intermediate frequencies and surface properties at low frequency [12].

The data generated from EIS measurements was fitted to a common equivalent circuit for a metal-paint-electrolyte system. The models were considered to be relevant to the Colorbond system: A, B and C, in Figure 15.



Figure 15. Common equivalent circuits used to describe a metal-coating-solution interface using EIS measurements.

Model 'C' was chosen as a standard analysis for the performance of coatings.

The constant phase element has the form given in equation 16, whereby a constant phase element can be used in the place of the double-layer capacitance [13].

$$Z = \frac{1}{T(Iw)^{P}} \qquad \dots \text{Eqn(16)}$$

where *T* and *P* are the Constant Phase constants.

The constant phase is the equivalent of a capacitor where *P* equals 1. If CPE-P equals 0.5, a 45 degree line is produced on the complex plane impedance graph. When a CPE is placed in parallel to a resistor, a Cole-Element (depressed semi-circle) is produced similar to that of the short-circuited Warburg impedance.

The CPE element is most commonly used in the place of a capacitor to compensate for non-homogeneity in the system. For example, a rough or porous surface can cause a double-layer capacitance to appear as a constant phase element with a CPE-P value between 0.9 and 1.

6.2 Experimental Details

EIS measurements were performed using a CompactStat electrochemical interface (Ivium Technologies). A cylindrical Perspex cell (typically 4 cm diameter) was used to contain a reservoir of 0.1 M sodium chloride over the surface of the Colorbond specimen. Each test required both a counter electrode (platinum or stainless steel) and a reference electrode (standard calomel electrode or silver/silver chloride). The magnitude of the solution resistance, R_s and the impedance associated with the platinum counter electrode was investigated using a three electrode system consisting of two identical platinum mesh counter electrodes and a Ag/AgCl reference electrode. 0.1 M NaCl was added to the three electrode system and a 15 mV AC potential was applied as a function of frequency.

6.3 Results for unexposed Colorbond®

The solution resistance determined at high frequency was $29.5 \pm 2.5 \Omega$ for a typical cell configuration used for gutter performance testing.

At the interface between the electrode and the counter electrode an electrical doublelayer exists, which creates a capacitive impedance. Normal values for the capacitance are of the order of 30 μ F cm⁻², although these values are highly dependent upon the characteristics of the metal. Figure 16 shows typical data for an undamaged topcoat.



Figure 16. Typical fit of data to model 'C'. $R_s = 29.5 \Omega$, $C_c = 8.45 \times 10^{.9}$ F, $R_c = 585.2 \Omega$, CPE-T = $C_{dl} = 1.11 \times 10^{.8}$ F (where CPE-P = 1) and $R_p = 5.34 \times 10^7 \Omega$. Surface area = 18.4 cm².

The undamaged backcoat was analysed according to model 'C', as shown in Figure 17.



Figure 17. Typical fit of data to model 'C'. $R_s = 358.5 \Omega$, $C_c = 1.038 \times 10^{-8} F$, $R_c = 18930 \Omega$, CPE-T = $C_{dl} = 3.74 \times 10^{-8} F$ (where CPE-P = 1) and $R_p = 3.42 \times 10^6 \Omega$. Surface area = 12.6 cm².

The following data was recorded using the portable EIS measurement equipment. Colorbond XRW was allowed to equilibrate in 0.1M NaCl for 48 hours. The data obtained using both laboratory and portable equipment yielded similar results.

