

The Effects of Chloride Ions on the Corrosion of Aluminium Alloys used in the Construction of *Australia II*

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Abstract

During a routine condition report and corrosion assessment of the hull of the historic 12-metre yacht, Australia II, a huddling liquid was found in the bilges. Rapid corrosion of structural aluminium alloys was occurring as a result of the accumulation of salty water under the floorboards. The offending liquid was removed and analysed before the surface was stabilised by a combination of desalination and the application of corrosion inhibitors. The most effective method involved the use of sodium metasilicate, acidified with phosphoric acid, since it inhibited corrosion whilst allowing removal of the highly aggressive chloride ions from the surface oxide layers. Subsequent commercial refurbishment, transport and corrosion have served to highlight the sensitivity of objects made of modern materials, designed for performance mode and not for longevity.

Introduction

Australia II was the first yacht to successfully challenge the Americas Cup and this took place at Newport Rhode Island in 1983. The cup had remained in the hands of the New York Yacht Club for 123 years, which represented the world's longest retention of an international sporting trophy. The yacht designer was the late Ben Lexcen and the builder was Steve Ward & Co. of Cottesloe, Western Australia. The yacht was completed in 1982 with the following dimensional characteristics: overall length 19.69m, waterline length 13.47m, breadth 3.682m, draught 2.659 m and a total sail area of 255m². The vessel was bought by the Australian Federal Government for the National Museum of Australia, and was sent on loan to the Western Australian Museum after a triumphal national tour. It had been taken out for a sail after

winning the cup and had been washed down by members of the victorious crew, prior to it going into storage. It was the first twelve-metre class yacht to use a 'winged' keel design, which provided much greater lift and a lower centre of gravity. It was principally constructed of series 5083 aluminium plates, with the yacht itself weighing 2.5 tonnes, with an 18 tonne keel of a lead-antimony alloy. This paper describes the treatment used to stabilise the *sewer* areas inside the hull of *Australia II* and the overall corrosion problems associated with the exhibition and storage of the vessel.

Description of *Australia II*

The series 5083 aluminium plates used in the construction of *Australia II* are an alloy of aluminium containing 4.5 % Mg and 0.7 % Mn, with H321 heat

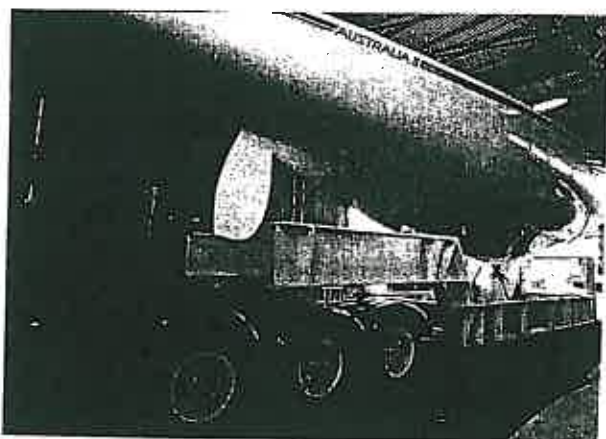


Figure 1. Overall exterior view of *Australia II* on its custom made trailer, Karrakatta storage facility, June 1987.

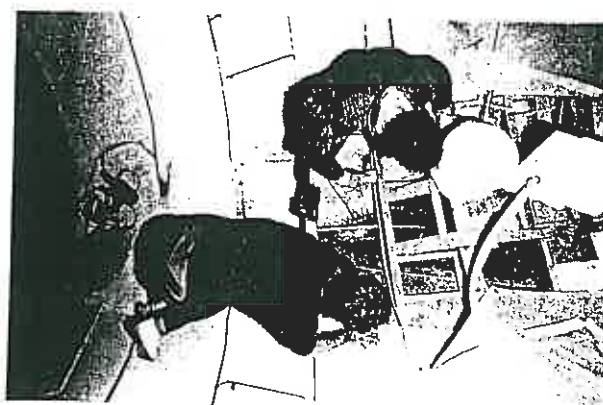


Figure 2. The authors inspecting the interior of *Australia II* sewer area, June 1987.

