Report on the corrosion of iron shipwrecks in South Australia: with particular reference to the River Murray

Ian Donald MacLeod
Department of Materials Conservation
Western Australia Museum
Western Australia

The *Santiago*

The *Santiago* was built in Scotland in 1856 and was used on the Australian run until it was turned into a coal hulk and ultimately taken to the "Ships Graveyard" in the Port River in Adelaide in 1945. The vessel now lies in the water with the bulwarks above water at low tide but awash at high tide. With the ebb and flow of the tide, a current of about 1.5 knots runs around the wreck whilst within the confines of the hull the water movement is significantly less, though at the flow of the tide a significant amount of water movement within the wreck does occur as the amount of sediment that was disturbed resulted in a fall of visibility from about two metres to half a metre. The bottom of the vessel is covered in a fine muddy-silty layer of sediment and this also forms a loose covering 1-1.5 cm thick on the flat surfaces of the vestiges of original iron plating that abuts the sides of the hull.

The outward appearance of the vessel is typical of iron wrecks that lie in and out of the water in that the stern has large lacunae in the zone that is defined by the rise and fall of the tide. The site is close to industrial areas associated with sanitary land fill and a nearby power station. The salinity of the water is based on data from the nearby Torrens Island power station—it varies from 41-45 parts per thousand (ppt) depending on the time of the year and the local evaporation rates. The pH of the sea water was 8.12 at a temperature of 10°C. The results of the corrosion survey on the vessel are summarised in table 1.

Table 1 ***corrosion parameters on the*** Santiago, ***Port River, Adelaide.***

Description	pH	Ecorr. vs. Ag/AgCl	Ecorr. vs. NHE
Starboard rib, badly corroded	7.2	-0.335	-0.056
Fe3O4 conc. rib, sound condition	6.96	-0.572	-0.293
Concreted rib, good white metal	6.82	-0.568	-0.289
Main mast, little concretion	-	-0.561	-0.282
Aft mast, siliceous slime	-	-0.577	-0.298
Port side sheet, about 1m below water line	-	-0.577	-0.278
Forward port sheet, good condition	-	-0.566	-0.287
Upper plating, totally corroded	-	-0.288	-0.009

The corrosion potentials were measured relative to the voltage of a Ag/AgCl reference electrode from the NSW Department of Transport. Since the electrode has a flow-through design, the voltage is dependent on the chloride ion activity of the surrounding water. It was therefore necessary to calibrate the reference electrodes for each type of environment. For the measurements on the *Santiago* the calibration voltage of this electrode was determined to be +0.279 volts vs. NHE (the normal hydrogen electrode). The average corrosion potential for the solid metal was -0.288 ± 0.007 volts vs. NHE. Using the pH value of 6.82 for the concreted rib it is possible to calculate that at the average corrosion potential of -0.288 volts there is an equilibrium concentration of Fe_3^{2+} ions at 7.3 ppm (1.3 x 10^{-4}M) with the solid phase being magnetite, Fe_3O_4 (Pourbaix 1977). This value represents a typical corrosion rate of approximately 0.08 mm./year, based on the data published for corrosion of concreted iron on historic shipwrecks (MacLeod 1989). In some sections of the vessel the average thickness of metal is of the order 1-2 mm and this will take between 12.5 and 25 years to totally disappear. However it should be noted that well before the total loss of metal the structural integrity of the vessel will be drastically impaired to the point of collapse. It is essential that action is taken in the very near future to minimise the corrosion of this vessel or else it will be lost to posterity.

Albion (Goolwa)

The *Albion* was a barge in the River Murray which had a timber hull with iron sides topped by wooden planking. It was apparently a government vessel that was unregistered. It is currently settled on the bottom of the river in about two metres of water adjacent to a reed bank and the stem post is within half a metre of a new wooden jetty upstream of the location of the *Uranus* at Goolwa. The stem post appears to be made of red gum (*Eucalyptus camaldulensis*) and it was covered with a thin layer of green algal slime. A measurement of the pH of the river water was taken and was found to be 7.90.

Table 2 ***pH profile of red gum on the*** Albion.

Location	pH	Depth into wood mm.
Stem post	7.90	0
"	7.12	2
"	7.45	3
"	7.50	3.5
Upper planking	7.05	3
"	7.02	3

It was impossible to penetrate the wood any further than the depths indicated in the table. Beyond the indicated depths, the original colour of the red gum was exposed and the flattened profile of the 10 mm diameter drill bit could not penetrate the undegraded wood. The maximum difference of 0.88 pH units between the wood and the surrounding water is indicative of the neutralising ability of the timbers acidic units (e.g. acetate units), to respond to the alkalinity of the surrounding waters. Since pH is a logarithmic function the difference of 0.88 in the pH value corresponds to a factor of 7.6 times difference in the analytical concentration of the hydrogen ions. The variability of the data from the stem post is due to experimental difficulties in locating the glass electrode on the area of freshly exposed materials. The pH profile of the wood is approximately -0.25 $pH.mm^{-1}$ for the upper planking and -0.39 $pH.mm^{-1}$ for the first two millimetres of the stem post.