	Rs(+)	Cc(+)	Rc(+)	CPE1-T(+)	CPE1-P(+)	Rp(+)	Estimated Icorr (A cm-2)
XRW backcoat 48 hrs	60.45	2.03E-08	34967	4.58E-08	0.99059	1.31E+06	2.40E-07
XRW topcoat 48 hrs	80.84	1.10E-08	34640	1.00E-08	1.162	2.64E+06	1.19E-07



6.4 Estimates of corrosion rate based upon polarization resistance

The corrosion current can be related to the Tafel slopes using the Stearn-Geary relationship:

$$i_{corr} = \left(\frac{1}{2.303R_p}\right) \frac{b_a b_c}{b_a + b_c} \qquad \dots \text{Eqn(17)}$$

Where R_p is the polarization resistance (Ω cm⁻²) and b_a and b_c are the Tafel slopes for anodic and cathodic polarization, respectively. Since the values of b_a and b_c are not accurately known the exact estimation of corrosion currents is uncertain. It has been shown previously that useful estimation can be obtained be assuming that the corrosion current is equal to the reciprocal of the polarization resistance multiplied by 0.025 V. Table 4 presents some typical values for the corrosion rate taken from field measurements at Queensland Schools, as details in Appendix A. The results show that the rate of corrosion increases according to the relative age of the component. This can be attributed to a break down in the performance of the paint film and an increase in the amount of under-paint corrosion at longer exposure times.

Table 4. Typical values for typicasaled on oblorbond backboats are.											
Sample	R _p	I _{corr}	Mass loss								
	$(\Omega \text{ cm}^{-2})$	(A cm ⁻²)	(µm yr⁻¹)								
Undamaged	2.71 × 10 ⁵	9.21 × 10 ⁻⁸	1.2								
7 years	3.29× 10 ³	7.59 × 10 ⁻⁶	98.9								
29 years	9.08×10^2	2.75 × 10 ⁻⁵	358.3								

Table 4. Typical values for Rp measured on Colorbond backcoats	are:
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Tables 5 and 6 detail the ability of modeled corrosion rates to predict those measured in the field. The results for a Colorbond backcoat are presented for the case of both clean and dirty gutters. In most cases the EIS measured corrosion rate falls between the predicted rates for clean and wet gutters. It should be noted that the corrosion rate estimated by the model does not change from year to year, rather damage is assumed

to occur at a specific site. The data from Table 4, which suggests that rates increase significantly, but are not compensated on an area basis. That is, it is assumed that the high rates measured after 29 years would be obtained from a much larger metal-solution contact area due to paint delamination. At present there has been no investigation regarding these increases in surface area. The key result from Tables 5 and 6 are however the correctly predicted magnitudes of corrosion and the reproducibility of the model to differentiate between high and low corrosivity sites.

Location	Age	Micron zincalume loss (fully wet &salt@3545 mg/m ²	тоw	Average salinity: clean gutter (mg/m ²)	T _{av}	RH _{av}	w	Fraction of Cr removed in 1 yr (10 yrs)	Estimated depth loss from EIS (µm/yr)	Estimated previous model (µm/yr)	Estimated Well- drained backcoat (µm/yr)	Time to failure (yrs)
Brookfield SS (clean)	7	98.99	37	1.15	26	60	2.00	0.01 (0.07)	0.0367	0.64	0.26	88
Chapel Hill SS (clean)	29	358.99	37	1.18	26	60	2.00	0.01 (0.07)	0.133	0.64	0.17	87
Townsville house (clean)	5	812.04	51	4.19	28.9	62	2.16	0.02 (0.11)	0.414	1.49	0.48	41
Townsville house (dirty)	5	1433.43	51	4.19	28.9	62	2.16	0.02 (0.11)	0.731	1.49	0.48	41
Payne Road (dirty)	9	1459.47	37	1.14	26	60	2.00	0.01 (0.07)	0.540	0.63	0.24	88
The Willows (dirty)	10	313.54	51	0.87	28.9	62	2.16	0.01 (0.09)	0.160	0.54	0.29	61

Table.5. Modelling results for the backcoat of a clean and well-drained gutter. A comparison of EIS measured corrosion rates, estimated corrosion rates for the equivalent time period (from model) and the estimated time to failure (given as the time to totally remove the protective zincalume).