treatment. It should be noted that the mast was made of a series 7075 alloy which contains 5.5 % Zn, 2.5 % Mg, 1.5 % Cu and 0.3 % Cr (American Society of Metals 1961). Like all aluminium alloys, the correct heat treatment is an essential step in ensuring that the correct microstructure is gained, since incorrect treatments can lead to catastrophic materials performance. During the construction of the yacht, the aluminium hull was sandblasted, coated with Alodine (a commercial coating that etch-primes the metal) sprayed with a zinc chromate-hydrofluoric acid inhibitor, followed by a high build epoxy undercoat which was fared down by hand and mechanical grinding and polishing. Prior to painting, the hull was fared with a West System Epoxy Resin system consisting of a two-pack epoxy mixture in a 5:1 ratio using special formulations of phenolic micro-balloons and Z 105 epoxy resin and hardener 206 (Smallwood, A. 1988, pers. comm.). A large number of coats of a two-pack polyurethane topcoat were applied, with each layer being hand sanded prior to the application of the next coat. This procedure was repeated until the hull was sanded down to a smooth mirror finish before the final painting (Figure 1). The *sewer* is the area where the corrosion problems appeared. It was described as the sewer by the yacht's crew and builder as it is the sail storage area below decks and forward of the winch grinder's and sail trimmer's pits. The floor was covered with marine ply, which provided a good working surface and easy access to sails, for sail changes by the *sewer men*.

The frames were constructed of a higher tensile alloy, series 6061 aluminium, which contained 1.0% Mg, 0.6% Si, 0.25% Cu and 0.25% Cr. The frames were evenly spaced through the boat with drainage holes along the floor to allow water to flow between frame sections. The 'mast box' consists of a series of aluminium boxes welded at the lowest point in the *sewer* to accommodate the hydraulic ram at the foot of the mast. The mast box was used as a pivot point to raise and lower the mast during racing. Slightly forward of the mast box and 20cm higher than the *sewer* floor, two drainage points facilitated water removal from the hull after racing when the yacht was removed from the water. The yacht was traditionally 'dry sailed', which is to say that after each race the vessel was removed from the water, hosed down and dried out with dehumidifiers during the preparation for the challenge and during the racing regime. Aluminium alloys are normally stable to dissolution in the environmental range determined by $8.5 < \text{pH} < 4$ and as such, it is a suitable material to be used in the

construction of seagoing vessels. The underlying reactivity of the parent aluminium metal is masked by the formation of a normally protective and very thin oxide film of the general composition $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, which normally incorporates a disproportionate amount of the alloying metal oxides such as MgO

Corrosion during Storage

Five years elapsed between the initial accessioning of *Australia II* by the National Museum of Australia and its journey to Western Australia as an exhibition loan item. A request of the Maritime History curator Sally May for a condition report on the vessel led to an initial inspection of *Australia II* which showed the tell tale signs of its previous racing history. The fittings on the deck and inside the hull appeared to be in a generally sound but 'knocked about' condition. However, a detailed inspection of the sewer showed approximately eight litres of water trapped below the drainage holes, since the holes were not at the lowest point of the hull (Figure 2). This area was also partially inaccessible due to the mast box assembly.

During the flushing and cleansing operation in the bilge area a small rectangular piece of aluminium was noticed. This piece was approximately 1/2 mm thick, 1 cm wide and about 4cm long and was lying flat on the hull plates. When this was removed from the surface of the hull plate the underlying metal was found to be deeply pitted. During the inspection all sorts of fragments of insulated copper wiring and stainless steel nuts and washers were removed. All of these would have had an accelerating effect on the corrosion phenomena. Copper ions will react with aluminium in the presence of chloride ions to produce metallic copper (cemented), which acts as an active site for the reduction of oxygen (Annamalai & Hiskey 1978). Since the reduction of oxygen on the aluminium alloy surface is often the rate-determining step in the corrosion reaction, any process, which facilitates this step, will have a most detrimental effect on the stability and durability of the alloy. The areas of most severe corrosion had lost at least 2mm, or some 40% of the total original thickness of the hull plate. The wet areas showed extensive pitting corrosion, with large bubble-like formations of a gel style precipitate of $\text{Al}(\text{OH})_3$ around active pit formations (Figure 3).

Thermodynamic data on the wide range of aluminium complex ions shows that $\text{Al}(\text{OH})_3$ is the dominant form at pH values above 7 at room temperatures, while $\text{Al}(\text{OH})_2^+$ is the dominant form in the range pH 7-6 and



Figure 3. Initial inspection, shiny areas in liquid are bubbles of hydrogen gas, June 1987.

$\text{Al}(\text{OH})_3$ is dominant between pH 6-5.5. The surface pH values in the *sewer* areas measured in 1987 (Table 1) were more acidic than the stability domain for aluminium-hydroxy species listed above. This indicates that active corrosion with the formation of soluble non-hydroxy containing aluminium species will be the dominant form of the initial metal corrosion products (Lowson 1974).