A corrosion survey on the iron fittings of the wreck was undertaken in order to ascertain the inherent corrosivity of the site. The stern section of the upper iron plating had a purplish-blue patina to it that was very reminiscent of an iron-tannate complex. This area was found 10 cm above the green algal slime line and may be due to complexation of the iron corrosion products reacting with soluble tannates in the water that came from the vegetation that had fallen into or grew on the river banks. The bulkhead in the midships was corroded right through in the area that was within 20 cm of the water line. In general only the heavier iron structural supports, in the form of frames, have survived above the waterline. The results of the corrosion survey are listed in table 3.

Table 3 *Corrosion potentials of iron fittings on the* Albion.

Fitting	Ecorr.volts vs. Ag/AgCl	Ecorr. volts vs. NHE
Plating near port bow	-0.552	-0.168
First bulkhead	-0.568	-0.214
"T" shaped frame near outer planking	-0.517	-0.163
Midships plating	-0.514	-0.160
Plating near stern	-0.462*	-0.018

**This plating was apparently in electrical contact with the "tannate" patinated material near the stem section of the vessel and the corrosion potential may be moved in the anodic direction through the formation of a passive film. Laboratory studies are needed to elucidate the cause of this effect. The voltage of the flow-through Ag/AgCl reference electrode was calibrated at +0.354 volts vs. NHE.*

The average corrosion potential of the iron plating was -0.163± 0.005 volts while the bulkhead was -0.214 volts which is indicative of the fact that the major part of the bulkhead is well below the water interface and as such the lower level of dissolved oxygen will result in a slower corrosion rate. The higher corrosion potential of the plating is due to the structure of the vessel which consists of an upper wooden planking above a steel plating section which in turn was above a wooden section that came up from the bottom of the vessel. The average corrosion potential of all the iron materials was -0.176 volts vs. NHE. The apparent contamination of the river water with sea water is reflected in the pH which was only 0.22 units less alkaline than the open sea value measured in the Port River at 8.12. The sites at Goolwa were only 12.8 km (8 miles) from the river mouth. The effectiveness of the barrage system in the river is indicated by the low reading of the chloride content of the water which was 410 ppm which is one forty sixth of the amount in normal sea water.

Uranus (Goolwa)

The *Uranus* was built in 1886 as a barge and currently lies in the River Murray in a partly submerged condition and has been built around by two arms of a modern jetty in front of the remains of the stern wheeler the *Captain Sturt* at Goolwa. It was sunk to form a breakwater. Some of the structure above the waterline remains but most of the vessel lies in a highly corroded state. The vessel has been in its current location for approximately fifty years. The results of the corrosion survey are listed in table 4. The water temperature at both sites at Goolwa was between 10.5 and 11°C.

Table 4 *Corrosion data from the wreck of the* Uranus.

Fitting	Ecorr. volts vs. Ag/AgCl	Ecorr. volts vs. NHE	pH
Stem post	-	-	7.42
Stern post	-	-	7.20
Rub rail	-0.516	-0.162	7.41
Plating at bow	-0.513	-0.159	-
Plating at stern	-0.511	-0.157	6.46
Plating near stern	-0.528	-0.174	-

The build-up of a mixture of corrosion products and the slime around and below the waterline, near the stern, had allowed a 1 cm layer of concretion-corrosion matrix to develop. This obviously facilitated the pH gradient from the water value of 7.92 to 6.46 at the corrosion product-water interface approximately 20 cm below the water line. The wood on the *Uranus* appeared to be more degraded than on the *Albion* although this is not reflected in different pH values—it should be noted that the original colour of the *Uranus* timber had not yet been exposed at a depth of 3 mm into the surface.

The average corrosion potential for the iron plating on the *Uranus* is -0.163 ± 0.008 volts vs. NHE which is 13 mV more positive (less negative) than the average value for the iron plating found on the *Albion*. The small difference in the average voltage of the vessel is probably a reflection of the location of the *Uranus* in the breakwater system which has more water flow around it than the *Albion* has in its location adjacent to the river bank. The recording of the pH profile on the wood from the *Uranus* stem post is seen in figure 1.

Figure 1 **Measurement of surface pH of wooden stem post in the** Uranus.

Crowie (Morgan)

The *Crowie* is a composite wood and iron Murray river barge that was built in 1911 and may have been abandoned as early as 1946 along with the *Corowa* with which it was commonly associated. The vessels are near Morgan and are located close to the 199 mile mark from the river mouth. The remains of the vessel lie parallel to the shore line and approximately ten metres from the bank. Only the ribs stand proud of the water with stern deck plating lying about 15 cm below the water line. A corrosion survey showed up interesting results that relate to not only metal sections that have part of their area exposed but also to metal sections that were fully immersed in the water. The temperature at a depth of one metre was 11.3°C while the temperature on the bottom at 6 m was only marginally lower at 11°C. The results of the measurements are shown in table 5.

Table 5 ***Iron corrosion potentials on the barge*** Crowie.