Table 6. Modelling results for the backcoat of a dirty and poorly maintained gutter. A comparison of EIS measured corrosion rates, estimated corrosion rates for the equivalent time period (from model) and the estimated time to failure (given as the time to totally remove the protective zincalume).

Location	Age	Micron zincalume loss (fully wet &salt@3545 mg/m ²	тоw	Average salinity: dirty gutter (mg/m ²)	Tav	RHav	w	Fraction of Cr removed in 1 yr (10 yrs)	Estimated depth loss from EIS (μm)	Estimated previous model (µm/yr)	Estimated loss (µm/yr) Dirty backcoat (100% TOW)	Time to failure (yrs)
Brookfield SS (clean)	7	98.99	100	11.46	26	60	2.00	0.02 (0.11)	0.0367	0.64	0.51	35
Chapel Hill SS (clean)	29	358.99	100	11.72	26	60	2.00	0.02 (0.11)	0.133	0.64	0.32	35
Townsville house (clean)	5	812.04	100	41.72	28.9	62	2.16	0.03 (0.17)	0.414	1.49	1.25	12
Townsville house (dirty)	5	1433.43	100	41.72	28.9	62	2.16	0.03 (0.17)	0.731	1.49	1.25	12
Payne Road (dirty)	9	1459.47	100	11.41	26	60	2.00	0.02 (0.12)	0.540	0.63	0.46	35
The Willows (dirty)	10	313.54	100	8.627	28.9	62	2.16	0.02 (0.13)	0.160	0.54	0.52	29

7 CONCLUSIONS

The model for predicting the longevity of Painted Metal Components has been updated and improved. The rates of corrosion predicted by the model have been validated to some extent by field measurements using Electrochemical Impedance Spectroscopy. The field measurements were limited to several schools in coastal areas of Queensland, and therefore, further validation would be required to ensure its accuracy for wider Australia. There are numerous factors that control the rate of degradation of painted components and some of these factors have yet to be investigated. For instance, the rate of delamination of paint and how this influences the removal of corrosion inhibitor and advance of corrosion damage. The performance of the currently presented model in predicting damage should ultimately be validated through further long-term experimental studies, which would be required to demonstrate statistical significance in its predictions.

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Appendix A. EIS Testing of Exposed Colorbond Panels

The following data was obtained by testing the current status of gutters at various field locations using a portable EIS analysis.

Brookfield State School, Qld.

Latitude: 27°29'42.74S Longitude: 152°54'47.87E Product: Colorbond backcoat Age: 7 years.

	Rs(+)	Cc(+)	Rc(+)	CPE1-T(+)	CPE1-P(+)	Rp(+)	Estimated Icorr (A cm- 2)
Brookfield	58.44	1.38E-07	3.508	3.07E-05	0.5352	41384	7.59132E-06



FigureA1. Left: Nyquist plot, Right (top): Bode plot, Right (bottom): Phase plot.

Chapel Hill State School, Qld.

Latitude: 27°29'58.20S Longitude: 152°56'37.69E Product: Colorbond backcoat Age: 29 years.



FigureA2. Left: Nyquist plot, Right (top): Bode plot, Right (bottom): Phase plot.

Monitored house, Townsville, Qld.

Latitude: 19°15'16.37S Longitude: 146°48'54.34E Product: Colorbond backcoat Age: 5 years.

	Rs(+)	Cc(+)	Rc(+)	CPE1-T(+)	CPE1-P(+)	Rp(+)	Estimated Icorr (A cm- 2)
Michelles house	34.84	7.08E-08	45.35	0.000255	0.50704	5045	6.22714E-05



FiguresA3. Left: Nyquist plot, Right (top): Bode plot, Right (bottom): Phase plot.

Payne Road State School, Brisbane, Qld.

Latitude: 27°26'53.51S Longitude: 152°57'05.81E Product: Colorbond backcoat Age: 9 years. State: Near the down pipe of a gutter full of leaves. Wet for the majority of time. There was visible damage to the backcoat, with approximately 30 % coating loss.

