

## Corrosion monitoring and the environmental impact of decommissioned naval vessels as artificial reefs

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### Abstract

The former Australian Naval vessels, HMAS Swan and HMAS Perth were scuttled as artificial reefs off the Western Australian coast in 1997 and 2001, respectively. In addition, the former HMAS Hobart was sunk in Gulf St Vincent, South Australia in 2002. During the preparation of the ships prior to sinking, significant quantities of metals, such as copper, copper alloys, aluminium, lead and steel, petroleum hydrocarbons and other potential pollutants were removed. Since it is possible that corrosion products and residual hydrocarbons may impact on the local marine environment, corrosion and sediment monitoring programmes were implemented on each of the three vessels. The concentrations of heavy metals, total petroleum hydrocarbons and butyl tins in the surrounding sediments were periodically monitored. The results demonstrate synergistic interactions between modern shipwreck materials, sediments, biota and the marine environment and the long-term stability of the vessels.

**Keywords:** artificial reef, marine environment, naval vessel, corrosion, environmental impact, sediment, butyl tin compounds

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### 1. Introduction

Artificial reefs are not a new concept. For centuries Japanese fishermen have attempted to increase the fishing productivity of their local waters by dumping rocks into the sea (Russel, 1975). By 1970 artificial reefs had been placed at more than 3500 sites around Japan. During the 1960's and 1970's over 100 artificial reefs had been constructed in the coastal waters of the USA and many other countries including Australia. In the 1970's, several tyre reefs were constructed in Gulf St Vincent and Spencer Gulf, SA and derelict ships and barges were sunk in the Pacific Ocean off the coast of Sydney, NSW. In the early 1970's artificial reefs were established in the lagoon at One Tree Island Reef in the Capricorn Group of the southern Great Barrier Reef. Similarly, three vessels were scuttled and three artificial tyre reefs were established off the Western Australian (WA) coast in an attempt to enhance recreational fishing and diving (Morrison, 2003a). The colonisation and/or corrosion of these artificial reefs were not monitored rigorously and there is little, if any data published for comparative studies.

The scuttling of decommissioned Royal Australian Navy (RAN) vessels as artificial reefs, the *Swan* in 1997, the *Perth* in 2001 and the *Hobart* in 2002, has provided the opportunity to study the environmental impact of these enormous contemporary ships on the local marine environment and obtain biological, physico-chemical and corrosion data from the time of 'wrecking'. The results provide important information on the synergistic interactions between modern shipwreck materials, sediments, biota and the marine environment and the long-term stability of the vessels. This knowledge is becoming more important as it is apparent that more of these decommissioned naval vessels and confiscated illegal fishing boats will be sunk as artificial reefs in the near future. Perhaps more importantly, the information can be used to better understand the deterioration of historic shipwreck sites and ultimately assist in the development of appropriate *in-situ* management strategies for underwater cultural heritage sites.

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## 1.1 The Vessels

The *Swan* (DE50) was an Australian built River class destroyer escort, laid down in the Naval Dockyard, Williamstown, Victoria in 1965 and first commissioned in 1970. It was 113m in length and 24m tall from keel to the tower, with a beam of 12.5m and a 5.3m draught. The *Perth* (DDG38) and the *Hobart* (DDG39) were American built Charles F. Adams class guided-missile destroyers, laid down in 1962 by the Defoe Shipbuilding Co., Bay City, Michigan, USA and commissioned in 1965. They were approximately 134m in length and 38m tall from keel to tower, with a beam of 14.2m and a draught of 6.1m (Chant, 1984; Gillet, 1986, 1988; Gillet & Graham, 1977; Odgers, 1989). The vessels' hulls were primarily mild steel plate and possibly small quantities of a carbon-manganese steel. The superstructure was aluminium alloy, probably 5083 (4.5% magnesium) primarily used for welded plate structures but thin material, such as furniture, ductwork, panel linings, awnings and general sheet metal work could have been 5052 (2.2% magnesium). In the late 1980's and 1990's the RAN had been using organotin self-polishing paint so the paint system below the waterline on the vessels would be a vinyl anti-corrosive plus antifouling International Intersmooth Self Polishing Co-polymer, which contains tributyl tin and cuprous oxide. The *Swan* was last painted with the anti-foul in 1994. The original paint above the waterline was probably zinc chromate primer with alkyd enamel undercoat and topcoat. Some or all of this may have been replaced in the 1980s and 1990s with zinc rich epoxy primer, epoxy intermediate coats and alkyd topcoat.

All hydrocarbons, hazardous material and liquids, debris and as far as was practicable, all metals of environmental concern were removed prior to scuttling in accordance with the Environmental Management Plans (EMPs). This was undertaken to minimise the environmental impact as a result of heavy metal and petroleum hydrocarbon contamination. During the preparation process, a number of measuring points were attached to predetermined positions on the hull and superstructure of the vessels to facilitate the corrosion monitoring programmes. After the preparations were completed and the vessels had passed rigorous inspections by Environment Australia, the *Swan* was scuttled on 14 December 1997 in Geographe Bay, Dunsborough, Western Australia, the *Perth* on 24 November 2001 in King George Sound, Albany, Western Australia and the *Hobart* was scuttled in Yankalilla Bay, Gulf St Vincent, South Australia on 5 November 2002. Post scuttling monitoring of the wrecks and surrounding sediments is required to provide information relating to the long-term stability of the vessels and establish the impact they have on the local marine environment. The monitoring regimes for each vessel varied however, they include a combination of sediment sampling for detection of heavy metals, total petroleum hydrocarbons and butyl tin, ecotoxicological assessments, recording the rate of colonization by fishes and encrusting marine life and corrosion surveys. The biological and sediment surveys were a requirement of the EMPs as prescribed by the Commonwealth or State environmental departments. However, the corrosion surveys were a proactive idea of the authors.

## 2. Experimental

### 2.1 Monitoring Programmes

The monitoring programme for the *Swan* required biological and sediment surveys in accordance with the Sea Dumping Act (1981) (Environment Australia, 1984; Morrison, 2003a). A baseline study of the fish community and the encrusting biota of the proposed wreck site and reference site was undertaken prior to sinking. The wreck was then monitored one month after scuttling, three times a year for the first two years and then annually for the next three years. The detailed results of these surveys will be reported separately. The sediment at the proposed wreck site and the selected reference site was analysed for a suite of heavy metals [aluminium (Al), iron (Fe), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb) and zinc (Zn)] and total petroleum hydrocarbons (TPH) prior to scuttling and repeated at 5 and 12 months after sinking. Baseline corrosion data was collected a few hours after scuttling, then again 12 months and 4 years after sinking.

The sediment sampling programme for the *Perth* involved baseline monitoring of the proposed wreck site and the selected reference sites followed by post scuttling monitoring after 6 and 12 months in accordance with the EMP governed by the Western Australian Environmental Protection Act under the supervision of the Department of Environmental Protection (DEP) (Morrison, 2003b). The sediment was analysed for nickel (Ni), tin (Sn) and mercury (Hg) in addition to the aforementioned heavy metals, TPH, total organic carbon (TOC) and tributyltin (TBT). Ecotoxicological assessment of the sediment during the baseline sediment survey was also performed in order to separate the ecological effects of the vessel from any existing contaminants. However, because the levels of TBT and metals in the sediments did not exceed ANZECC/ARMCANZ (2000) guidelines the toxicity testing was not carried out after the initial baseline assessment and hence, the ecotoxicological results will not be presented in this paper. The rate of colonisation of the *Perth* by fishes and encrusting marine

organisms was not recorded. The results of the five-year biological survey of the *Swan* could be extrapolated to this site so it was deemed unnecessary. The baseline corrosion survey was undertaken shortly after sinking then further monitoring occurred after 6 and 16 months.

A baseline benthic survey of the proposed wreck site for the *Hobart* prescribed by the Environmental Protection Authority (Morrison, 2002) was conducted to determine the existing assemblage and sediment quality. Unfortunately, no further sediment or biological monitoring has been undertaken due to monetary constraints, therefore the results of this survey will not be presented. The corrosion monitoring programme involved measurements at 3 and 6 months post-scuttling. The corrosion surveys will continue for five years after which time the programmes will be reviewed and continued if deemed necessary.