Fitting	Ecorr.*volts vs. Ag/AgCl	Ecorr. volts vs. NHE
Port beam	-0.523	-0.149
Iron decking plate	-0.521	-0.147
Outside hull plate	-0.510	-0.136
Frame, port side	-0.495	-0.121
Totally submerged frame	-0.554	-0.180
Submerged frame near bow	-0.547	-0.173
Submerged stern plating	-0.522	-0.148
Stern deck beam	-0.517	-0.145

** The potential of the flowing water Ag/AgCl electrode from the NSW Department of Transport was +0.374 volts vs. NHE.*

The average of all the corrosion potential measurements was -0.150 ± 0.019 volts vs. NHE and as such the voltage is indicative of a slightly elevated corrosion rate compared with the two vessels located at Goolwa. The increased amount of the iron structure that was exposed and the greater amount of water movement all contribute to the differences in the measurements. The only totally submerged iron frame that was measured was 36 mV more negative in corrosion potential than the average value of the other frames that were partly exposed. The chloride concentration in the water at Morgan was 185 ppm compared with 410 ppm at Goolwa.

P.S. *Corowa* (Morgan)

The remains of the 1868 paddle steamer *Corowa,* which was abandoned at Morgan on the River Murray in 1946 after sinking, lies about 15 metres from the shore on the town side of the river. Part of the stern wheel lies above the water and a small section of a steam-pipe lies proud of the water to a height of about 10 cm, as can be seen in figure 2. A corrosion survey of the vessel and its remains was made using the AGA full face mask with communication facilities to facilitate the coordination of measurements and the recording of the data, which is summarised below in table 6. A divers knife was used to clear a small area of the surface and a torch showed up the white metal where the platinum electrode was placed. Without the use of the torch it would have been impossible to accurately place the electrode and ensure good electrical contact.

Table 6 ***Corrosion potentials for the*** Corowa.

Fitting	Ecorr.*volts vs. Ag/AgCl	Ecorr. volts vs. NHE
Boiler	-0.519	-0.145
Wrought iron engine fitting	-0.516	-0.142
Horizontal pipe#	-0.526	-0.152
Cast iron pipe	-0.508	-0.134
Steam pipe	-0.525	-0.136
Stern paddle section	-0.542	-0.170
Base of paddle system	-0.590	-0.216
Wooden deck beam	+0.200	+0.574

* The corrosion potentials were measured against the NSW instrument and this was calibrated against a standard Ag/AgCl reference electrode which had been calibrated against the platinum electrode using a quinhydrone solution buffered at a pH of 4.0. The reference voltage was + 0.374 volts vs. NHE.

This potential was measured using another reference electrode.

