Accelerated corrosion of zinc alloys exposed to ultraviolet light

E. A. Thompson[1] and T. D. Burleigh[*2]

The present study demonstrated that alloying had an effect on the photo corrosion rates of zinc coated steel. The corrosion rates of 99·9%Zn, galvanise (>99Zn), galfan (95Zn–5Al), galvanneal (90Zn–10Fe) and galvalume (43Zn–55Al–1·5Si–0·5Fe) were all compared by immersion in flowing fresh water for four months. One set of samples was exposed to ultraviolet (UV) fluorescent lamps, while the second set was up stream and illuminated only by the natural day–night lighting. The field test demonstrated that the UV light exposure increased the corrosion rates of all the zinc alloys tested. Laboratory experiments with photoelectrochemistry showed that alloying changed both the flat band potential and the photospectrum. The flat band potential is the potential where the photocurrent goes to zero. The samples with the more negative flat band potentials also had the higher corrosion rates. This correlation between the flat band potential and the corrosion rate provides a possibility for designing corrosion resistant alloys.

Keywords: Galvanised, Galvalume, Zinc, Corrosion, Photo corrosion, Photo induced

Introduction

Zinc coated steel sheet is manufactured by either electroplating steel sheet or hot dipping the steel sheet in a molten zinc bath. Zinc coated steel sheet has a multitude of uses which include automotive bodies, appliances and roofing sheet. The zinc is a sacrificial coating that corrodes very slowly and cathodically protects the underlying steel. In atmospheric corrosion or in fresh water immersion, the predominant corrosion products on the surface are zinc carbonates and zinc bicarbonates.[1] There are several alloys of zinc used for cathodically protecting steel, e.g. galvanise (>99%Zn), galfan (95Zn–5Al), galvanneal (90Zn–10Fe), and galvalume (43Zn–55Al–1·5Si–0·5Fe). The galvalume, with 55%Al, is a two phase alloy but works on the same principle where the zinc corrodes and provides the sacrificial protection, but in this case aluminium dendrites hold the zinc corrosion products on the surface.[2] The present study was undertaken to determine if ultraviolet (UV) light or sunlight inhibited or accelerated the corrosion rates of these different zinc alloys under outdoor exposure. The questions were also asked whether photo corrosion was significant when compared to dark corrosion, was the effect due to infrared heating or to an UV photo electronic effect, and was the rate of photo corrosion affected by the alloying content of the zinc?

Several previous researchers have studied the effect of illumination on the corrosion rate of zinc. Spathis and Poulios[3] compared the corrosion behaviour of Zn (99·99% pure) in an aerated 3·5%NaCl solution both in light and dark conditions. They concluded that the corrosion products were mostly $Zn(OH)_2$, but under illumination a small amount of zinc oxychlorides formed which had a high degree of compactness that protected the Zn from further corrosion. For times greater than 2 h, the amount of zinc oxychlorides increased, thereby reducing the corrosion rate. They also proposed that the electronic holes generated as a result of the photo energy, acted as strong oxidising species. The corrosion products formed more rapidly, helping to suppress further corrosion.

Juzeliunas[4] measured the corrosion rate of zinc in a deaerated 5%NaCl solution while illuminated with a defocused laser beam (λ=488 nm). Their results showed that the illumination increased the rate of the electrode mass gain and the corrosion rate. They found that the electrons moved to the oxide/solution interface and the electronic holes moved to the metal interface. They proposed that light accelerated the electron transfer to the oxygen in the solution, resulting in enhanced corrosion rates.

Rudd and Breslin[5] experimentally determined that the polychromatic illumination caused the photo decomposition of the anodically formed ZnO passive layer in sodium borate solutions with pH=9·2, 10·3 and 13·0.

Kalinauskas et al.[6] studied the corrosion of pure zinc in NaCl solution containing different amounts of dissolved oxygen. They reported accelerated corrosion during the first stages of illumination, but photo inhibition during long term illumination (for their study, long term was several hours).