## 2.2 Corrosion Monitoring

The corrosion monitoring programmes of the scuttled vessels involved measuring the corrosion parameters ( $E_{\text{corr}}$  and surface pH of the metal surface) of a number of stainless steel (316) bolts attached to various positions on the steel hull and the aluminium superstructure of the *Swan*, *Perth* and *Hobart* prior to scuttling. The attachment and documentation procedure is outlined in Richards (2003a). The corrosion potentials ( $E_{\text{corr}}$ ) of the various positions on the vessel were measured on a high impedance digital multimeter, sealed in a custom-built plexiglass waterproof housing, set to read at 2V direct current. The measured voltage refers to the difference in electrical potential between a platinum working electrode and a silver/silver chloride/seawater electrode. The  $E_{\text{corr}}$  of the point was measured by firmly pressing the platinum electrode onto the head of the stainless steel bolt. Good electrical contact was made when the voltage reading was very stable, changing only  $\pm 1\text{mV}$ . Measurements of surface pH were effected by a BDH GelPlas flat surface pH electrode connected to a Cyberscan 200 pH meter sealed inside the custom-built plexiglass waterproof housing. The surface pH was measured by mechanically removing a small area ( $\sim 2\text{cm}^2$ ) of paint directly adjacent to the stainless steel measuring point then quickly placing the tip of the flat surface pH electrode onto the bare metal surface. The minimum pH reading was recorded. The water depth at each position was measured with a digital dive computer. The temperature, salinity and dissolved oxygen concentration of the seawater column was measured on-site at 0.5-1m intervals to a maximum depth of 24m with the appropriate sensors connected to a TPS 90DC Microprocessor Dissolved Oxygen and Conductivity meter.

## 2.3 Sediment Monitoring

### 2.3.1 Sampling Procedure

Replicate sediment samples from the *Swan* (Morrison, 1998) scuttling and reference sites (3km north west of the wreck site) were collected by divers from random locations along a 100m north-east transect using a polycarbonate hand corer inserted to a depth of 2cm. Replicate sediment samples from the *Perth* scuttling and reference sites were obtained at the prescribed locations using a Van Veen grab. Samples from the wreck site were collected at distance intervals of 10m, 50m 125m and 500m away from the vessel, along two perpendicular axes (south and west). The reference area is approximately 1.7km north of the scuttling site. The sampling and reference sites were located using a GPS. A sub-sample of the surface sediment (top 2cm) was obtained for analysis. All sediment samples were frozen prior to analysis.

### 2.3.2 Analysis

A representative sample of sediment was acid digested and the metals in solution (Al, Cd, Cr, Cu, Fe, Ni, Pb, Sn and Zn) measured by atomic absorption spectroscopy (AAS). Mercury ions were reduced by stannous chloride reagent in acidic solution to elemental mercury. This mercury vapour was then purged by nitrogen into a cold cell in an atomic absorption spectrometer or mercury analyser. The concentrations of TPH in the sediment samples were determined by gas chromatography using a flame ionisation detector (GC/FID) after solvent extraction with dichloromethane (DCM). TBT analyses were performed using quartz furnace atomic absorption spectrophotometry and TOC was determined on a dried and pulverised sub-sample by LECO induction furnace. The TBT results were normalised to 1% TOC. The detailed sediment sampling and analytical procedures used on the *Swan* are described fully in Morrison (1998), for the *Perth* in Morrison (2003b) and for the *Hobart* in Morrison (2002).

### 3. Results

#### 3.1 Corrosion Monitoring Programme

The baseline corrosion survey of the *Swan* was performed on 14 December 1997, four hours after sinking then repeated after 1 year (351 days) and 4.25 years (1562 days) post-scuttling. The surface pH of the metal surfaces were not measured until the 4.25 year survey to allow the vessel to attain some form of ‘steady state’ with the local environment. The measuring point positions are shown diagrammatically on the general arrangement plan of the former HMAS *Swan* in Figure 1 and their positional descriptions outlined in Table 1. The corrosion potential and surface pH of each point measured on the *Swan* at the specified time intervals are shown in Table 2.

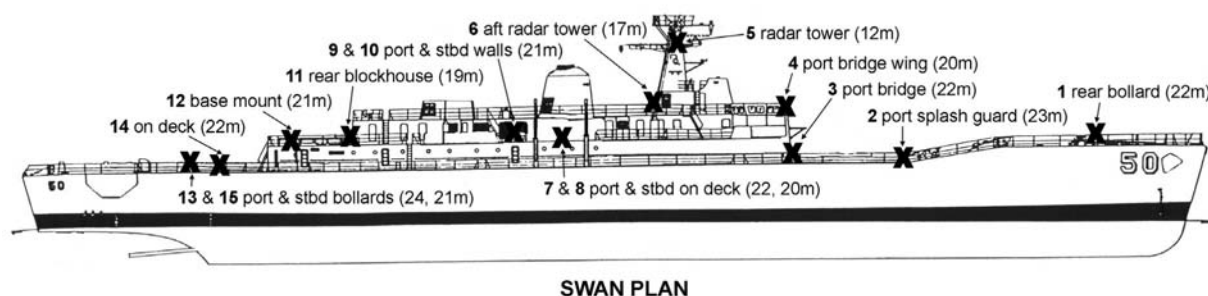


Figure 1. General arrangement plan of the HMAS *Swan* indicating the position of the 15 measuring points on the vessel.

Table 1. Positional descriptions of the measuring points on the *Swan*.

POSITION NO.	POSITIONAL DESCRIPTION
1	Bow, main deck, rear bollard
2	Bow, main deck, aft spray guard (B), port end facing bow
3	Superstructure below bridge, 1.4m above lower main deck, midway towards port side
4	Upper deck, open wing bridge, port side, directly above door on upper deck
5	Radar tower, main mast, first stage down from top, on deck, left of ladder, starboard side
6	Aft of radar tower, starboard side, 1.4m up from upper deck, right of two door close together directly below “CHECK YOUR AIR”
7	Between boat rest V’s on stanchion, on octagonal plate, upper deck, port side
8	Upper deck, starboard side, aft of forward davit
9	Upper deck, starboard side, forward of aft door on wall approximately 1.4m from upper deck, aft of aft lifeboat cradle, aft of grill but forward of stairs
10	Upper deck, port side, between large square cut out and aft door approximately 20cm aft of door and 1m up from upper deck, forward of grill, directly below “CHECK YOUR AIR”, yellow triangle and 2 x red arrows
11	Rear of blockhouse on wall, about 20cm left of pipes, upper deck
12	Stern, upper deck directly aft of 11, on aft of manhole cover
13	Stern, main deck, port side, on aft bollard
14	Stern, main deck, starboard side, forward of bollards on deck
15	Stern, main deck, starboard side, on forward bollard

Table 2. Corrosion potential, surface pH and average depth of the measuring points on the *Swan*.

Position	Metal	Average depth (m)	FOUR HOURS	ONE YEAR	FOUR YEARS	
			$E_{corr}$ (14/12/97)	$E_{corr}$ (30/11/98)	$E_{corr}$ (26-27/3/02)	pH (26-27/3/02)
1	Fe	21.7	-0.595	-0.506	-0.518	8.84
2	Fe	23.7	-0.577	-0.517	-0.514	8.59
3	Fe	22.3	-0.597	-0.522	-0.514	8.61
4	Al	20.9	-0.586	-0.525	-0.558	8.13
5	Al	12.1	-0.597	-0.527	-0.410	7.99
6	Al	17.3	-0.563	-0.535	-0.554	7.64
7	Fe	22.2	-0.500	-0.524	-0.550	7.47
8	Fe	20.3	-0.585	-0.532	-0.564	7.94
9	Al	20.1	-0.556	-0.522	-0.546	8.26
10	Al	21.1	-0.522	-0.523	-0.382	8.15
11	Al	19.7	-0.559	-0.517	-0.368	nd
12	Fe	20.3	-0.582	-0.508	-0.502	8.27
13	Fe	24.2	-0.605	-0.512	-0.368	8.29
14	Fe	21.8	-0.599	-0.509	-0.492	8.30
15	Fe	21.3	-0.584	-0.508	-0.508	8.28

nd Not determined.

The inaugural corrosion survey on the *Perth* was performed on 26 November 2001, two days after the scuttling then repeated after six months (199 days) and sixteen months (473 days) post-scuttling. The surface pH of the metal surfaces were not measured until the sixteen-month survey. The measuring point positions are shown diagrammatically on the general arrangement plan of the former HMAS *Perth* in Figure 2 and their positional descriptions outlined in Table 3. The measuring point positions, 19 and 20 were inadvertently cut out some time after attachment, prior to scuttling. The corrosion potential and surface pH of each point measured on the *Perth* at the specified time intervals are shown in Table 4.