Corrosion reactions involve at least two steps in the overall process, one of which is the oxidation reaction and the other is the reduction reaction. In the case of aluminium corrosion, the anodic reaction of interest is simply the oxidation of the metal to the trivalent ion, Al^{3+} and the cathodic or reduction reactions are primarily dependent on the location of the reaction. If the dominant reaction zone is the surface of the metal, the reduction of molecular oxygen to produce hydroxide ions is the major cathodic process. In the case of pitting reactions, where the geometry of the pit is such as to inhibit the ingress of oxygen, then reduction of water or hydrogen ions to produce hydrogen gas and hydroxide ions, is the controlling cathodic process. Since the rate at which metals corrode is dependent on the voltage of the metal in an aqueous solution, a measurement of the voltage provides an insight into the state of health of the metal.

The rest potential, the voltage the metal has when no external current or voltage source is being applied, is also called the corrosion potential, E_{corr} , which is dependent on both the anodic and cathodic reactions. The voltage at which the anodic and net cathodic reactions have the same current is the E_{corr} or the corrosion voltage.

The corrosion potential of the pits was measured as being -0.397V relative to the Normal Hydrogen Electrode (NHE), with active hydrogen evolution from the corroding pits (see Table 1). Since the values of the E_{corr} are above the voltages required for the initiation of pits, the corrosion rate is necessarily quite high (Dexter 1980). Using Lowson's relationship between E_{corr} of pure aluminium and chloride concentration,

$$E_{\text{corr}} = -0.475 - 0.060 \log[\text{Cl}^-]$$

it is possible to estimate the chloride concentration, as represented by the observed E_{corr} (Lowson 1978). The calculated chloride activity at the observed E_{corr} was 1,770 ppm, which was of the same order as measured in the area of the pits with the flat surface chloride ion electrode. In the absence of a specific relationship for the aluminium alloy from which the plates were made, which contains 94.87% aluminium, the correlation of the data is good. It should be noted that the difference between the surface pH of the pitting areas (2.67) and that of the surrounding water (8.64) is characteristically large and typical of acidity observed in pitting corrosion (Table 1). The pH of normal seawater is 8.2 ± 0.1 and so the stale bilge water was somewhat more alkaline than would be expected for fresh seawater. The somewhat more alkaline nature of the bulk water – compared with seawater – is due to the concentration of the brine solution and the increasing value of the concentration of carbonate ions. A guide as to the severity of the nature of the physical, chemical and corrosion environment on the hull plates can be obtained by placing the corrosion data on a Pourbaix diagram for aluminium (Figure 4). The 'star'

Table 1. 1987 corrosion environments for hull plates in the sewer of *Australia II*

Date	E_{corr} volts vs. NHE	pH	Chloride ppm
19 June 1987		8.64 <small>solution</small>	13,100
24 July 1987 starboard	-0.497	2.67 <small>pit</small>	3,500
24 July 1987 port	-0.397.		6,125
14 August 1987 either side of mast step		4.25 ± 0.05	n.d.
Second silicate wash	-0.700	9.05 <small>solution</small>	230
After metasilicate		9.70 <small>surface</small>	25

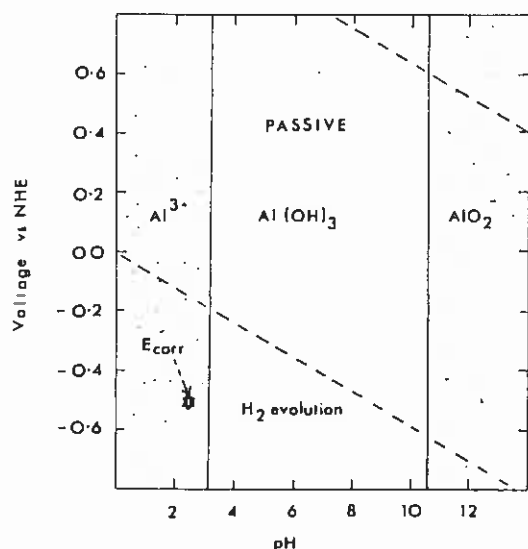


Figure 4. Pourbaix diagram showing location of E_{corr} in the zone of film free active corrosion.

symbol locates the pH and E_{corr} of the pit listed in Table 1 in the zone where the free Al^{3+} ion is the thermodynamically stable form of aluminium i.e. the metal is in a zone of active corrosion (Pourbaix 1974). Analysis of the sewer solution showed a chloride content of 13,100ppm, compared with normal seawater, which had a chloride content of 18,600 ppm. This indicates that the normal hosing down procedures had been at least partially effective in removing the bulk of the salty water from the interior of the vessel. Given the high concentration of chloride ions, it is likely that the ionic species present in the pits would have included some aluminium chloride complexes. Gas chromatography confirmed that, apart from salinity, the solution contained amino acids and a high content of urea. This analysis is consistent with the oxidation of human urine and sweat, which had accumulated inside the vessel during its service life as a racing yacht.