	Rs(+)	Cc(+)	Rc(+)	CPE1-T(+)	CPE1-P(+)	Rp(+)	Estimated Icorr (A cm-2)
Payne Road	40.82	8.49E-07	56.55	0.00024	0.69072	2807	0.00011192



FigureA4. Left: Nyquist plot, Right (top): Bode plot, Right (bottom): Phase plot.

Sandringham College Highett Campus, Vic

Product: Colorbond backcoat Age: 20 years. State: ½" of leaf litter. Wet prior to testing.

	Rs(+)	Cc(+)	Rc(+)	CPE1-T(+)	CPE1-P(+)	Rp(+)	Estimated Icorr (A cm-2)
Sandringham1	58.82	1.26E-08	147.8	3.39E-05	0.52814	31268	1.00473E-05



FigureA5. Left: Nyquist plot, Right (top): Bode plot, Right (bottom): Phase plot.

Sandringham College Highett Campus, Vic

Product: Colorbond backcoat Age: 20 years. State: No leaf litter, well drained.

	Rs(+)	Cc(+)	Rc(+)	CPE1-T(+)	CPE1-P(+)	Rp(+)	Estimated Icorr (A cm-2)
Sandringham2	71.66	1.91E-08	1517	2.13E-05	0.41606	1.21E+05	2.59851E-06



FigureA6. Left: Nyquist plot, Right (top): Bode plot, Right (bottom): Phase plot.

Sandringham College Highett Campus, Vic

Latitude: 37°57'03.12S Longitude: 145°01'18.50E Product: Colorbond backcoat Age: 1 years. State: Leaf litter (eucalyptus), wet.

	Rs(+)	Cc(+)	Rc(+)	CPE1-T(+)	CPE1-P(+)	Rp(+)	Estimated Icorr (A cm-2)
Sandringham3	44.59	8.25E-09	51.58	6.92E-07	0.51146	2.81E+05	1.11872E-06



FigureA7. Left: Nyquist plot, Right (top): Bode plot, Right (bottom): Phase plot.

Sunshine Beach State School, Sunshine Coast, Qld.

Latitude: 26°24'07.90S Longitude: 153°06'04.87E Product: Colorbond topcoat Age: 16 years. State: Leaf litter, damp.

	Rs(+)	Cc(+)	Rc(+)	CPE1-T(+)	CPE1-P(+)	Rp(+)	Estimated Icorr (A cm-2)
Sunshine Beach	3846	3.02E-10	8837	5.70E-07	0.77946	93045	3.37642E-06



FigureA8. Left: Nyquist plot, Right (top): Bode plot, Right (bottom): Phase plot.

The Willows State School, Townsville, Qld.

Latitude: 19°18'16.41 S Longitude: 146°43'18.58 E Product: Colorbond backcoat Age: 10 years. State: Leaf litter, dry.

	Rs(+)	Cc(+)	Rc(+)	CPE1-T(+)	CPE1-P(+)	Rp(+)	Estimated Icorr (A cm-2)
The Willows leaves	36.68	5.72E-07	704.8	5.87E-05	0.57612	13066	2.4044E-05
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FigureA9. Left: Nyquist plot, Right (top): Bode plot, Right (bottom): Phase plot.

Site 1 – Naval Base (Flinders)

Latitude: Longitude: B5 Site 1 10 years Sheltered Backcoat

	Rs(+)	Cc(+)	Rc(+)	CPE1-T(+)	CPE1-P(+)	Rp(+)	Estimated Icorr (A cm-2)
B5110Sb	125	1.05E-08	9.82E-05	0.000401	0.19943	1241	0.00025315









Site 3 – CSIRO (Highett)

Latitude: Longitude: B535Sb Colorbond B5 Site3 5 years Sheltered/Open Backcoat

	Rs(+)	Cc(+)	Rc(+)	CPE1-T(+)	CPE1-P(+)	Rp(+)	Estimated Icorr (A cm-2)
B535Sb	279.2	1.25E-09	8219	1.80E-08	0.7548	6.32E+06	4.97127E-08
B535Ob	573.4	2.74E-09	36140	7.63E-09	0.97904	3.17E+07	9.90726E-09







Appendix B. ICP-AES analysis of leaching solutions. *

The solution analysis results are tabulated. Sample 12 indicates the first cell, second experimental run. Letters indicate time sampling periods within an experimental run.