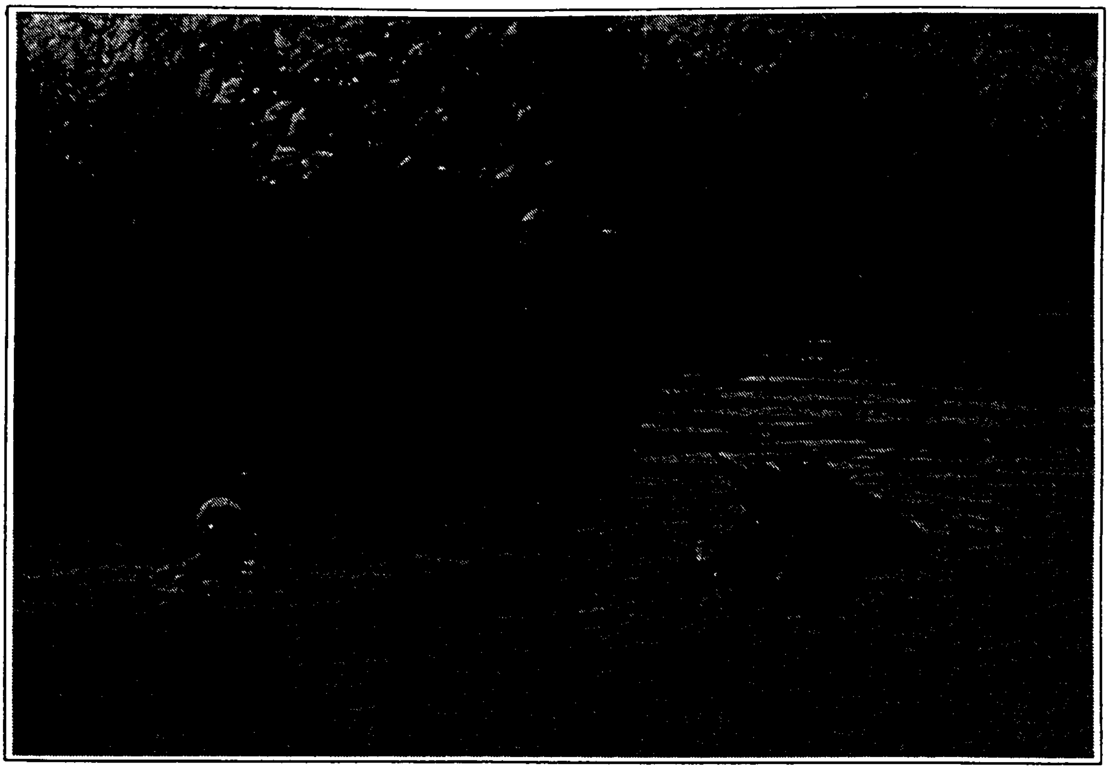

Figure 2 *Bill Jeffery inspecting the steam pipe from the* Corowa *engine.*

The average of all the iron corrosion potentials measured on this site was -0.156 ± 0.028 volts vs. NHE. Part of the reason for the larger standard deviation of these corrosion potentials compared with the previous sites is that, with an increased range of water depth, the *Corowa* site can exhibit a wider range of micro environments. The other major factor is that we note the more anodic (less negative) potentials associated with the cast iron fittings associated with the engine. The most negative potential was recorded at the base of the paddle system. Given the juxtaposition of the *Corowa* and the *Crowie* it is not surprising to see that they have essentially the same average corrosion potential and the same inherent rate of corrosion.

Cobar (Waikerie)

The *Cobar* lies close to lock 2 on the River Murray about 224 miles from the mouth of the river and about thirteen miles downstream from Waikerie. It was a composite barge that was built in 1882 that was abandoned and sank sometime between 1925 and 1961. Currently the vessel lies parallel to the shore about three metres into the water though in one part the shore almost reaches out to the vessel. Above the waterline the wreck consists of a series of frames with some wooden planking just visible at the waterline, as shown in figure 3. The water temperature was 11°C. The results of the corrosion potential survey are summarised in table 7.

Table 7: ***Corrosion survey of the barge*** Cobar.

Object	Ecorr. volts vs. Ag/AgCl	Ecorr. volts vs. NHE
L shaped stringer, near bow	-0.495	-0.118
Second stringer down, poor condition	-0.387	-0.002
Frame near bow	-0.486	-0.109
Bulkhead	-0.490	-0.113
Corroded frame	-0.269	+0.008
Outside hull plating	-0.489	-0.112
Outside stern plating	-0.479	-0.102
Stern deck plating, badly corroded	-0.286	+0.081
Stern	-0.360	+0.015

** The reference electrode was calibrated in river water against a previously calibrated Ag/AgCl electrode and was +0.377 volts vs.NHE.*

The mean corrosion potential of the solid iron fittings, frames and plating on the *Cobar* was -0.111 ± 0.006 volts vs. NHE. This average value is higher (more corrosive) than the *Corowa* and the *Crowie* and this is due in part to the fact that more of the iron in the vessel is protruding from the surface which gives increased access to oxygen and to the setting up of a series of differential aeration cells.

The higher voltage for the submerged stern deck plating of +0.081 volts is indicative of a corroded matrix rather than a true corrosion potential reading which requires some solid metal to be in electrical contact with the point of measurement. The measurement of the corrosion potential of the stern at +0.015 is also consistent with this area being heavily corroded since the both potentials lie in the domain of the Pourbaix diagram (Pourbaix 1974) where FeO.OH is the thermodynamically stable form of iron. An example of a Pourbaix diagram is shown in figure 4 where the corrosion potentials for the *Jolly Miller* are plotted. Pourbaix diagrams are thermodynamic plots of stability of metals, metal ions and associated solid phases consisting of corrosion products. Such diagrams are a very convenient way of displaying corrosion data.

P.S. *William R. Randell* (Waikerie)

The *William R. Randell* was a wooden paddle steamer built in 1905 and abandoned in the 1930's. It is located in the same area as the *Cobar* and sank during a flood some two kilometres below lock 2. The only visible part of the vessel is a section of one of the iron paddle frames of the side wheel, as seen in figure 3. Corrosion measurements were done on fittings associated with the engine and on some of the supporting structural members. Owing to the submerged nature of this vessel it was necessary to use a platinum electrode with the double junction reference Ag/AgCl electrode. Both these electrodes had 15 metre lengths of insulated cables attached to them to facilitate underwater contacts while allowing the digital multimeter to be read on board the work boat. The advantage of the double junction reference electrode is that the isolation of the reference compartment means that the voltage is not sensitive to the chloride content of the local waters.

The salinity data listed in table 13 shows that the chloride concentration of the river changes significantly and this also affects the voltage of the "flow-through" reference electrodes. The use of the long wires meant that they could be taped to the communications system and the safety line. The pH of the water was 7.61 and the chloride level was 168 ppm (see table 13). The results of the measurements are shown below in Table 8 where the effects of contact of iron with non-ferrous materials is clearly seen i.e. the corrosion potentials for the iron fittings connected to brass are elevated by some 144 mV which is probably an increase in corrosion rates of the order of between

Figure 3 *View of the exposed frames of the* Cobar *and the stem wheel of the* William R.Randell.

eight and ten times. The attachment of brass and copper fittings to the iron associated with the boiler will, in the environment of the wrecksite, accelerate the corrosion of the associated iron work.