Prior to attempting an overall treatment of the interior of the hull, a surface chloride ion activity measurement was done in the region of the plates between the fourth and the fourteenth frame and the results are summarised in Table 2. Analysis of the data shows that

Table 2. Surface chloride ion activity and pH values for hull plates in *Australia II*.

Hull plate	Chloride, ppm	Surface pH	E_{corr} vs. NHE
4	21,500	8.06	-0.575
5	21,500	7.99	-0.562
6	21,500	8.03	-0.564
7	21,500	7.84	-0.525
14	14,377	8.13	-0.499

for the four hull plates forward of the mast step, there is a strong linear correlation between the surface pH and the E_{corr} given by

$$E_{corr} = -0.221 \text{ pH} + 1.2069$$

with an R^2 value of 0.9828 for the linear regression. An R^2 value of 1 is obtained for a perfect correlation between two variables. The one data point aft of the mast step, zone 14, does not lie anywhere near the fall of the other points. The most likely reason for this is that the physical location of the measurement point is a significant distance from the main corrosion zone where the accumulated debris had formed and that it is significantly higher, i.e. above the drainage points, than the other four plates. This zone also had a much lower chloride content. Using Lawson's relationship between the corrosion potential and chloride content, to correct the E_{corr} value for the differences in chloride ion activity, this correction brings the value of the 14th plate potential towards those of the other plates but not sufficient to make them fall into the same category of data.

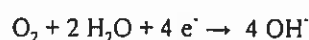
Apart from indicating the differences that exist in the microenvironment of the interior of the vessel, the data shows that both the E_{corr} and the pH and chloride concentration are all inter-connected kinetic corrosion parameters, which relate to the degradation of the aluminium alloys used in the construction of the vessel.

Effect of Chloride Concentration on Aluminium Corrosion

In the presence of extremely low chloride ion concentrations, the anodic reaction involves the oxidation of aluminium to the tri-positive ion Al^{3+} , followed by reaction with water to form the octahedrally coordinated ion, $Al(H_2O)_6^{3+}$ which can undergo further reaction with water. The hydrolysis reaction, which is favoured by alkaline and neutral conditions, gives various aluminium hydroxides with a concomitant drop in pH, i.e.



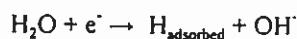
In the same chemical environment, the surface cathodic sites are dominated by the reduction of molecular oxygen, which produces hydroxyl ions and a consequent rise in the surface pH, i.e. the cathodic reaction



provides hydroxyl ions, which favour the formation of

inert and protective corrosion products of the form $Al_2O_3 \cdot xH_2O$. The initial gel-like precipitate of aluminium hydroxide ages with time, moving from being an amorphous matrix to various crystalline forms. Whilst the formalisation of the corrosion products has the stoichiometry of $Al(OH)_3$, the solids appear in the form of hydrargillite (gibbsite) as hydrated aluminium oxide $\alpha Al_2O_3 \cdot 3H_2O$. At room temperature, other commonly formed aluminium corrosion products include bayerite, $\beta Al_2O_3 \cdot 3H_2O$ (Lowson 1974). In these situations aluminium and its alloys provide a good resistance to corrosion and the vessel would have a good lifetime expectancy.

However, the situation is very different in the presence of moderate to high concentrations of chloride ions. After the primary corrosion product has been formed it can undergo a series of hydrolysis reactions to form hydroxy or hydrated oxide species, chloride complexes or an admixture of the above. For pitting corrosion reactions the cathodic reaction can be dominated by the formation of adsorbed hydrogen via reactions such as



which then controls the rate of oxidation of the aluminium metal, i.e. the overall corrosion reaction would then be deemed to be under cathodic control. The anodic dissolution of aluminium in the presence of aggressive anions, in particular chloride ions has been well documented in the literature (Despic et.al. 1988). Electric field inversion, caused by the accumulation of negatively charged chloride ions, triggers the fast anodic dissolution of aluminium oxide films since the primary electrostatic attraction between the metal ions and the negative oxides is fundamentally changed with the accumulation of chloride ions. The acidic microenvironment around the pits results from the hydrolysis reaction on aluminium in the absence of a protective oxide layer. Once a pit has initiated and developed into a cavity, it propagates by local cell action, which is reinforced by the difference in acidity between the anode and the cathode. Since chloride ions form soluble complexes with aluminium (III) ions, they tend to promote the overall corrosion reaction since they prevent the reaction sites becoming clogged with insoluble corrosion products (Richardson & Wood 1970).