Burleigh et al.[7] studied the photo corrosion of the pure zinc under exposure to UV light for five months in

[1]US Steel Irvin Works, Dravosburg, PA, 15642, USA
[2]Materials & Metallurgical Engineering Department, New Mexico Tech, Socorro, NM 87801, USA

*Corresponding author, email burleigh@nmt.edu

a flowing water stream, and found that the UV light doubled the corrosion rate. Burleigh proposed that the UV light accelerated electron flow through the surface film to the electrolyte interface and accelerated the cathodic reaction (oxygen reduction), which increased the pitting corrosion rate of the zinc.

Experimental

The experimental procedure consisted of two parts, field experiments and laboratory experiments, which are described in detail below. Five different zinc alloy compositions were tested (*see* Table 1); 99·9%Zn, galvanise (>99%Zn), galfan (95Zn–5Al), galvanneal (90Zn–10Fe), and galvalume (43Zn–55Al–1·5Si–0·5Fe). For completeness, three samples with surface treatments were also included in the test programme. The terms 'chem treat' and 'acrylic' refer to proprietary surface treatments applied to the surface of the galvanised and galvalume steel. The 'chem treat' is a hexavalent chromium rinse that converts to trivalent chromium on the surface. The 'acrylic' is a 1–2 μm thick coating of acrylic polymer containing both trivalent and hexavalent chromium.

Field experiments

In the field experiments, the samples were immersed in the flowing discharge water stream at the Franklin Township Municipal Sanitation Authority (FTMSA), Murrysville, PA, from 30 October, 2000 to 1 March, 2001. The average water flow in the channel was 2·5 million gallons of water per day (8 m^3 min^{-1}) at an average temperature of 10°C. Triplicate coupons of each sample were immersed in this outdoor water channel at two different locations. The first set of triplicate coupons were immersed under 0·5 m of flowing fresh water beside high intensity UV lamps (Trojan System UV3000) used to disinfect the treated water before it was discharged into Turtle Creek. The UV system consisted of 112, parallel, 27 W, 147 cm (58 in.) long, fluorescent UV lamps. The second set of coupons (dark control) was immersed 20 m upstream, at the same depth, and was exposed to the natural day–night cycles.

The test coupons were cut from each of the original eight types of alloyed zinc into 3·8 × 7·6 cm (1·5 × 3·0 in.) rectangles for a total of 48 coupons. Each coupon was stamped with a code for identification. The six sets of coupons were bolted to nylon racks using nylon nuts and bolts. The bolt and nut crevices were sealed with vacuum grease [(Apiezon (L)] to prevent crevice corrosion. The racks were designed to allow aerodynamic flow of the water, and to maintain a separation distance between each of the individual samples, as well as between the samples and the channel walls. The distance from each rack to the nearest UV
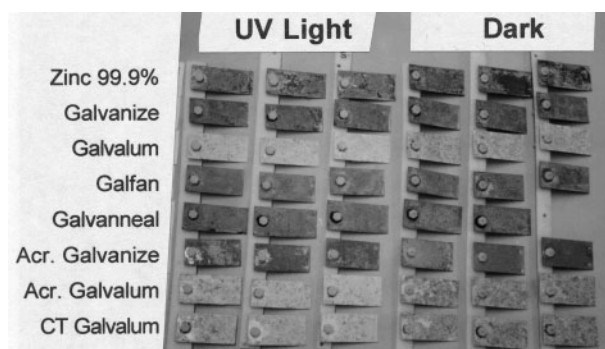
1 Triplicate zinc samples are shown after four months of immersion in water stream, both in UV light and in dark

lamp was ~2·5 cm. Both sides of the coupons were exposed to the UV light and the cut edges of each sample were not sealed. Every week or two weeks, the channels were drained for 1–2 h and rinsed with fresh water. At the end of the four month period, the racks were removed, rinsed and allowed to dry in the air (*see* Fig. 1). Each coupon was then carefully removed from the rack and weighed. The corrosion product was next removed using ammonium persulphate per ASTM-G1[8] and then these cleaned coupons were reweighed.