Since the vessel was primarily made of wood the metal corrosion measurements relate to materials associated with the vessels propulsion system. The apparent stable voltages measured for the sight glass on the boiler and for the wooden beam are redox potential measurements, since there is no solid metal present, and the high voltages are consistent with the red-brown patina of iron(III) corrosion products being impregnated into the materials that were measured. If the corrosion products on the wooden beam had been black that would have indicated either magnetite or an iron sulphide - the latter possibilities are also shown to be unlikely because of the positive voltages. The voltage reading of the wooden beam may also in part be due to the presence of dissolved oxygen in the degraded structure. The corrosion potential of -0.045 for the brass fitting on the boiler is typical of material that is corroding in a film free environment with the corrosion products consisting of copper chloride complexes (MacLeod 1992).

Table 8 *Corrosion survey of the paddle steamer* William R. Randell.

Fitting	Ecorr. volts vs. Ag/AgCl	Ecorr. volts vs. NHE
Paddle wheel brace	-0.522*	-0.129
Support at wheel base	-0.326	-0.160
Thin plating at top of beam	-0.225	-0.059
Non ferrous, part of boiler	-0.142	-0.024
Iron on boiler with brass fitting	-0.165	-0.001
Possibly glass	+0.167	+0.333
Possibly wooden beam	+0.207	+0.373
Iron hull frame	-0.228	-0.062
Cast iron fitting	-0.219	-0.053

** This measurement was made using the NSW instrument while the rest were made using the remote instruments which were calibrated using the known voltage of a platinum electrode in a saturated quinhydrone solution at a pH of 4.*

The average corrosion potentials for all the wrought iron materials on the site was -0.102 ±0.052 volts vs. NHE while the cast iron fitting, which was significantly corroded was -0.053 volts. It was noted that only a few of the iron materials measured were in good condition and when these results are averaged the mean corrosion potential for the wrought iron is -0.145 ± 0.022 volts. The differences between the corrosion potentials cannot be easily correlated with site conditions such as water depth because of the practical technical difficulties of determining this measurement when carrying out a survey in blackout conditions. The water depth on the site was dependent on the part of the wreck that was being measured but it generally ranged from 1-3 metres.

P.S. *J.G. Arnold* (Waikerie)

The *J.G. Arnold* was built in 1917 at Mannum as a River Murray paddle steamer which came to grief near Waikerie at the 240 mile upstream post near Holder Bend. The pH of the water was measured and found to be 7.61 and the chloride concentration was 168 ppm. The site is fully submerged and the average water depth was six metres. It lies on the outer curve of the river and as such it will be more prone to a localised increase in average water velocity. If the corrosion rate is determined by the flux of dissolved oxygen, as is the case for concreted marine iron, then any factor that increases the flux of dissolved oxygen to the corroding metal will result in an increase in the overall corrosion rate. The results of the survey are shown in table 9.

Table 9 ***Corrosion potentials for the*** J.G. Arnold.

Fitting	Ecorr. volts vs. Ag/AgCl	Ecorr. volts vs. NHE
Hull plating	-0.356	-0.190
Corroded deck beam	-0.398	-0.232
Top deck beam	-0.411	-0.245
Wooden beam	+0.244	+0.410
Wooden beam, red coloured surface	+0.247	+0.413
Deck beams	-0.428	-0.262
"T" piece on deck beam for hatch	-0.370	-0.204
Hatch	-0.411	-0.245
Hull material	-0.392	-0.226

The average corrosion potential for the iron fittings in this composite vessel was determined to be -0.229 ±0.025 volts vs. NHE which is significantly more negative than the average values of the other wrecks listed in the preceding tables. The low voltage is indicative of a low overall corrosion rate. As noted in the discussion for the wooden beams on the wreck of the *William R Randell*, the positive voltages measured on this site are indicative of iron(III) corrosion products impregnated into the wood itself.

P.S. *Jolly Miller* (Pyap)

The *Jolly Miller* is the oldest iron paddle steamer built in South Australia on the River Murray and it was built in 1866 and it sank near Pyap some time before 1944. It was an iron vessel that was built at Goolwa. The pH of the river water was measured and found to be 7.66 and the chloride concentration of the water was 154 ppm. The site is located near the 298 mile upstream post and some six miles downstream from Loxton. This was the second totally immersed site and the first where the influence of the effects of the silt layer on the corrosion behaviour of the iron was clearly demonstrated. The results of the corrosion survey are noted below in table 10 and representative values are plotted in the Pourbaix diagram in figure 4.

Table 10 **Corrosion potentials for the wreck of the** Jolly Miller.

Fitting	Ecorr. volts vs. Ag/AgCl	Ecorr. volts vs. NHE
Beam	-0.427	-0.261
Hull plating	-0.437	-0.271
Wrought iron	-0.421	-0.255
Hull plating, out of silt by 20 cm	-0.453	-0.287
Timber planking	+0.268	+0.434
Iron bolt in timber, just out of silt	-0.503	-0.337

The average corrosion potential for all of the iron fittings on the vessel is -0.282 ±0.014 volts vs.NHE. The average water depth of the site was between 4 and 8 metres with the remains of the vessel resting on the edge of the river bank which falls away quite quickly once one moves away from the shore line. The low values of the corrosion potentials is indicative of a good state of preservation of this material.