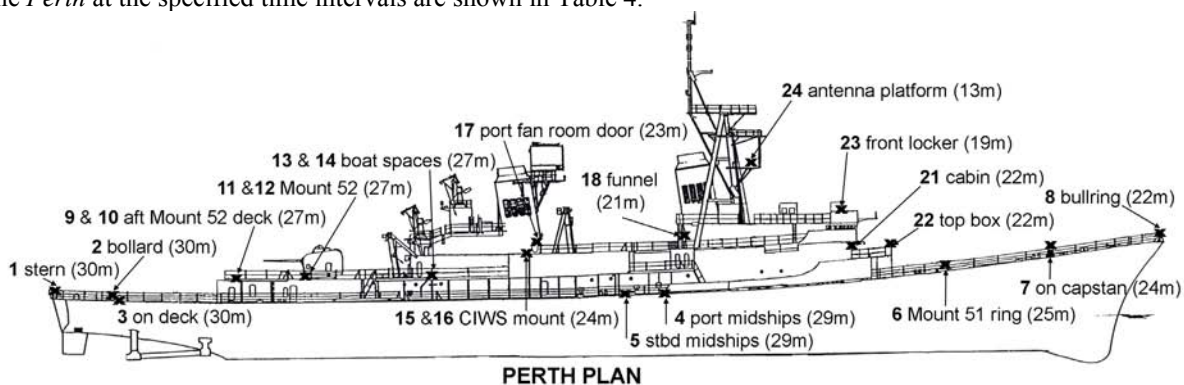


Figure 2. General arrangement plan of the HMAS *Perth* indicating the position of the 22 measuring points on the vessel.

Table 3. Positional descriptions of the measuring points on the *Perth*.

POSITION NO.	POSITIONAL DESCRIPTION
1	Base of aft anchor light support on 1 Deck (stern main deck)
2	Top of forward bollard on stbd side aft 1 Deck (stern main deck)
3	On main deck (~1m) forward of position 2 bollards on stbd side aft 1 Deck (stern main deck)
4	Port midships 1 Deck (main deck) attached to small plate on outside of scuppers
5	Stbd midships 1 Deck (main deck) attached to scupper aft of hawse and forward of bollards
6	Aft Mount51 ring forward 1 Deck (bow main deck)
7	On top of capstan centre forward 1 Deck (bow main deck)
8	Bullring on bow (main deck)
9	Port side aft end of Mount52 Deck (01 Level). Mounted on brackets on deck
10	Stbd side aft end of Mount52 Deck (01Level). Mounted on brackets on deck
11	Bottom aft edge port side Mount52 (01 Level)
12	Bottom aft edge stbd side Mount52 (01 Level)
13	Aft end of port boat spaces Mount52 Deck (01 Level)
14	Aft end of stbd boat spaces Mount52 Deck (01 Level)
15	Forward port corner of port CIWS mount base remains on Ikara Missile Deck (02 Level)
16	Forward stbd corner of stbd CIWS mount base remains on Ikara Missile Deck (02 Level)
17	Forward of port side fan room door (directly below aft funnel) ~1.5m above Ikara Missile Deck (02 Level)
18	Eyebolt on rear of forward funnel (~2m above deck 02 level)
21	Above cut out (~1.8m above deck) into captain's cabin on Torpedo Deck (01 level)
22	On top of box forward Torpedo Deck (01 level)
23	On front of (store locker) Ikara tracking unit platform (~1.5m above 03 level)
24	On stbd side ECM DF Antenna platform

Table 4. Corrosion potential, surface pH and average depth of the measuring points on the *Perth*.

Position	Metal	Average depth (m)	TWO DAYS	SIX MONTHS	SIXTEEN MONTHS	
			$E_{corr}$ (26/11/01)	$E_{corr}$ (11-12/6/02)	$E_{corr}$ (12-14/3/03)	pH (12-14/3/03)
1	Fe	28.8	-0.494	nd	-0.546	7.97
2	Fe	29.0	-0.504	nd	-0.531	7.99
3	Fe	29.3	-0.498	nd	-0.535	8.18
4	Fe	28.9	-0.510	-0.508	-0.538	8.15
5	Fe	28.9	-0.538	-0.498	-0.565	7.81
6	Fe	24.8	-0.520	-0.478	-0.525	8.22
7	Fe	23.2	-0.434	-0.480	-0.523	8.17
8	Fe	21.9	-0.504	-0.490	-0.534	8.06
9	Al	26.9	-0.492	-0.500	nd	nd
10	Al	26.8	-0.496	-0.502	-0.554	7.98
11	Fe	27.3	nd	-0.502	-0.556	8.19
12	Fe	26.8	-0.486	-0.502	-0.554	8.19
13	Al	27.4	nd	-0.508	-0.567	8.12
14	Al	27.4	nd	-0.512	-0.564	8.11
15	Al	24.5	nd	-0.514	-0.570	8.05
16	Al	24.3	nd	-0.516	-0.570	8.17
17	Al	23.3	nd	-0.524	-0.579	6.38
18	Al	21.4	nd	-0.528	-0.581	nd
21	Al	22.5	-0.518	-0.510	-0.565	nd
22	Al	22.4	-0.518	-0.500	-0.552	8.17
23	Al	18.7	-0.518	-0.508	-0.560	8.17
24	Al	13.6	-0.510	-0.526	-0.569	8.16

nd Not determined.

Corrosion surveys of the *Hobart* were performed on 28 January 2003, two months (84 days) after the sinking and on 10 May 2003, six months (186 days) post-scuttling. The measuring point positions are almost identical to those of the *Perth* (Figure 2; Table 3) however, the Mount 51 gun on the main deck towards the bow of the *Hobart* remains intact. The corrosion potentials measured on the *Hobart* at the specified time intervals are shown in Table 5. No surface pHs of the metal surfaces have been measured to date.

Table 5. Corrosion potential and average depth of the measuring points on the *Hobart*.

Position	Metal	Average depth (m)	TWO MONTHS	SIX MONTHS
			E <sub>corr</sub> (28/1/03)	E <sub>corr</sub> (10/5/03)
1	Fe	22.5	-0.512	-0.496
2	Fe	22.2	-0.520	-0.503
3	Fe	22.9	-0.521	-0.505
4	Fe	22.2	-0.534	-0.534
5	Fe	21.3	-0.525	-0.523
6	Fe	18.4	-0.494	-0.505
7	Fe	16.5	-0.505	-0.507
8	Fe	15.0	-0.515	-0.513
9	Al	20.3	-0.531	-0.522
10	Al	20.2	-0.535	-0.520
11	Fe	20.3	-0.532	-0.519
12	Fe	20.3	-0.531	-0.520
13	Al	20.0	-0.543	-0.526
14	Al	20.2	-0.542	-0.524
15	Al	17.4	-0.554	-0.536
16	Al	17.4	-0.550	-0.539
17	Al	16.3	-0.561	-0.548
18	Al	13.2	-0.562	-0.568
21	Al	15.6	-0.551	-0.547
22	Al	15.4	-0.534	-0.543
23	Al	11.1	-0.540	-0.544
24	Al	6.2	-0.549	-0.550

### 3.2 Sediment Monitoring Programme

The baseline sediment survey of the *Swan* site was performed on 15 November 1997, one month prior to scuttling then five months (153 days) and twelve months (363 days) after the sinking. The heavy metal and TPH results are outlined in Table 6.

Table 6. Sediment analysis results for the *Swan*.

Contaminant	EA (2002) Guidelines <sup>1</sup>		BASELINE (15/11/97)		5 MONTHS (16/5/98)		12 MONTHS (12/12/98)	
	Screening	Max	Reference	Swan	Reference	Swan	Reference	Swan
Aluminium <sup>2</sup>	na	na	1450±71	1650±71	1000±0	965±191	1650±636	14000±0
Cadmium	1.5	10	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chromium	80	370	11±1	25±1	14±1	17±1	14±7	47±1
Copper	65	270	2±0	3±0	2±0	7±2	<1	69±16
Iron	na	na	6400±141	6850±71	3500±283	2250±778	2500±141	88500±212
Lead	50	220	<1	<1	<1	7±7	<1	5±0
Zinc	200	410	5±0	5±0	3±0	19±18	8±3	80±3
TPH	na	na	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

<sup>1</sup> Environment Australia (2002).

<sup>2</sup> All contaminants levels are quoted in mg/kg.

na Not applicable (no screening or maximum levels quoted in the EA (2002) Guidelines).