Sample	Time (hrs)	AI	Cr	Fe	Sr	Zn	Final pH
	0	ppm	ppm	ppm	ppm	ppm	
11A	0.0833	2.15	0	< 0.004	0.003	0.84	
11B	1	1.92	0	< 0.004	0.003	0.45	
11C	5	2.64	0	< 0.004	0.004	0.98	
11D	24	1.99	0	< 0.004	0.001	0.5	
21A	0.0833	2.39	0	0.04	0.003	81.7	
21B	1	0.87	0.022	0.044	0.003	78.2	
21C	5	0.75	0.022	0.046	0.003	76.3	2.11
21D	24	0.81	0.025	0.083	0.004	74.36	2.09
31A	0.0833	2.31	0.05	0.12	0.002	14.8	
31B	1	7.31	0.096	0.203	0.006	55.3	
31C	5	39.84	0.18	0.28	0.019	74.9	
31D	24	96.3	0.26	0.26	0.051	75.5	4.15
41A	0.0833	1.51	0	0.05	0.002	5.62	
41B	1	1.99	0.007	0.09	0.002	8.21	2
41C	5	2.39	0.014	0.14	0.002	10.8	
41D	24	0.97	0	0.03	0.002	0.59	
51A	0.0833	0.99	0.004	0.043	0.002	1.74	
51B	1	1.1	0	0.027	0.002	2.62	
51C	5	2.73	0	<0.004	0.004	8.07	
51D	24	2.32	0	< 0.004	0.002	9.18	
61A	0.0833	2.01	0	< 0.004	0.003	0.897	
61B	1	1.85	0	< 0.004	0.003	1.77	
61C	5	2	0	< 0.004	0.003	2.56	
61D	24	3.76	0	<0.004	0.001	9.53	
71A	0.0833	0.13	0.44	1.92	0.002	1.15	
71B	1	0.2	0	< 0.004	0.002	1.28	
71C	5	0.39	0	< 0.004	0.002	3.25	2
71D	24	8.81	0	< 0.004	0.002	16.5	2.02
12A	24.083	0.19	0	<0.004	0.001	0.97	
12B	25	0.056	0	< 0.004	0.002	0.96	
12D	48	0.076	0	< 0.004	0.002	1.09	2
22A	24.083	0.038	0	< 0.004	0.002	0.99	
22B	25	0.06	0	<0.004	0.002	1.08	
22D	48	< 0.004	0	0.027	0.002	3.07	2
32A	24.083	2.08	0	0.099	0.004	9.2	
32B	25	17.5	0.057	0.442	0.019	40.2	
32D	48	89.8	0.25	0.503	0.06	111.8	
42A	24.083	< 0.004	0	0.024	0.001	0.83	