Laboratory experiments

Six of the eight zinc alloys were also tested in the laboratory. (There was a shortage of material for the galfan and the galvanneal, so these two were not laboratory tested). The samples were attached to copper wires, and then the backs and edges were coated with epoxy to expose a 1 cm^2 window on the front of the sample to the solution. The samples were then allowed to corrode for several weeks in separate beakers of quiescent municipal tap water which were near neutral pH. They were periodically tested using an EG&G 263 A potentiostat and a 100 W xenon arc lamp filtered with schott colour glass filters. Two types of tests were performed. First the potential was held constant near the open circuit potential (OCP). The current was measured as the sample was illuminated with a pulse of light filtered by different coloured glass filters. The percentage differences of the normalised photocurrent were then determined for the energy range of each filter.[9] With this test, it was possible to determine whether infrared (heating) or UV light caused the photo corrosion. For a second test, the potential was increased in steps of 20 mV and the current was measured at each potential using the unfiltered beam of white light from the Xenon arc lamp. The potential at which the photocurrent approached zero was of particular interest and is referred to as the 'flat band potential'. This flat band potential was measured for each of the six zinc alloys; unfortunately, the samples measured in the lab were not exposed to the identical conditions as the samples corroded in the field.

Results and discussion

Field experiments: precleaned weight

Each coupon was weighed before the removal of the corrosion product. The change in weight per area during the four months was calculated for each coupon and the individual data points are plotted in Fig. 2. Positive

Table 1 Nominal compositions of zinc samples, wt-%

Alloy	Zn	Al	Fe	Si
Acrylic galvalume	43	55	0·5	1·5
Chem treat galvalume	43	55	0·5	1·5
Acrylic galvanise	>99	0·4	0·5	–
Galvalume	43	55	0·5	1·5
Galvanise	>99	0·4	0·5	–
Galvanneal	90	0·2	10	–
Galfan	95	5	–	–
Pure zinc	99·9	–	–	–
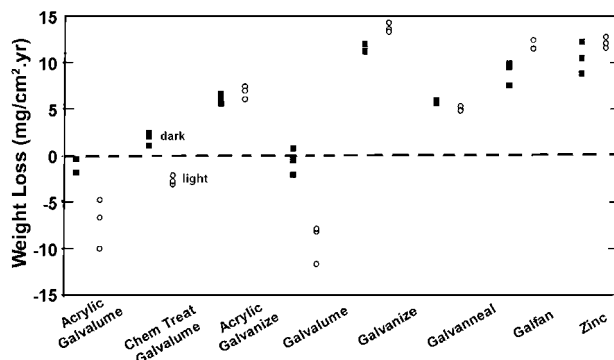
2 Weight loss (or gain) of zinc samples are shown before removal of corrosion products: solid black squares are control samples in dark, while hollow circles are samples exposed to UV light

3 Weight loss of zinc samples after removal of corrosion product: samples exposed to UV light (hollow circles) lost more weight on average than control samples in dark (solid black squares)

values are a weight loss, and negative values are a weight gain. The open circles are the weight change under the UV lamps, and the solid squares are the weight change in the 'dark'. The white corrosion product was more adherent on some samples than other samples. Localised corrosion (pitting) was the dominant form of corrosion during this fresh water immersion.

Field experiments: cleaned weight

Figure 3 shows the weight loss after the corrosion product was chemically removed with the ammonium persulphate.[8] All the coupons exhibited a weight loss, and the weight loss was greater for the coupons that had been exposed to the UV light. The samples are ranked in the following order from the least to the largest weight loss, with pure zinc corroding the most:

(i)   acrylic galvalume
(ii) chem treat galvalume
(iii) acrylic galvanise
(iv) galvalume
(v)   galvanise
(vi) galvanneal
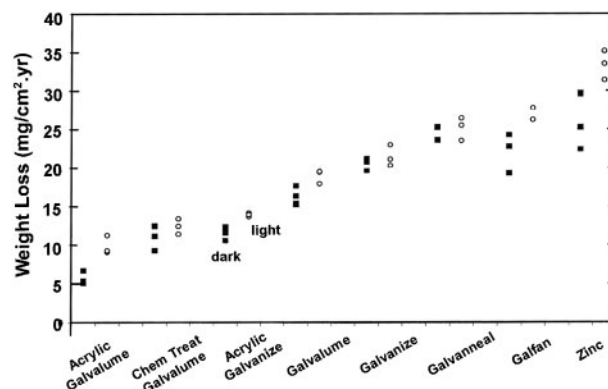(vii) galfan
(viii) zinc.