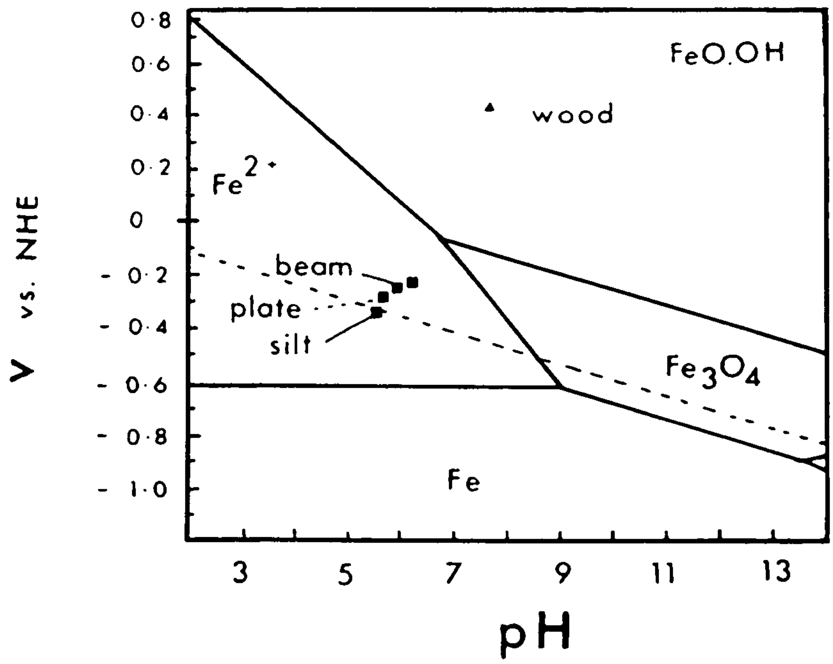

Figure 4 **Pourbaix diagram showing corrosion potentials for materials on the** Jolly Miller.

Undaunted/Ventura (Berri)

This site is located 300m downstream from the waste disposal site at Berri, which is approximately 2 km downstream from the ferry. The pH of the water was 7.67 which seems to be normal for this part of the river system and the chloride level was 113 ppm. Owing to the fact that the remains of the vessels appear to have fallen away from the river bank area off into deeper water there was very little information that was able to be measured on these two contiguous sites. The material that was observed tended to be covered in a layer of silt. The few results from this area are listed below in table 11.

The average water depth was about 6 metres and it appears that the remains of the vessels have fallen into the steep river bed—at a distance of some ten metres from the shore line a virtually shear drop-off occurs. The average corrosion potential for this site is -0.227± 0.016 volts vs. NHE.

Table 11 ***Corrosion parameters on the*** Undaunted/Ventura ***site.***

Fitting	**Ecorr. volts vs. Ag/AgCl**	**Ecorr. volts vs. NHE**
Concreted deck beam	-0.404	-0.238
Wooden beams	+0.228	+0.394
Deck beam near silt	-0.382	-0.216

Discussion of results

Corrosion potential measurements of submerged and partially submerged wrecks in the River Murray have been performed for the first time. This is also the first time that measurements of this type have been performed under black water conditions. The use of corrosion potentials to assess the condition of the wrecked barges and paddle steamers will provide heritage managers with a very useful tool for assessing the stability of the metal fittings and fixtures that remain on the sites. One of the practical consequences of this work is that since the turbid waters of the river precludes visual inspection methods, the corrosion measurements can act like a sensitive set of "remote sensing" eyes. Since the traditional methods of assessment cannot be used in the river, electrochemical measurements can produce an accurate data base to check on changes in the site conditions. An example of the use of such data is outlined in the following section.

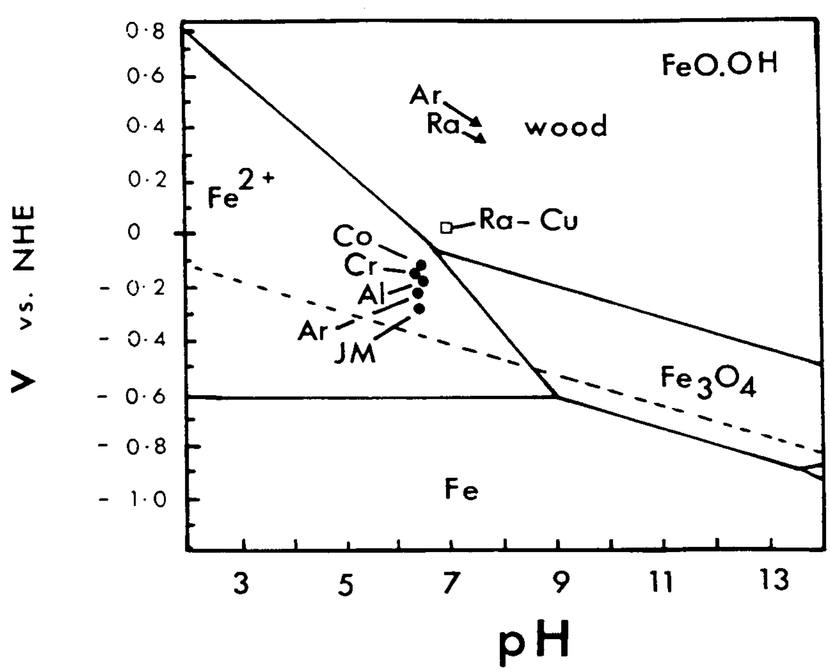

Figure 5 ***Pourbaix diagram showing corrosion parameters for wrecked barges and paddle steamers in the River Murray. The symbols used are : Ar(Arnold), Ra(Randell), Ra-Cu(galvanically coupled), Co(Cobar), Cr(Crowie), Al(Albion) and JM(Jolly Miller).***