Sample	Time (hrs)	AI	Cr	Fe	Sr	Zn	Final pH
42B	25	3.19	0	0.046	0.003	6.49	
42D	48	92.9	0.028	0.13	0.008	102.9	3.25
52A	24.083	< 0.004	0	0.03	0.002	0.69	2
52B	25	< 0.004	0	0.036	0.002	0.91	2
52D	48	0.69	0.012	0.087	0.002	4.66	2
62A	24.083	<0.004	0	0.021	0.002	1.27	
62B	25	0.062	0.002	0.03	0.002	1.64	
62D	48	13.6	0.01	0.073	0.003	23.4	2.03
72A	24.083	<0.004	0	0.02	0.002	1.27	
72B	25	0.13	0	0.037	0.002	1.59	
72D	48	24.4	0.002	0.18	0.002	34.8	2.08
13A	48.083	<0.004	0	0.029	0.001	1.19	2
13B	49	< 0.004	0	0.029	0.001	1.19	
13C	52.583	< 0.004	0	0.043	0.002	1.18	
13D	72	< 0.004	0	0.033	0.002	1.14	
23A	48.083	< 0.004	0	0.04	0.002	1.22	2
23B	49	0.056	0	< 0.004	0.001	0.1	
23C	52.583	0.04	0	< 0.004	0.001	0.18	
23D	72	0.26	0	< 0.004	0.002	0.26	2
33A	48.083	0.085	0	< 0.004	0.001	0.59	
33B	49	0.94	0	< 0.004	0.004	3.16	
33C	52.583	15.6	0	< 0.004	0.012	31.1	
33D	72	47.9	0	< 0.004	0.027	64.3	4.18
43A	48.083	52.5	0	< 0.004	0.066	87.2	
43B	49	0.37	0	< 0.004	0.002	0.46	
43C	52.583	2.61	0	< 0.004	0.005	4.63	2.01
43D	72	88.6	0	< 0.004	0.047	140.2	
53A	48.083	0.64	0	< 0.004	0.002	0.17	2
53B	49	0.64	0	< 0.004	0.002	0.21	
53C	52.583	0.86	0	< 0.004	0.002	0.57	
53D	72	3.69	0	< 0.004	0.003	7.62	2
63A	48.083	0.67	0	< 0.004	0.002	0.32	
63B	49	0.81	0	< 0.004	0.002	0.58	
63C	52.583	1.61	0	< 0.004	0.003	2.94	2
63D	72	13.4	0	< 0.004	0.005	23.6	2.07
73A	48.083	0.75	0	< 0.004	0.002	0.35	
73B	49	0.72	0	0.057	0.002	0.55	
73C	52.583	2.13	0	0.075	0.003	3.78	
73D	72	16.9	0	0.12	0.005	28.3	
14	192	0.77	0	0.032	0.001	0.33	
24	192	3.16	0	0.023	0.002	7.24	
34	192	140.8	0.13	2.72	0.21	188.2	4.86
44	192	107.4	0	0.107	0.14	130.9	
54	192	18.3	0	0.06	0.012	35.6	
64	192	51.6	0	0.051	0.022	56.7	

Sample	Time (hrs)	AI	Cr	Fe	Sr	Zn	Final pH
74	192	64.9	0	0.45	0.018	87.2	2.42
15	360	0.89	0	< 0.004	0.001	0.36	
25	360	14.1	0	<0.004	0.004	23.9	
35	360	243.7	0.104	0.13	0.17	199.5	5.32
45	360	108.9	0	< 0.004	0.082	125.7	4.15
55	360	36.8	0	<0.004	0.022	52.2	
65	360	65.2	0	< 0.004	0.039	62.7	
75	360	79.2	0	< 0.004	0.034	119.9	2.72
16	528	0.89	0	<0.004	0.001	0.64	
26	528	72.4	0	<0.004	0.009	59.8	
36	528	182.5	0.069	0.046	0.23	129.8	5.43
46	528	104.6	0	<0.004	0.12	131.4	4.18
56	528	65.5	0	< 0.004	0.048	63.8	
66	528	85.7	0	< 0.004	0.066	64.9	3.15
76	528	97.6	0	< 0.004	0.048	67.4	
17	1032	1.4	0	< 0.004	0.001	1.63	
27	1032	115.2	0	<0.004	0.048	120.2	
37	1032	262.9	0.18	0.21	0.31	211.7	5.67
47	1032	126.1	0	< 0.004	0.13	140.5	4.15
57	1032	105.6	0	< 0.004	0.078	130.1	
67	1032	106.4	0	< 0.004	0.092	131.8	4.08
77	1032	115.5	0	< 0.004	0.01	133.1	



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