The baseline sediment survey of the *Perth* site was performed on 15 November 2001, 9 days prior to scuttling, then repeated after six months (174 days) and twelve months (388 days) post-scuttling. The heavy metal, TPH and TBT results are outlined in Tables 7, 8 and 9, respectively.

## 4. Discussion

### 4.1 Corrosion Monitoring Programme

#### 4.1.1 General

The main objectives of the corrosion monitoring programmes are to measure the corrosion parameters of previously designated sites on each of the vessels at specified time intervals, to ascertain any discernible

differences in the corrosion rates between the various locations on the vessels and to ultimately monitor the long-term stability of the vessels. The *Swan* lies 2.4km north-east of Point Piquet, Dunsborough in Geographe Bay, Western Australia (Figure 3) in 31m of water at high tide whilst the tower reaches to within 8m of the water surface. The vessel rests on the keel, the bow facing north-west with a 10° list to port.



Figure 3. Location of the *Swan* including the sediment sampling positions (Morrison, 1998).

The *Perth* lies in King George Sound, Frenchman Bay, Albany, Western Australia about 9.5km south-east of Albany (Figure 4). The vessel rests on the keel with the bow facing approximately east with no noticeable list to either side. The total depth to the keel at the sediment line is about 34m. The remains of the radar tower rises 4m out of the water surface to act as a navigation marker.



Figure 4. Location of the *Perth* including the sediment sampling positions (Richards & MacLeod, 2004).



Table 7. Baseline sediment analysis (15/11/01) results for the *Perth*.

Sample	Al <sup>3</sup>	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Sn	Zn	TPH	TBT <sup>4</sup>
West 10m	5850±71	0.1±0.0	20±1	7±0	3750±71	0.02±0.00	5±0	6±0	0.45±0.07	9±4	8±0	0.5±0.0
West 50m	7050±354	nd	24±2	7±0	4550±354	0.02±0.01	6±0	7±0	0.55±0.07	9±0	5±3	0.5±0.1
West 125m	6850±636	0.1	22±2	8±1	4250±354	0.01±0.00	5±1	6±1	0.60±0.14	8±1	6±1	0.5±0.0
West 250m	6000±848	nd	20±2	6±1	3350±919	0.01±0.00	4±1	6±1	0.45±0.07	6±4	11±5	0.7±0.3
West 500m	5900±566	nd	21±3	7±0	3900±283	0.01	5±0	6±1	0.50±0.00	6±1	26±8	1.2±0.0
South 10m	5800±424	nd	19±1	6±0	3250±354	nd	4±1	6±1	0.50±0.00	4±0	54±26	0.5±0.0
South 50m	5550±212	nd	18±1	6±0	3050±212	0.01	4±0	5±0	0.50±0.14	9±4	60±28	0.4±0.0
South 125m	6300±283	nd	20±0	6±0	3400±141	0.01±0.00	5±0	6±0	0.50±0.00	10±1	35±5	0.4±0.1
South 250m	5050±636	nd	16±1	6±1	2500±566	0.01	3±1	5±0	0.45±0.07	6±2	65±30	0.5±0.2
South 500m	3000±283	nd	11±1	6±1	1100±141	nd	2±1	3±0	0.30±0.00	7±1	28±2	0.5±0.1
Reference 1	6550±1061	0.1	20±1	6±0	3750±919	0.01	4±1	6±1	0.60±0.00	6±1	115±49	0.7±0.2
Reference 2	7050±212	0.1±0.0	10±0	8±1	4250±212	0.01±0.00	4±0	12±8	0.60±0.00	10±2	115±7	0.5±0.1
<i>Perth</i> Site <sup>1</sup>	4950±212	nd	18±1	7±0	3000±0	0.01	4±0	6±0	0.50±0.00	6±3	82±1	0.7±0.2
Screening value <sup>3</sup>	na	1.5	80	65	na	0.15	21	50	na	200	na	5
Maximum value <sup>2</sup>	na	10	370	270	na	1	52	220	na	410	na	70

<sup>1</sup> Samples from the proposed *Perth* scuttling site prior to sinking.

<sup>2</sup> Environment Australia (2002) guidelines.

<sup>3</sup> All contaminant levels are quoted in mg/kg with the exception of TBT, which is quoted in µg/kg.

<sup>4</sup> Normalised to 1%TOC.

na Not applicable (no screening or maximum levels quoted in the EA (2002) guidelines).

nd Not detected (both replicates below Practical Quantitation Limit, PQL).

Table 8. Six month sediment analysis (7/5/02) results for the Perth.

Sample	Al <sup>2</sup>	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Sn	Zn	TPH	TBT <sup>3</sup>
West 10m	9185±262	0.1±0.0	33±7	10±1	6050±636	0.03±0.00	8±1	10±1	0.7±0.0	20±2	nd	39.9±56.1
West 50m	10200±141	0.1±0.0	32±0	6750	6750±212	0.03±0.00	9±0	10±1	0.8±0.1	18±2	nd	0.2±0.0
West 125m	9965±474	0.1±0.0	32±1	8±0	6600±141	0.03±0.00	9±1	10±0	0.8±0.0	19±1	5±1	0.3±0.1
West 250m	8780±56	0.1	28±3	8±0	5700±141	0.03±0.00	8±0	8±0	0.6±0.1	14±1	3±1	0.3±0.0
West 500m	6335±1096	nd	23±1	6±1	4150±495	0.02±0.00	7±1	6±1	0.6±0.1	11±1	8±1	0.3±0.0
South 10m	8490±254	0.2±0.0	31±4	16±6	5500±283	0.04±0.00	10±3	8±1	0.6±0.1	24±8	21	0.2±0.0
South 50m	8920±792	0.1	30±3	14±1	5500±707	0.03±0.00	8±1	10±0	0.6±0.0	20±2	nd	0.2±0.0
South 125m	7670±976	0.1	26±2	8±2	4700±424	0.02±0.01	7±0	8±1	0.6±0.1	16±1	nd	0.2±0.0
South 250m	7885±318	nd	29±7	8±0	4750±212	0.02±0.01	6±0	8±0	0.6±0.1	14±1	nd	0.2±0.0
South 500m	6390±14	nd	20±1	7±0	3500±141	0.02±0.00	6±1	7±0	0.6±0.1	12±4	nd	0.5±0.2
Reference 1	6615±855	0.2±0.1	22±4	8±1	3700±566	0.02±0.00	7±3	8±4	0.8±0.1	10±1	7±1	0.4±0.1
Reference 2	18420±18498	nd	24±7	6±0	2850±71	0.01±0.00	4±1	6±1	0.5±0.0	10±4	nd	0.5±0.1
Screening value <sup>1</sup>	na	1.5	80	65	na	0.15	21	50	na	200	na	5
Maximum value <sup>1</sup>	na	10	370	270	na	1	52	220	na	410	na	70

<sup>1</sup> Environment Australia (2002) guidelines.

<sup>2</sup> All contaminant levels are quoted in mg/kg with the exception of TBT, which is quoted in µg/kg.

<sup>3</sup> Normalised to 1%TOC.

na Not applicable (no screening or maximum levels quoted in the EA (2002) guidelines).

nd Not detected (both replicates below Practical Quantitation Limit, PQL).

Bolded values indicate that the guideline screening value has been exceeded.

Table 9. Twelve month sediment analysis (17/12/02) results for the Perth.