When defects cannot be naturally repaired by the formation of a protective oxide film, pits deepen and begin to accumulate insoluble corrosion products, forming a porous cap of aluminium hydroxide, which further separates the anode from the cathode. The

alternative cathodic reaction in the pits is the reduction of hydrogen ions to produce hydrogen gas and hydroxide ions. Pits start because of electrochemical action brought about by natural oxide film defects and particles such as $FeAl_3$ or any other cathodic constituent, such as copper, in an electrolyte containing oxygen and anions such as chloride, sulphate and bicarbonate (Johnson 1971). Simple washing procedures, utilising solutions of deionised water, proved unsuccessful in stabilizing *Australia II*, and it soon became apparent a corrosion inhibitor was needed to halt corrosion whilst desalination of the hull took place. Ultimately there exists equilibrium between the pitting corrosion reactions and passivation; Lowson (1978) found that a bulk concentration of 1.6 M chloride was needed to maintain pit growth. Thus the main aim of the conservation treatment was to remove as much of the soluble chloride salts as was technically feasible for a vessel which was initially in a storage regime before going on exhibition in the Historic Boats Museum at B Shed on Victoria Quay in Fremantle inner harbour.

Initial Conservation of the Hull Plates

Corrosion of the hull-plates was initially halted by siphoning off the foul smelling deep brown liquid, swabbing the pits before scrubbing down the affected areas with local tap water, which averages 120 ± 25 ppm chloride. Tap water was chosen as this form of water was the only one available in the storage facility, which was located more than 8km from the conservation laboratories in Fremantle. There was the additional complication of the hazards of trying to get water up a rickety old wooden ladder to *Australia II*. After washing, the hull-plates were dried with a hot air gun in an attempt to rapidly form a coherent passive oxide film. However, this simple solution proved to be totally ineffective since fresh outbreaks of the initial frothy corrosion products on top of the pit sites, showed that simple swabbing was not effective at managing the corrosion process. Changes in relative humidity had allowed the aluminium surface to absorb water and propagate rapid corrosion in the pits. The configuration of the mast box prohibited access to the worst corrosion site and proper drying was impossible.

Having established the underlying cause of the continued corrosion, an inhibitor was sought that could shift the pitting initiation potential of the aluminium to the positive side of the rest potential (i.e. the corrosion potential) whilst exhibiting a low current density i.e. a

low corrosion rate. Since Steve Ward, the builder of the yacht, had used a sodium chromate inhibitor, in conjunction with hydrofluoric acid as an etchant, in preparing the interior of the hull, it was thought that we should initially try to passivate the corrosion spots with the same chromate inhibitor. Owing to the highly toxic and corrosive nature of hydrofluoric acid, it was decided to capitalise on the amphoteric nature of aluminium and use alkaline sodium carbonate as an etchant. A series of measurements on the hull-plate electrode were made to assess the suitability of such a system to stabilise the hull of *Australia II*. By monitoring the corrosion current at given voltages, which varied in both anodic and cathodic directions by 250mV from the E_{corr} , it was found that high chromate concentrations of 60,000ppm (60 g/litre) were very effective inhibitors. When the chromate concentration fell below 250ppm, the solutions accelerate the corrosion rate. The results of these experiments formed the basis of the second attempt at controlling the corrosion processes i.e. using a wash solution containing 60g/litre sodium chromate (Na_2CrO_4) and 120g/litre sodium carbonate (Na_2CO_3). The treatment involved soaking the affected areas for several hours and then drying the hull sections with hot air from an electrically operated hot-air gun. Although our corrosion inhibitor experiments indicated that this treatment would reduce the corrosion rate by a factor of more than 110 times, it was clearly not sufficient for these hull plates. Despite the effective repatination of the aluminium with a bright yellow colour, indicative of the formation of an aluminium chromate coating, there were still major problems. A further inspection several weeks after the final chromate treatment showed the aluminium to be actively corroding. The reason why this inhibitor system failed is most probably due to a combination of relative humidity in excess of 60% and the presence of the high concentration of chloride on the aluminium surface (Oakes 1973; Awad et.al. 1981).