The above ranking demonstrates that the hexavalent chromium (in the acrylic coating and the chem treat) was most effective at reducing the corrosion rate. The next best corrosion resistance was the galvalume (55Al–43Zn). The galvanise (>99%Zn) was better than galvanneal (90Zn–10Fe). The galfan (95Zn–5Al) showed a much scatter in the data. The pure zinc had the greatest weight loss in the UV light.

Lab results: photospectra

Corroded zinc samples were tested in the laboratory using a xenon arc lamp. The samples were polarised near their open circuit potential, and then they were illuminated with light from a xenon arc lamp. All of the corroded lab samples showed an increase in the cathodic current. A representative photospectrum for pure zinc is shown in Fig. 4a, and for galvalume is shown in Fig. 4b. Infrared light (<1·5 eV) had no effect on the current density, indicating that heating was not the cause for the photo corrosion. Although there were significant variations in the photospectra, most of the photocurrent was caused by visible and UV light with energy >2·5 eV. The galvalume sample in Fig. 4b shows a shifting of the photospectrum to higher energies than the pure zinc in Fig. 4a. None of these films correspond to crystalline ZnO, which is an *n* type semiconductor with a bandgap of 3·2 eV. However, ZnO is not expected on the surface since the corrosion product on zinc in fresh water is typically zinc carbonate or bicarbonate.[1]

Figure 5 illustrates the mechanism by which light lowers the dark current temporarily, but accelerates localised corrosion in the long run.[7] The photons excite an electron from the valence band to the conduction band, where it flows downhill to the electrolyte interface. The excess electrons at the electrolyte interface accelerate the cathodic reaction. This increased cathodic reaction increased the localised pitting corrosion of the zinc (Fig. 5b).[7]

Lab results: flat band potentials

The flat band potential is the point where the applied potential results in zero photocurrent. A typical experimental curve is shown in Fig. 6 for the pure zinc. Starting at the open circuit potential, the potential was increased in +50 mV steps, and the corrosion current
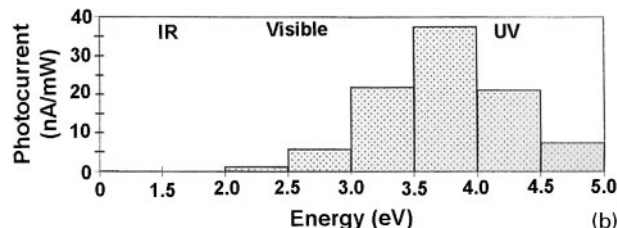

4 Representative photospectrum of *a* galvanised after 11 weeks in tap water and *b* galvalume after three weeks in tap water: neither sample showed photocurrent caused by infrared heating (<1·5 eV); galvalume (Zn–Al) photospectrum was shifted to higher energies
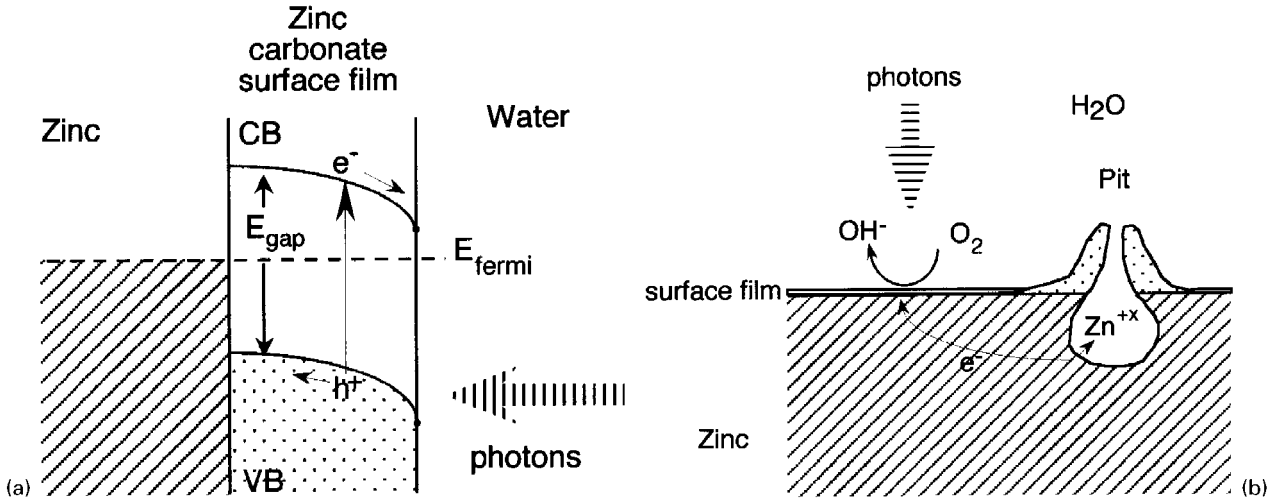
a photons excite electrons into conduction band where they flow down to water interface; *b* electrons are replenished by pitting corrosion of zinc