Sample	Al <sup>2</sup>	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Sn	Zn	TPH	TBT <sup>3</sup>
West 10m	7405±417	0.1±0.0	27±0	14±4	4850±495	0.02±0.00	7±0	12±6	1.0±0.2	24±2	6±1	3.2±2.7
West 50m	7855±276	0.1	27±1	7±0	4700±424	0.02±0.00	6±1	8±0	0.6±0.1	16±1	9±4	0.5±0.3
West 125m	7765±78	0.7	28±1	6±0	4750±212	0.02±0.00	7±1	10±4	0.6±0.1	12±1	5±1	0.3±0.1
West 250m	7075±417	nd	24±2	5±0	4050±212	0.02±0.00	5±1	6±1	0.4±0.1	10±2	4±0	0.2±0.0
West 500m	5905±262	nd	20±1	6±1	3350±353	0.01	4±0	6±1	0.4±0.0	8±1	6±1	0.3±0.0
South 10m	7640±396	0.2	22±8	9±1	4950±212	0.02±0.00	7±0	12±1	0.6±0.0	33±1	9±6	<b>48.4±17.7</b>
South 50m	8825±757	nd	31±1	7±1	5450±354	0.02±0.00	8±2	10±0	0.9±0.3	17±1	5±0	1.0±0.5
South 125m	9840±184	nd	33±11	7±0	6150±71	0.02±0.01	8±1	10±0	0.6±0.1	16±1	12±2	0.3±0.0
South 250m	8595±544	0.6	33±3	6±1	5450±354	0.01±0.00	7±0	9±0	0.6±0.0	14±1	8±1	0.3±0.3
South 500m	6735±841	nd	22±2	5±0	4400±283	0.02±0.01	4±1	7±1	0.4±0.0	11±1	9±1	0.3±0.0
Reference 1	6225±35	nd	20±0	5±0	3600±141	0.02	4±1	6±0	0.4±0.1	12±3	9±7	0.3±0.1
Reference 2	6075±559	nd	20±0	4±1	3400±283	0.01±0.00	4±1	6±1	0.5±0.1	8±1	6±4	0.4±0.1
Screening value <sup>1</sup>	na	1.5	80	65	na	0.15	21	50	na	200	na	5
Maximum value <sup>1</sup>	na	10	370	270	na	1	52	220	na	410	na	70

<sup>1</sup> Environment Australia (2002) guidelines.

<sup>2</sup> All contaminant levels are quoted in mg/kg with the exception of TBT, which is quoted in µg/kg.

<sup>3</sup> Normalised to 1%TOC.

na Not applicable (no screening or maximum levels quoted in the EA (2002) guidelines).

nd Not detected (both replicates below Practical Quantitation Limit, PQL).

Bolded values indicate that the guideline screening value has been exceeded.

The *Hobart* lies offshore, about 7.5km west of Marina St Vincent, Wirrina Cove in Yankalilla Bay, Gulf St Vincent, South Australia (Figure 5). It lies in a roughly east-west orientation with no noticeable list to either side, with the bow facing approximately east. The total depth to the keel at the sediment line is about 28m, the depth to the main deck is 23m, while the remains of the radar tower rises to within 5-6m of the water surface dependent on the tidal range.



Figure 5. Location of the *Hobart* (Richards 2003a).

The dissolved oxygen, salinity and temperature of the water column on each of the sites was measured at 0.5–1m intervals and the pH and redox potential of the seawater was measured at an average depth of 3–5m. The results are presented in Table 10.

Table 10. Seawater column measurements for the *Swan*, *Perth* and *Hobart*.

Vessel	Date	Average Salinity (ppt)	Average Seawater Temperature (°C)	pH Seawater	Redox Potential Seawater (V)	Average Dissolved Oxygen Content (ppm; % Sat)
<i>Swan</i>	30/11/98	34.7±0.1	19.3±0.1	8.21	0.221	7.87±0.14 85%@19°C
<i>Perth</i>	11/6/02	37.4±0.1	17.8±0.7	8.26	nd	6.92±0.09 72%@18°C
<i>Perth</i>	14/3/03	37.9±0.1	20.8±0.1	8.26	0.310-0.349	6.52±0.05 72%@21°C
<i>Hobart</i>	10/5/03	38.5±0.0	17.8±0.0	8.04	0.275	6.85±0.11 71%@18°C

nd Not determined.

The pH and the redox potentials measured on the sites indicated typical open circulation, well mixed, aerobic marine environments. There were no significant changes in the salinity with depth on the sites. The usual salinity range for the open ocean is 32–36ppt however, enclosed seas, embayments and estuaries may have higher average salinities, such as 38.6ppt for the Mediterranean and 41ppt for the Red Sea (Pearson, 1987, p. 4). Therefore, the higher average salinity for the *Hobart* site may be expected towards the head of the Gulf in the summer months due to decreased water exchange and increased evaporation and also during dudge tide periods when tidal movement is minimal. The temperature of the water columns did not vary significantly with depth, with the exception of the *Perth* site during the winter survey. The average water temperature was  $17.8 \pm 0.7^\circ\text{C}$  and there was a marked temperature differential below 15m where the temperature decreased  $1\text{--}2^\circ\text{C}$ , which would account for the relatively larger standard deviation.

The average dissolved oxygen contents are typical of aerobic seawater. Each site exhibited the general decreasing trend of dissolved oxygen concentration with increasing water depth, which is typical for an open circulation ocean environment. Factors contributing to this trend are decreasing water movement, which leads to less oxygen exchange with the atmosphere and decreasing photosynthetic activity due to less light penetration. The solubility of oxygen in seawater decreases with increasing temperature and salinity. Since the salinity of the seawater did not change significantly from winter to autumn on the *Perth* site, the dissolved oxygen concentrations measured in autumn were corrected for the  $3^\circ\text{C}$  temperature difference using Grasshoff's (1976) oxygen solubility in seawater table (Pearson, 1987, p. 5). Hence, the average corrected dissolved oxygen concentration of the water column in autumn was  $6.95 \pm 0.05\text{ppm}$  and in winter the average dissolved oxygen content was  $6.92 \pm 0.05\text{ppm}$  ( $\sim 72\%$  saturation at  $18^\circ\text{C}$ ). When the dissolved oxygen contents are corrected for the temperature difference there is very little variability between the dissolved oxygen contents of the water column between winter and autumn. Since the cathodic reduction of oxygen is the rate controlling step in the corrosion of concreted metals in seawater, a knowledge of the seasonal variation of dissolved oxygen on a site is vital.

#### 4.1.2 Corrosion Surveys

Corrosion monitoring of the vessels was facilitated by measuring the corrosion potentials of stainless steel bolts that had been attached to the hull and superstructure, prior to scuttling. This provided high profile, long-term electrical ohmic contact with the vessels, ensuring that the same positions were measured over the course of the monitoring programmes. The surface pH of the metal surfaces were not routinely measured until after at least one year of immersion to allow the vessel to attain some form of 'steady state' with the local environment. The physical structure and the nature of the alloys used in the original manufacture of these vessels will significantly affect the measured corrosion potentials. The sacrificial anodes that were attached to the steel hull under the waterline were probably not removed during the preparation of the vessels prior to scuttling, however there was a relatively large time lapse of at least 4-5 years between the ships being decommissioned and their sinking. Hence, any protective effect afforded by the sacrificial anodes would be minimal as they would have most likely been consumed during this time period. The range and average corrosion potentials for the iron and aluminium alloys measured on the *Swan*, *Perth* and *Hobart* are summarised in Table 11. The average surface pH of the iron and aluminium points measured on the *Swan* after four years were  $8.29 \pm 0.40$  and  $8.03 \pm 0.24$  and on the *Perth* after sixteen months were  $8.09 \pm 0.13$  and  $8.12 \pm 0.07$ , respectively.

Table 11. The range and average corrosion potentials measured during the corrosion monitoring programmes for each vessel.

Vessel	Date	Time (yr)	Iron Alloy Corrosion Potential (V)			Aluminium Alloy Corrosion Potential (V)		
			Min	Max	Average	Min	Max	Average
<i>Swan</i>	14/11/97	0	-0.500	-0.605	$-0.580 \pm 0.032$	-0.552	-0.597	$-0.569 \pm 0.018$
	30/11/98	1	-0.506	-0.532	$-0.515 \pm 0.009$	-0.517	-0.535	$-0.525 \pm 0.006$
	26/3/02	4.3	-0.492	-0.565	$-0.521 \pm 0.025$	-0.369	-0.559	$-0.470 \pm 0.092$
<i>Perth</i>	26/11/01	0	-0.434	-0.538	$-0.499 \pm 0.029$	-0.492	-0.518	$-0.509 \pm 0.012$
	11/6/02	0.5	-0.480	-0.508	$-0.494 \pm 0.012$	-0.500	-0.528	$-0.512 \pm 0.010$
	12/3/03	1.3	-0.523	-0.565	$-0.541 \pm 0.014$	-0.552	-0.581	$-0.566 \pm 0.009$
<i>Hobart</i>	28/1/03	0.2	-0.494	-0.534	$-0.519 \pm 0.013$	-0.531	-0.562	$-0.546 \pm 0.010$
	10/5/03	0.5	-0.496	-0.534	$-0.512 \pm 0.011$	-0.520	-0.568	$-0.539 \pm 0.014$

The total amount of water movement generally decreases with increasing depth thereby reducing the total amount of oxygen flux to a metal surface. The general rate of deterioration of concreted metals on shipwreck sites is very dependent on the water depth and the flux of oxygenated seawater over the objects lying proud of the seabed. Therefore it is expected for concreted iron alloy artefacts that the corrosion potentials will decrease with increasing depth. The corrosion potentials and the average depths of the points measured at the specified time intervals for each vessel were graphed to ascertain if there was any emergent relationship between the two variables since the time of scuttling (Figure 6).