Characterisation of Corrosion Processes

In order to characterise the nature of the processes occurring on the hull plates of the *sewer*, a section of hull plate, which had been removed from the bow after it had been damaged in a collision during match racing before the Cup in Rhode Island, was sectioned and fabricated into an electrode. The aluminium hull-plate-electrode was prepared by taking a 1cm² section, tapping a small bolt hole into it and then attaching an insulated multi strand copper wire before embedding

the metal block in Araldite D casting resin. For tests using cyclic polarisation methods, one face was exposed by freshly grinding with silicon carbide wet and dry 1200 grit papers. After the surface had been exposed it was placed in an aerated test solution for 48 hours before being used in cyclic voltametric measurements. Cyclic voltammetry involves the use of standard three-electrode configuration with the working electrode and the reference electrode being used for voltage measurement and the current being passed through an auxiliary platinum electrode and the hull section. The voltage was controlled by an Amel 551 potentiostat and the cyclic voltage ramp was generated at the rate of 50 mV/sec. The resultant current-voltage curve is recorded on a flat bed X-Y recorder and both oxidation and reduction reactions are characterised by peaks in the trace. The voltages, which determine the location of the peaks, are dependent on the nature of the alloy, the solution environment and any absorption processes.

Corrosion testing was carried out on deoxygenated inhibitor solutions using 20 g/litre sodium metasilicate (Na_2SiO_3) solutions in deionised water. Such solutions were found to inhibit pitting. Cyclic voltammetry measurements indicated that the metasilicate solutions were much more effective at reducing corrosion than the chromate solutions which had previously been applied to the surface.

Treatment with Sodium Metasilicate Solutions

Given the encouraging data from the corrosion simulation experiments with sodium metasilicate and the previous failure of the chromate treatment, it was decided that it was necessary to flood the lower section of the vessel. Such action would not only introduce the corrosion inhibitor but it would also assist in the removal of chloride ions. A total volume of 130 litres of a 2 wt. % sodium metasilicate, acidified to pH 9.0 with phosphoric acid, was therefore poured into the *sewer* in order to bring about the desalination and repassivation of the hull plates. The pH, corrosion potential (E_{corr}) and chloride concentration in the wash solution were taken every twelve hours. Within forty-eight hours the E_{corr} had moved from -900 mV (vs. NHE) at pH 9.0 to -560 mV at pH 8.6 whilst the chloride concentration increased from a background level of 2 ppm to 1290 ppm chloride. The initial solution was siphoned out and replaced with 260 litres of a fresh sodium metasilicate solution of the same initial composition. The corrosion potential stabilized

at -700mV whilst removing a further 230ppm chloride over a period of two weeks.

In order to understand the implications of the changes in the values of E_{corr} , it is important to be aware of some of the other factors controlling the electrochemical processes of corrosion. In the absence of any films to protect the underlying metal from corrosion, any shift in the E_{corr} towards more anodic values, i.e. less negative, is normally associated with an increase in corrosion rate. However, when a protective film is formed, such as in the case with chromate and the metasilicate treatments, the relationship is not as simple. For general corrosion reactions there exists a fundamental relationship between the corrosion rate and the corrosion potential, E_{corr} , which is defined by the overvoltage η , and the corrosion current i via the Tafel relationship,

$$\eta = a + b \log i$$

where a is an empirical constant which relates to the inherent reversibility of the corrosion reaction, and b is the slope of the plot of the voltage versus the log of the corrosion current. The overvoltage η is a measure of the difference between the applied voltage E and the reversible voltage at net zero current flow E^0 , or the reversible potential (Stern & Geary 1957).

The slope of the plot of the voltage against the log of the corrosion current gives a measure of the number of millivolts needed to bring about a ten fold change in corrosion rate. The slope of the anodic branch of the plot is given by β_a and the slope of the cathodic branch is given by β_c . The Tafel relationship means that for most practical situations, there is a linear relationship between the logarithm of the corrosion current (rate) and the observed voltage of the corrosion cell.

Since the addition of the metasilicate solution brings about formation of a more protective film over the metal, the primary mechanism of corrosion reduction is the inhibition of the anodic reaction. Thus a drop in the oxidation (corrosion) rate brings about an increase in the E_{corr} since the voltage at which the reduction reaction equals the rate of the anodic reaction takes place at a less negative voltage. In this way the shift to less negative potentials during the treatment of the hull plates with the sodium metasilicate solution is to be viewed as a sign that the corrosion rate has been reduced. Thus the 340 mV anodic shift in the E_{corr} values of the hull plates during the passivation treatment with the metasilicate solution indicates that the overall corrosion rate has fallen by several orders

of magnitude owing to the formation of a protective passive film i.e. there is inhibition of the anodic corrosion reaction.