5   Band bending schematic
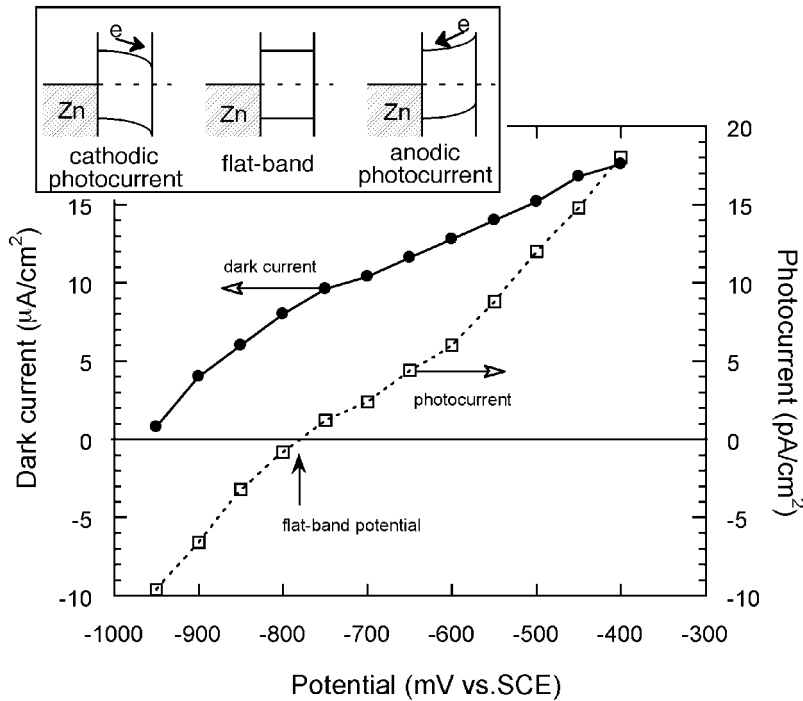
6   Flat band potential was measured by polarising zinc near its OCP in municipal tap water [about −950 mV saturated calomel electrode (SCE)], and then stepping potential anodic in +50 mV steps, and measuring dark current and photocurrent at each step: flat band potential is potential where photocurrent goes to zero, or goes from negative to positive

(dark current) and the photocurrent were both measured at each step. The photocurrent was initially negative, and decreased in magnitude as the potential increased. At −800 mV, the photocurrent became very small, and at higher potentials, the photocurrent changed signs and increased with potential. The flat band potential is the potential where the photocurrent extrapolates to zero, or changes from negative to positive.

Figure 7 shows the range of flat band potentials for samples measured, versus the range of weight loss in the dark. There is good reproducibility for the measured flat band potentials for zinc, galvanise, and acrylic galvalume. Poor reproducibility was seen in the acrylic galvanise. There was no significant change in the flat
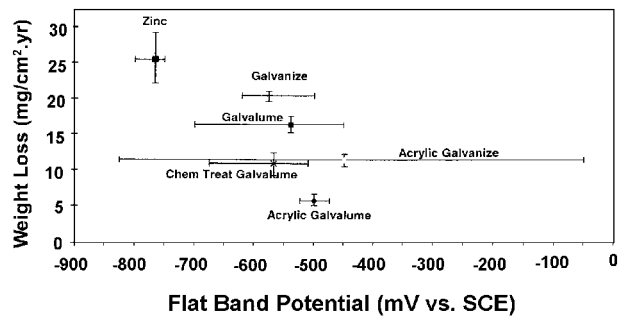
7   Measured flat band potentials versus corrosion rates for zinc and Al–Zn samples show downward trend
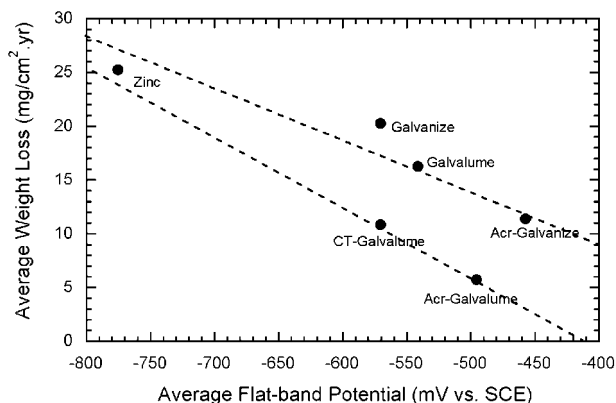
8 Average flat band potential and average corrosion rates show trend that more positive flat band potentials correspond to lower corrosion rates