### Change in Iron Alloy Corrosion Potential with Depth

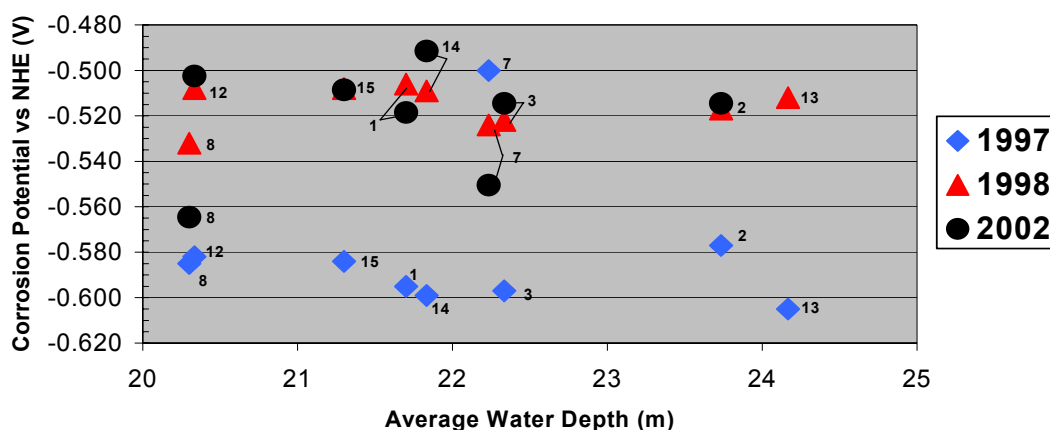


Figure 6. The relationship between the iron alloy corrosion potentials and depth for the *Swan*.

As is evident from Figure 6, there appears to be no correlation between changes in corrosion potential with average water depth on the *Swan* even after four years of submersion. There was also no emergent trend between the aluminium alloy voltages measured on the *Swan* and the average water depths. Similarly, the corrosion potentials for the iron and aluminium alloys on the *Perth* and the *Hobart* showed no correlation with increasing water depth. The lack of any apparent dependence of  $E_{corr}$  on depth is simply a reflection of the inter-connected nature of the structural elements of the vessel and that large sections of the ships are still electrically connected with each other and therefore the voltages expressed do not relate directly to the measurement point. The ships are very much still in the initial stages of deterioration and although there has been some colonisation of the vessel's surfaces, due to the anti-foul present below the waterline of the vessel and the protective paint systems, no significant concretion formation has occurred on the steel hulls during their period of immersion. Therefore, the usual film free iron corrosion mechanism applicable to concreted iron objects where the anodic and cathodic sites are separated by a semi-permeable concretion membrane does not apply to these vessels at this point in time. Experience with the wreck of the *Fujikawa Maru* (1944) in Chuuk Lagoon has shown that this wreck is only now just beginning to have  $E_{corr}$  values that are sensitive to water depth (MacLeod, 2003). The *Fujikawa Maru* has a very similar site orientation to the *Perth* in that it is lying upright on its keel on a flat seabed so it is expected that a decade or two will be needed before any  $E_{corr}$  values on the naval vessels show any systematic behaviour with regard to water depth.

It is vital that the data from the modern naval vessels are viewed in their own right since the fundamental corrosion microenvironment is different to that of historical concreted marine iron that has been immersed for more than 100 years. The different processes mean that the rate-determining step in the overall corrosion process at this stage is not the reduction of oxygen on the surface but the oxidation of the metal. All three vessels are painted with an anti-corrosive paint system, which will have an effect on the corrosion mechanisms and significantly reduce the corrosion rate of the underlying metals. In an attempt to understand changes in the corrosion potentials with time, the voltages of the aluminium and iron alloy points on each vessel were plotted against the time of submersion since the scuttling. In addition, by plotting the measured corrosion potentials and the corresponding surface pH's of the residual metal surface on the Pourbaix diagram for the appropriate metal, the thermodynamic stable state of the metal in that particular environment can be ascertained.

The corrosion behaviour of the *Perth* and the *Hobart* for the first six months is very similar, therefore only the *Perth* results will be presented. The aluminium alloy points on the *Perth* are reacting similarly to the iron alloy points (Figure 7) and there appears to be a relatively random scatter of points during the first six months of immersion. The baseline corrosion potential of point 7 on the *Perth* appears to be anomalous and may have been caused by partial electrical connection between the platinum electrode and the bolt during measurement. This random scatter for the *Perth* and the *Hobart* may reflect differences in the amount of sea water penetration through and under the paint film in the vicinity of the measuring points and this, in turn, would lead to a range of dry to wet corrosion cell mechanisms occurring under the paint layers. Therefore, interpretation of any differences between individual data points or sets of the same is not possible for the first six months of immersion. However, after sixteen months there was a small, relatively consistent decrease in the average corrosion potentials of both the aluminium (0.055V) and iron (0.045V) alloy measuring points on the *Perth*, reflecting more effective and uniform penetration of the seawater under the protective paint film and the establishment of a series of localised corrosion cells after a further ten months of submersion.

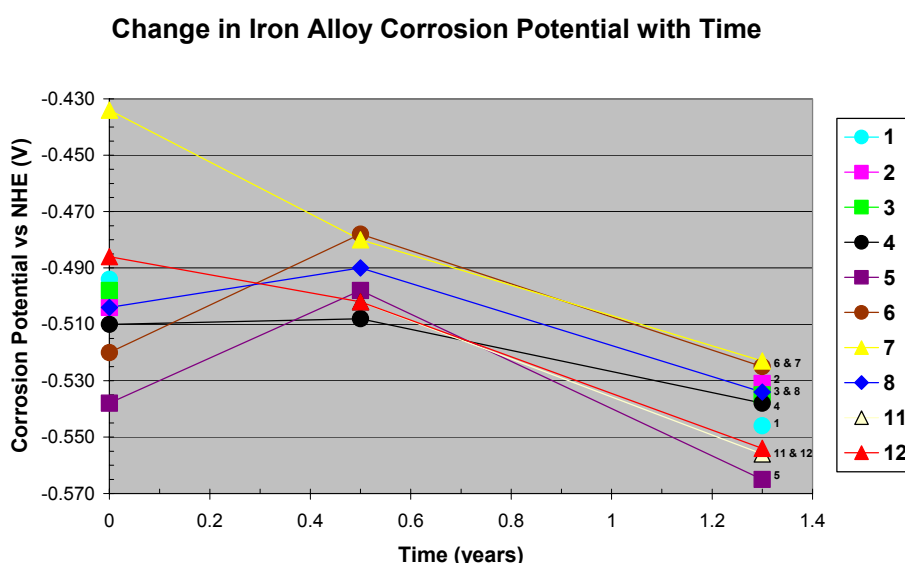


Figure 7. The change in iron alloy corrosion potentials on the *Perth* with time.

This decrease in the average voltages after sixteen months could also indicate a relatively small decrease in the corrosion rate of the vessel. This may be caused by the increase in secondary colonisation of the hull and superstructure after this time but there is no significant uniform formation of concretion, which would cause some partial separation of the anodic and cathodic sites effectively slowing the corrosion rate. Therefore, it may be that this decrease in the average corrosion potentials coupled with slightly more acidic pHs at the metal surfaces after sixteen months is more consistent with a slight increase in the corrosion rate due to the development of localised corrosion cells on the vessel as the seawater penetrates the paint layers, causing pitting corrosion of the iron and aluminium under this passive paint film. Unlike film free corrosion mechanisms, with pitting corrosion a decrease in corrosion potential indicates an increase in the corrosion rate.

The changes in the iron and aluminium alloy corrosion potentials of the *Swan* over the four years of submersion are shown graphically in Figures 8 and 9, respectively.