By plotting the average corrosion potentials for the iron fittings and structural materials, from the different sites, on a Pourbaix diagram, it is very easy to appreciate the different nature of the sites at a glance. Some of the data is shown in figure 5 where sites with essentially the same average Ecorr. were omitted for the sake of clarity.

When the site parameters are summarised in this form we see that all the average Ecorr. values for sound iron are in the region of active corrosion. The equilibrium reactions appear to be related to the corrosion of iron to produce Fe^{2+} ions which are in equilibrium with magnetite, Fe_3O_4 according to the following reactions,

$Fe \longrightarrow Fe^{2+} + 2e^-$ ....(1)

$3Fe^{2+} + 4\ H_2O \longrightarrow Fe_3O_4 + 8H^+ + 2e^-$ ....(2)

The pH of the micro environment associated with this equilibrium is given by the relationship

$Eo = 0.980 - 0.2364\ pH - 0.0886\ \log[Fe^{2+}]$ ....(3)

which for the pH of 6.46 observed on the concreted sections on the *Uranus* at Goolwa, gives a ferrous ion concentration of 3.9x10-5 M or approximately 2.2 ppm Fe2+ in equilibrium with magnetite. Assuming that this pH value is typical, the average corrosion potentials on the *Jolly Miller* correspond to approximately 200 ppm Fe2+ ions. The individual Ecorr. measurements on the extensively corroded iron materials on the *Wm. Randell* and the *Cobar* are seen to be in the region where FeO.OH is the stable form of iron. This data also is consistent with the observation that these fittings appeared to be extensively degraded. In a similar fashion we see that the voltages recorded for the wooden beams on the *J.G. Arnold, Wm. Randell* and the *Ventura/Undaunted* are typical of iron(III) corrosion products such as FeO.OH being impregnated into the matrix.

A tabular summary of the average corrosion potentials for the iron fittings and iron structural material on the vessels is found below in table 12. It is interesting to note that each of the pairs of vessels at each of the main sites at Goolwa, Morgan and Waikerie presented similar values of the corrosion potentials. The more corrosive environment measured for the vessels at Morgan, compared with Goolwa, are probably a reflection of the greater amount of water movement over the wrecks located at Morgan since those at Goolwa were in only what could be described as a very sheltered environment. The average values for the *Cobar* are significantly higher than those measured for the four vessels at Goolwa and Morgan. This is probably due to the much more exposed nature of the metal frames and plates that were being measured.

The more negative values for Ecorr. found for the vessels upstream of Waikerie and at Loxton and Berri are in part due to the greater depth of water over the sites. It has been observed in the ocean sites that water depth has a major affect on the values of Ecorr. and, in turn, on the rate of corrosion (MacLeod 1989:2). Although the corrosion mechanism has not yet been validated for river sites, it is most likely that the reduction of dissolved oxygen is involved in the rate determining step in the overall corrosion process. Support for this mechanism is found in the way in which the individual corrosion potentials vary with site conditions. A good example of this is seen on the site of the *Jolly Miller* where the Ecorr. of the iron in the silt was 82 mV more negative (less corrosive) than values obtained on similar iron sections at shallower depth which were lying proud of the river bed (figure 4).

Table 12 Corrosion parameters for wrecks in the River Murray.

Wreck	Water depth (metres)	Ecorr. volts vs. NHE	Nearest town
ALBION	1-2	-0.176±0.025	Goolwa
URANUS	1-2	-0.163±0.007	"
COROWA	2-3	-0.156±0.024	Morgan
CROWIE	1-2	-0.150±0.019	"
COBAR	1-2	-0.111±0.006	Waikerie
Wm. RANDELL	1-4	-0.145±0.052	"
J.G. ARNOLD	6	-0.229±0.025	"
JOLLY MILLER	6-8	-0.282±0.033	Loxto
VENTURA II- UNDAUNTED	4-6	-0.227±0.016	Berri

The changes in the nature of the River Murray water are indicated by the changing pH and chloride content of the water measured on the various sites that ranged from being close to the mouth at Goolwa to being some three hundred miles away at Loxton. The data is dramatically portrayed in table 13.

It is essential that future studies be done on these wrecksites as it will only be possible to asses the stability of the sites by comparing sets of data collected over an extended period. Any parameter that increases the amount of water movement in the area of the wrecks will increase the rate of deterioration of the metals. Examples of avoidable water movements are water skiing where the wash from the speed boats can have a major effect on the localised site parameters.