band potential over the several weeks of laboratory testing. Arranging the metals from most positive average flat band potential to most negative average flat band potential gave the following ranking:

  (i)   galvalume
  (ii) galvanise
  (iii) zinc.

Field and lab results combined

The average values for the ranges shown in Fig. 7 are replotted in Fig. 8 for the six samples. As the flat band potential increases to more positive potentials, the weight loss decreases. In other words, the alloy with the more positive flat band potential corroded less. Although this comparison is intriguing, it does not take into account the changing corrosion product composition for the different alloys. However if the zinc carbonates were the identical, a suggested way to improve the pitting resistance of a zinc alloy would be to raise the flat band potential. The flat band potential can be shifted to the right (more positive) by doping the carbonate more p type. The challenge, therefore, is to alloy with an element that has a valence of $+1$ and that can form a solid solution with zinc, such as lithium. This p type doping to increase pitting resistance of zinc is the opposite of the Burleigh's previous work which found that n type doping increased the erosion–corrosion resistance of copper–nickel alloys.[10] Therefore the benefits of n type doping versus p type doping of

corrosion product films depend on the mechanism of corrosion one is attempting to reduce.

Summary

After four months of exposure in a discharge water stream, the UV light increased the corrosion rate for all of the zinc alloys tested, with the largest effect seen for the purer zinc alloys and the smaller effect seen for the galvalume (Zn–Al) alloys. The photo corrosion effect was caused by the light exciting electrons from the valence band to the conduction band, where they flowed to the electrolyte interface. It is proposed that this accelerated the cathodic reaction which accelerated the pitting corrosion of these alloys. Comparing the weight loss with the flat band measurements showed that the more negative the flat band potential, the greater the corrosion rate. The authors have proposed that doping the zinc corrosion product more p type could lead to improved pitting corrosion resistance of zinc alloys.

Acknowledgements

References

1. D. C. H. Nevison: in 'ASM handbook', Vol. 13, 'Corrosion', 755–769; 1987, Materials Park, OH, ASM International.
2. E. Palma, J. M. Puente and M. Morcillo: *Corros. Sci.*, 1998, **40**, (1), 61–68.
3. P. Spathis and I. Poulios: *Corros. Sci.*, 1995, **37**, (5), 673–680.
4. E. Juzeliunas, P. Kalinauskas, A. Stankeviciute, A. Sudavicius and A. Survila: *Corrosion*, 1995, **51**, (9), 672–678.
5. A. L. Rudd and C. B. Breslin: *J. Electrochem. Soc.*, 2000, **147**, (4), 1401–1407.
6. P. Kalinauska, I. Valsiunas, M. Samulevicience and E. Juzeliunas: *Corros. Sci.*, 2001, **43**, 2083–2092.
7. T. D. Burleigh, C. Ruhe and J. Forsyth: *Corrosion*, 2003, **59**, (9), 774–779.
8. S. P. Canning, *et al.* editors, ASTM: in 'Annual book of ASTM standards'; 1991, Philadelphia, PA, ASTM, Vol. 3.02, p. 35–41.
9. T. D. Burleigh and R. M. Latanision: *J. Electrochem. Soc.*, 1987, **134**, (1), 135–138.
10. T. D. Burleigh and D. H. Waldeck: *Corrosion*, 1999, **55**, (7), 800–804.