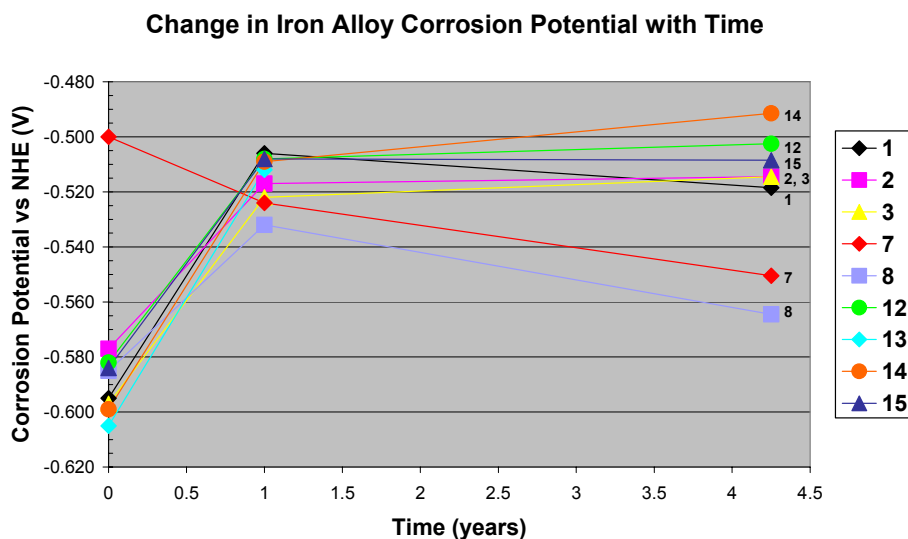


Figure 8. The changes in iron corrosion potentials on the *Swan* with time.

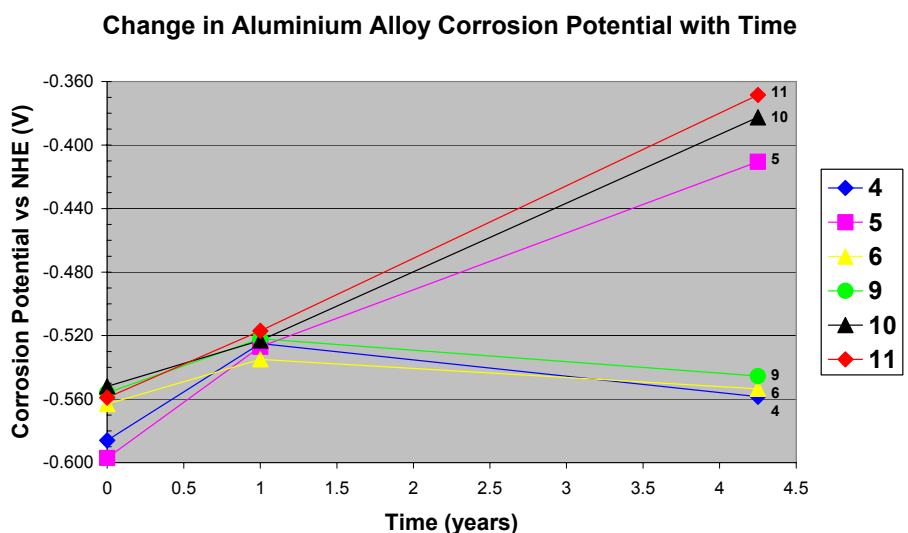


Figure 9. The change in aluminium corrosion potentials on the *Swan* with time.

The baseline iron and aluminium corrosion potentials measured four hours after scuttling are indicative of dry cell corrosion mechanisms as the seawater would not have had time to effectively penetrate the protective paint system. Again the voltage of point 7 appears to be anomalous. After one year, the voltages become more positive, similar to the voltages measured on the *Perth* and *Hobart* after the first six months of immersion, reflecting increased deterioration and penetration of the paint barrier with seawater causing a corresponding increase in the formation of localised wet corrosion cells. However, after four years the vessel appears to have attained some form of ‘steady state’ with the local environment and differences in corrosion potentials are becoming more apparent, which may indicate some slow changes in corrosion mechanisms occurring on the vessel.

The more positive voltages of the iron alloys measured on the stern (12, 13, 14 and 15) and the bow (1, 2 and 3) suggests that these areas are subjected to a more corrosive environment than the more protected points (7 and 8) located on the upper deck, midships on the vessel. There is a significant amount of scouring around the stern and bow of the vessel, which indicates that considerable water movement is occurring in these areas and increased water movement increases the oxygen flux to metal surfaces thus, in turn, increasing corrosion rates.



The voltage of point **13** at  $-0.368\text{V}$  is very close to the open circuit potential for iron in flowing seawater ( $-0.383\text{V}$ ). This voltage could simply be erroneous but the more likely explanation is the bollard is not in good electrical contact with the rest of the hull. If the latter is the case then this supports the fact that isolated iron artefacts corrode at a faster rate than a large, intact iron structure. This is due to the massive difference in surface area and therefore, the current density is dispersed over a larger area and the corrosion rate of the hull will significantly decrease in comparison to the isolated iron fitting.

The aluminium alloy points are reacting similarly to the iron alloys with respect to total water movement and localised turbulence factors. The less negative corrosion potentials of aluminium points **5**, **10** and **11** indicate they are subject to a more corrosive environment than positions **4**, **6** and **9**. Point **4** is positioned on the port side corner of the bridge behind a large splash guard, point **6** is mounted on the wall on the rear of the radar tower and point **9** is mounted on the wall, behind a ladder on the starboard side of the superstructure. All three points are considerably more protected from excessive water movement than the other more exposed positions.

Galvanic corrosion may also be contributing to the emerging differences in the iron and aluminium alloy corrosion potentials on the *Swan*. The effects of galvanic corrosion are most readily discerned when the iron alloy hull and the aluminium of the superstructure are in direct electrical contact. When this occurs the aluminium will act as an enormous sacrificial anode for the steel hull promoting galvanic corrosion of the aluminium and protecting the steel structure. Naval architects make enormous efforts to ensure electrical isolation of the different alloys used in the construction of these vessels to prevent galvanic corrosion occurring during service so it will be only after these insulating techniques have begun to fail and the seawater has penetrated the isolation barriers that galvanic corrosion will be observed. The anode or cathode resistances in the galvanic cells are controlled by protective oxide films and the resistance associated with the custom-made industrial paint system. Data from the *Swan* indicates that breaches in the electrical barriers have commenced but they appear to still be intact after six and sixteen months immersion for the *Hobart* and *Perth* respectively. The midships of the steel hull of the *Swan*, points **7** and **8**, appear to be receiving some cathodic protection by the aluminium superstructure after four years, while the stern and bow are the least protected (more positive voltages). It should also be noted that the structural profile of the bow and stern are such that they present zones of greater turbulence for the flowing seawater than in the midships areas. Preferential corrosion of the aluminium is also indicated by the decrease in the average pH of the aluminium elements and an increase in the pH of the iron measurement points. The absence of significant build up of concretion mitigates against ready discernment of such changes in local acidity and alkalinity.

Six months after being sunk the average corrosion potential of the iron alloy points on the *Hobart* was about  $0.130\text{V}$  more negative than the open circuit potential of iron in seawater ( $-0.383\text{V}$ ); the *Perth* about  $0.160\text{V}$  more negative after sixteen months and the *Swan* about  $0.120\text{V}$  more negative after four years. Normally cathodic protection will result in a  $150$  millivolt drop in average corrosion potentials but the differences between the  $E_{\text{corr}}$  of the vessels cannot be directly compared with the open circuit value of iron in seawater since the latter refers to bare iron and not the painted systems on the naval vessels. The intercepts of the iron and aluminium alloy points for the *Swan* on the corresponding Pourbaix diagrams (Figure 10 and 11) support the results from the potential/time graphs and also indicate the *Swan* is relatively protected even after four years immersed in an aerobic marine environment. The intercepts for the *Perth* and *Hobart* are very similar to the results for the 1997 and 1998 measurements on the *Swan* indicating these vessels are obviously less deteriorated than the *Swan* because they have been submerged for much shorter periods of time.

There were a significant number of discrete areas of aluminium corrosion products visible on the planar surfaces of each vessel's aluminium superstructure, which increased significantly with the time of immersion. Pitting and crevice corrosion are causing this deterioration of the aluminium as the protective paint system is slowly failing in these areas but it has not significantly affected the overall corrosion rates even after four years of submersion. These results signify that these contemporary vessels are corroding albeit at a relatively slow rate and this is most probably due to the protection afforded by the paint barrier remaining on the vessels. The monitoring programmes for the *Perth*, *Swan* and *Hobart* are the first systematic corrosion survey programmes established in Australia for monitoring the long-term stability of twentieth century warships after scuttling as artificial reefs. Complex corrosion behaviour are being exhibited by these vessels but it is still too early in the monitoring programmes to make any definitive statements regarding the long-term stability of these vessels.