The final wash solution was siphoned off and the interior of the hull was dried over several days by drawing air through the interior of the hull with electric fans. The desalination and repatination treatment removed a total of 228g of chloride and resulted in a natural looking patina on the aluminium hull. The badly etched and deeply pitted sections of the hull plates remained stable for two years following this treatment, despite being stored in a damp, salt-rich environment of the B-Shed Historic Boats Museum on the Victoria Quay in Fremantle

Re-treatment to Original Specifications for Australian National Maritime Museum

The transfer of the loan agreement from the Western Australian Museum to the emerging Australian National Maritime Museum brought about a commitment to ensure that the vessel was handed over in pristine condition. Since we could not guarantee the longevity of the metasilicate treatment (Aylor & Moran 1986), it was decided to retreat the hull. The National Museum of Australia provided the funding for this work, since they were the owners of the vessel. Steve Ward and his team, who had originally built the yacht in their yard in Cottesloe, Western Australia, carried out the treatment program. The interior of the vessel was refurbished according to the US Military Specification No C5541, which involved the application of chromate conversion coatings, after phosphoric acid treatment with Deoxidine 624. This work involved stripping all interior fittings before the hull plates were all scrubbed down with *Scotchbrite* (3M Company) and given the same Alodine 1000L treatment used during the initial construction phase. This work was completed prior to *Australia II* travelling to the Australian National Maritime Museum in January 1991, where it became a focal point in the Leisure Gallery at the Darling Harbour site in Sydney.

During the conservation treatment, the hull was separated from the keel to facilitate an inspection, as our previous inspections had shown that there were signs that seawater had penetrated the bedding compound and the interface between the two surfaces. One of the effects of ingress of water at the interfaces between the paint film, the micro-balloons and metal is blisters forming beneath the painted surface (Figure 5).



Figure 5. View of bubbles underneath the finished painted hull surface, June 1987.

Corrosion products were subjected to analysis by X-ray diffraction, which characterised a basic lead oxide carbonate, $Pb_{10}(CO_3)_6(OH)_6O$, a mixed lead antimony oxide $Pb_3Sb_2O_8$, a mixed lead antimony sulphide $Pb_3Sb_2S_{17}$, a mixed lead antimony sulphide chloride $Pb_{17}Sb_{14}S_{35}Cl_{64}$ and some galena, PbS . The presence of the mixed lead antimony corrosion products is entirely consistent with the nature of the lead-antimony alloy used in the construction of the keel. The presence of the three sulphides indicates that the dominant form of corrosion was anaerobic with sulphides, emanating from the biological activity of sulphate reducing bacteria, appearing as the major anionic species. Microorganisms, such as *desulfovibrio desulfuricans*, produce sulphide ions and hydrosulphide ions as they consume the sulphate in the seawater. Owing to the extremely low solubility of metal sulphides, the oxidation products are readily trapped in the confined matrix of the interface between the hull and the keel.

A recent review of lead corrosion products found on historic shipwreck sites has shown that the oxides and basic carbonates relate to corrosion reactions that take place in well oxygenated waters (MacLeod & Wozniak 1996). Thus the presence of the hydroxy carbonate oxide of lead supports the supposition that there was initially aerobic corrosion of the lead-antimony alloy before the corrosion products filled the void and created anaerobic conditions. It is likely that the lead-antimony-oxide was formed during the high temperature pouring of the molten alloy into the mould that formed the shape of the keel.

A major part of the refurbishment of the vessel included the complete stripping of the damaged paint film from the mast. The higher chromium and copper content in the 7075 alloy of the mast, compared with the high tensile 6061 of the frames and the presence of 5.5% zinc would have resulted in much greater



Figure 6. Filiform corrosion on the mast of *Australia II*, prior to stripping and repainting.

strength. However, the paint film had failed spectacularly during the combined service and storage life. This difference perhaps serves to highlight the difference between mechanical strength and materials performance in terms of resistance to corrosion. Large sections of the mast showed filiform corrosion and blistering of the paint from the metal surface (Figure 6), which was also seen to be covered with white corrosion products. The old paint film was ground off and the abraded surface provided a good key-in for the new paint film. There have been no reports of any subsequent corrosion problems on the mast.

Discussion

The likely mechanism of corrosion inhibition of the hull plates involves silicon atoms in the silicate molecules bonding to the octahedral sites occupied by aluminium within the hexagonal close packed array of oxygen atoms on the oxide surface. Atanasoska et al. (1985) showed that the concentration of chloride ions is predominantly in the oxide layer that develops a chloride saturated aluminium-oxide coating. The rapid chloride release experienced in this treatment may possibly be attributed to the strong chemisorption of silicate onto the aluminium surface, displacing the remaining oxide layer and the chloride content within the surface. As the chloride concentration in solution increased, the corrosion potential gradually moved into a range of voltages, which represent a more passive environment. It should be noted that the adsorption of chloride ions is localized at corroding pits (Berzins et al. 1977) and so there is only a small percentage of the bulk chloride concentration that leads directly to pitting formation.