Table 13 The effect of distance from the sea on river water pH and chlorinity.

Nearest town	pH	Distance from the sea miles	[Cl-] ppm.
Goolwa	7.90	5	410
Morgan	7.86	199	185
Waikerie	7.67	224	168
Pyap	7.67	298	154
Berri	7.61	326	113

An example of the effects of water movement on the preservation of timber is seen in the degradation patterns on the bottom of the P.S. *Colonel*. The timber has apparently been degraded to a much greater extent in the area adjacent to the wash from the paddles than in the sections where the water flow is less turbulent. The iron corrosion products have apparently preserved the wood in the vicinity of the bolts, see figure 6, whereas iron is normally associated with the increased rate of chemical and biological deterioration. Further work need to be done to clarify the mechanism of this apparent reaction—the surface profile may also be due to specific biological degradation mechanisms that pertain to the riverine and riparian environments.

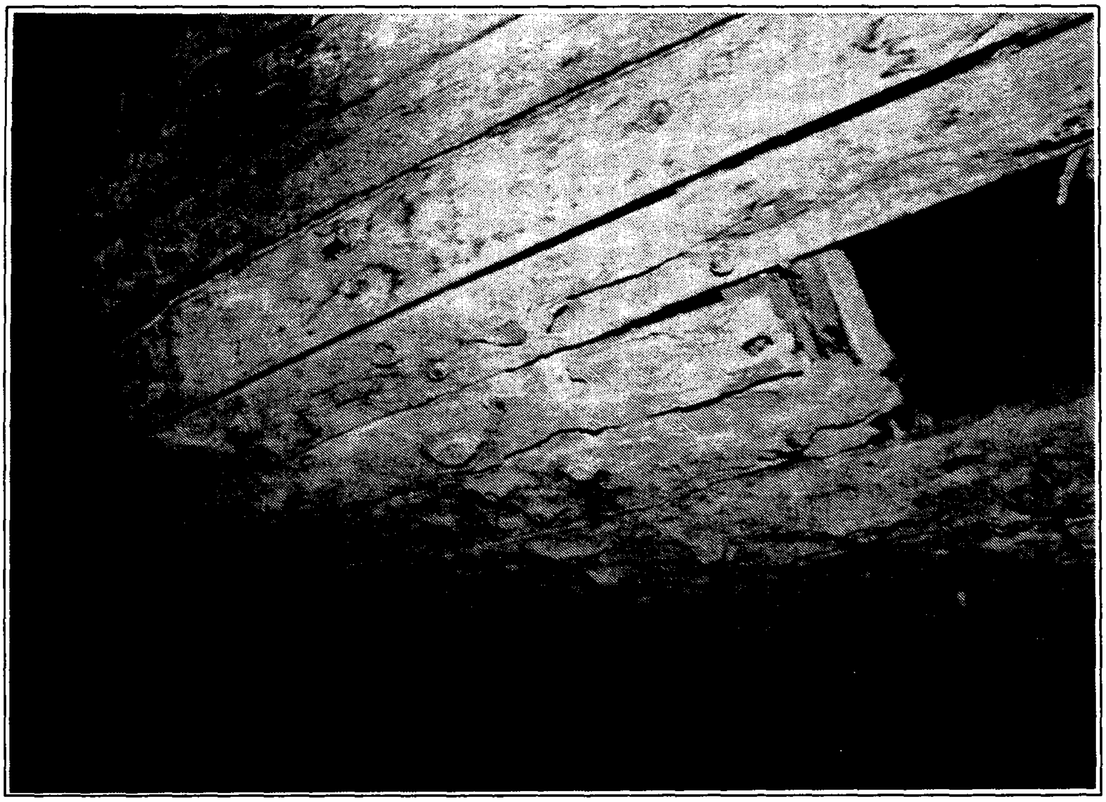

Figure 6 ***Hull planking on the P.S.*** Colonel.

Acknowledgements

The assistance, cooperation and patience of my colleagues Bill Jeffery and Sarah Kenderdine is gratefully noted. The trialing of the modified equipment presented more than a few challenges. Without the support of the Trustees of the Western Australian Museum and the permission of the Minister for the Arts, I would not have been able to carry out this very significant project. The financial support of the Murray-Darling Basin Commission is gratefully acknowledged.

References

MacLeod, I.D., 1989, Electrochemistry and conservation of iron in sea water. *Chemistry in Australia*, 56(7): 227-229.

MacLeod, I.D., 1989, The application of corrosion science to the management of maritime archaeological sites. *Bulletin of the Australian Institute of Maritime Archaeology*, 13(2):7-16.

MacLeod, I.D., 1992, Conservation of corroded metals- a study of ships fastenings from the wreck of HMS Sirius(1790). *Conservation of Ancient and Historic Metals*, Getty Museum, Los Angeles -in press.

Pourbaix, M., 1974, Atlas of Electrochemical Equilibria in Aqueous Solutions. *National Association of Corrosion Engineers*, Houston, Texas, Second Edition.