The lack of subsequent corrosion problems with *Australia II* after the sodium metasilicate solution treatment indicated that it has been possible to

simultaneously desalinate the interior hull plating in *Australia II* after five years of immersion in saline water, and to re-passivate the alloy. The metasilicate treatment resulted in rapid chloride release and good subsequent stability of the hull. However, to ensure the long-term stability of the vessel and to reduce the inherent risk of further corrosion from absorbed salts over the whole area of the interior of the hull, it was decided to strip the interior of the vessel of all fittings and to re-passivate the surfaces by repeated application of the original surface treatment. This ameliorative treatment cost a total of \$30,000 in 1990 and involved the removal of the keel from the boat to assess the internal corrosion between the lead-antimony alloy keel and the aluminium alloy hull, sandblasting the bottom of the boat, treating the cleaned surface with Alodine 1000L and painting the surface with an epoxy primer before rebedding the keel with 5200 silicon adhesive, followed by refairing the keel joint line. The interior of the hull was descaled by hand in the worst corrosion areas and the whole of the interior was to be re-treated with Alodine (Henkel Australia).

Analysis of the corrosion products on 6061 aluminium alloy materials, used in the construction of the frames, showed that exposure to seawater resulted in a matrix that consisted of 14.5% sulphate and only 1.3% chloride. This analysis is believed to be a reflection of the selective adsorption of the doubly charged sulphate ion from seawater, since it has a much higher electrostatic attraction for aluminium ions than does the singly charged chloride ion (NACE, 1960). Surface re-touching of the deck coating was to use the original two pack Epiglass paint system with a mixture of blue and yellow paints to gain the desired muted green finish. The running rigging and gear was serviced before the vessel was transported across to Sydney for exhibition. Although the vessel left Western Australia

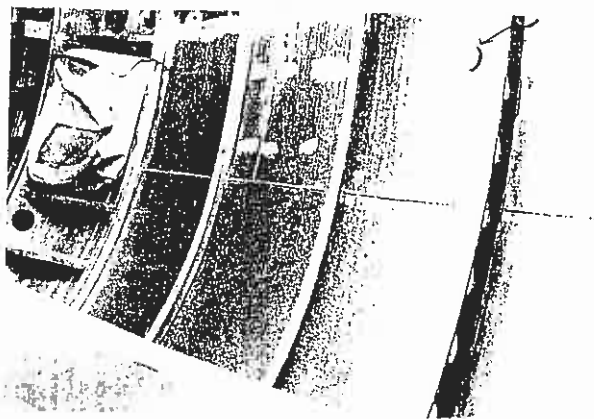


Figure 7. Streaked corrosion lines on interior of *Australia II* after transport and storage in Sydney.

in a fine condition, as noted in a November 29 1990 condition report, the interior of the hull was streaked with aluminium corrosion products by the time it had been shipped across to Sydney and inspected after five weeks of storage in the off-site facility in St Mary's (Figure 7). This change of condition serves to highlight the inherent instability of these high tensile aluminium alloys and the need to maintain them in a stable museum environment. It can also be a reflection of the sensitivity of the passivated surfaces to exposure to moisture containing chloride ions (Panitz & Sharp 1984). Given that these changes in the condition of the vessel took place during and after transport from Perth to Sydney, it does bring into question the ethics of taking such vessels out of the museum for the purpose of promotional activities such as racing by former crew members.

In April 2001 *Australia II* was taken from its storage location in Fremantle and made ready to sail once again. This work involved fitting a new mast, navigational equipment and a set of sails to allow the vessel to be trialed off Fremantle. Prior to being allowed into the water, an acoustic survey of the integrity of the paint film was undertaken, using a 'holiday' detection device which finds discontinuities e.g. pinholes, in the paint film. Defects were made good by application of a transparent coating which could be rubbed down and removed after the yacht returned to Australia. After the fitting of the new components and careful documentation of the original fixtures, the vessel underwent sea trials before it was taken by boat to Cowes in England to engage in a series of races associated with the 150th anniversary of the America's Cup regatta. During one of the races the yacht grounded and sustained some damage to the keel. This has subsequently been repaired. It is anticipated that once the yacht has been returned to the museum, it will undergo an extensive conservation treatment program before it is installed in the new maritime museum building at Forrest Landing at Victoria Quay in Fremantle Harbour.

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