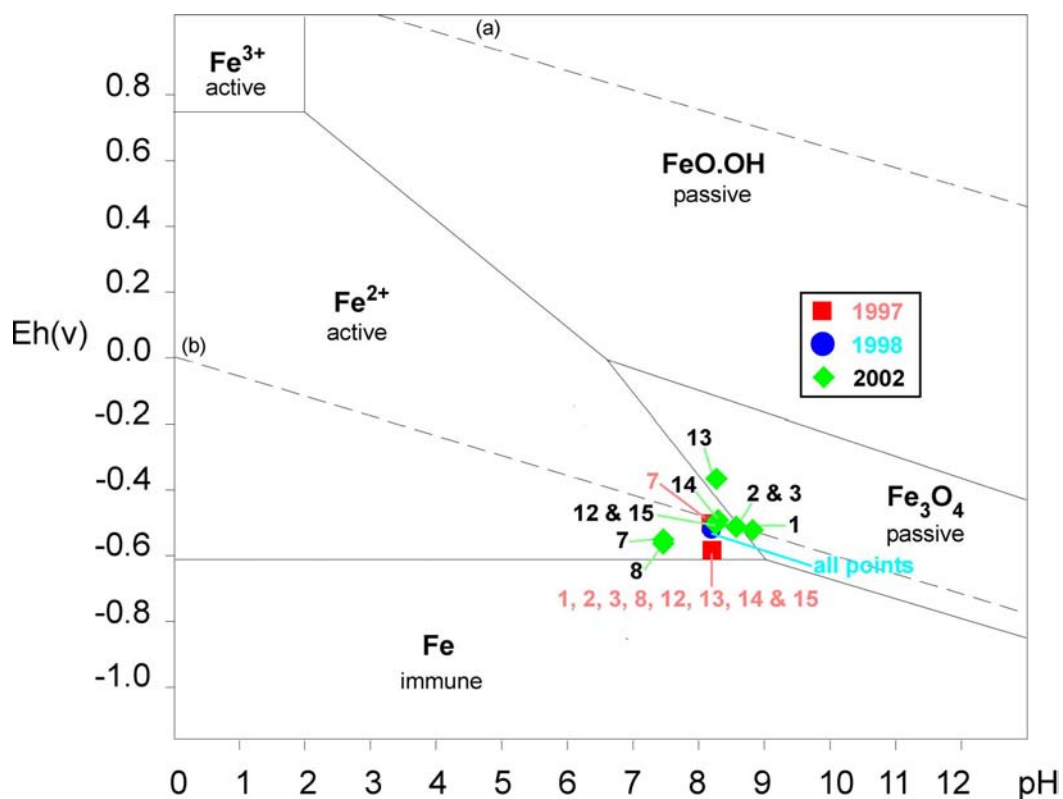


Figure 10. Iron ( $10^{-6}$ M) Pourbaix diagram in aerobic seawater at 25°C on the Swan after four years.

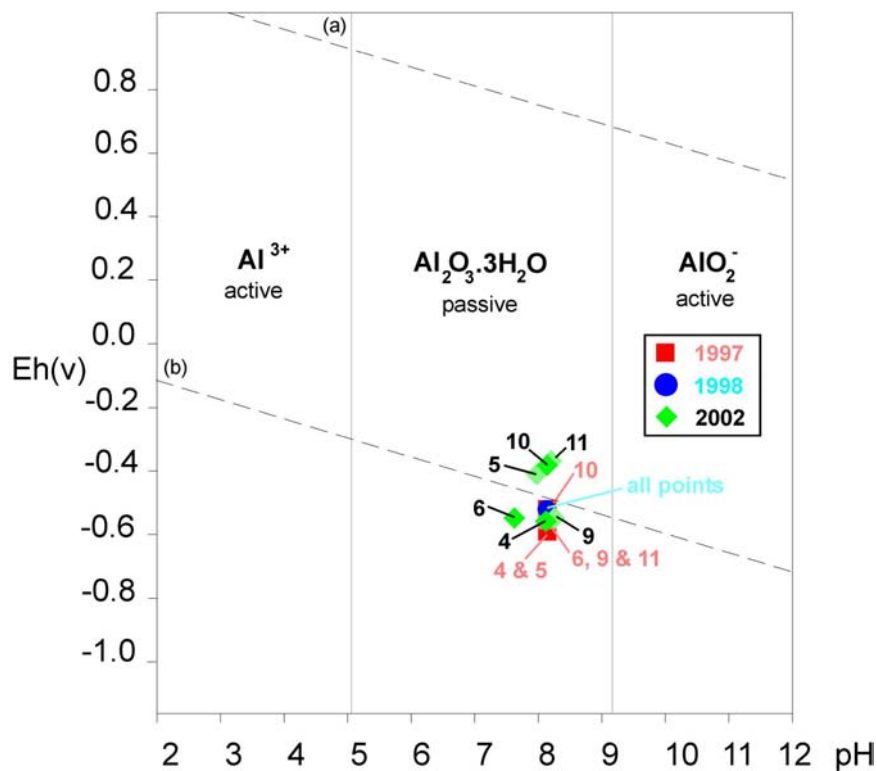


Figure 11. Aluminium ( $3.7 \times 10^{-6}$ M) Pourbaix diagram for aerobic seawater at 25°C on the Swan after four years.

## 4.2 Sediment Monitoring Programme

The main objectives of the sediment analysis programmes are to ascertain any environmental impact resulting from the scuttling of these contemporary vessels, to ascertain the extent of metal enrichment of the sediments surrounding the submerged vessel, to ascertain if any change in corrosion mechanism has an impact on the extent of metal enrichment in the sediment and to ultimately monitor the long-term stability of the vessels. During the decommissioning of the ex-naval vessels significant quantities of metals and oil were removed as scrap for both the purposes of salvage and for reducing the potential for impact on the environment. Vast quantities of copper, brass, aluminium, lead and steel were removed however, it was not possible to remove all traces of metals, especially copper and brass from the engine rooms. The metals remaining on the vessels will corrode and diffuse into the surrounding environment, therefore it is imperative that the sediments in close proximity to these vessels are monitored for these major contaminants and the environmental impact assessed.

The results of the sediment surveys for the *Swan* are tabulated in Table 6. Prior to scuttling, chromium and iron were found to be significantly elevated indicating that the site had naturally elevated levels of these two metals compared with the reference site. No statistically significant differences in sediment metal concentrations between the reference and *Swan* site were noted after five months. After 12 months there was a marked enrichment of aluminium, chromium, copper, iron, lead and zinc in the sediments directly adjacent to the vessel. Only copper was found to exceed the Environment Australia (2002) guidelines and none of the sediments contained measurable quantities of total petroleum hydrocarbons from either site that were measured on the three sampling occasions.

Metal enrichment of sediments surrounding metal structures and jetties is common. Since the area of enrichment around such structures is dependent on distribution by currents, the sediments on the *Perth* site were monitored at increasing distances away from the vessel in the major current directions for that area. The results of the *Perth* sediment surveys are summarised in Tables 7, 8 and 9. The concentrations of these metals in the sediment have increased significantly since the baseline survey however, none are above the Environment Australia (2002) guideline levels. The concentration of cadmium and mercury did not increase significantly above the Practical Quantitation Limit. Whilst there was some variability in metal levels measured at the reference locations, none were statistically significant (Morrison, 2003b). The TBT results indicate that there has been some contamination of the *Perth* site at four locations within 50m of the vessel after one year however, the data shows that the TBT is below screening levels at all locations with the exception of one site 10m west of the vessel. It is possible that a paint flake had dislodged from the hull during the scuttling process and the prevailing current from the east deposited it on the seabed at this location. The significant variation between replicate samples supports this suggestion however, further sampling will investigate whether TBT is decreasing due to degradation or increasing through further contamination. The TPH concentrations have not increased since the baseline survey.

Typically the amount of metal enrichment in the sediment decreases with increasing distance from the vessel. On average, the metal concentrations in the sediments are relatively similar from the vessel out to a distance of 125m along both transects, decrease slightly at distances greater than 125m and then decrease markedly at distances greater than 250m away from the vessel. There appears to be no significant differences in the heavy metal distribution in the sediment measured along the west and south transects. Metal enrichment of the sediment surrounding the *Swan* and the *Perth* is a direct result of metal corrosion and the degradation of the protective paint layers. The major source of aluminium and iron in the sediment would originate from the corrosion of the superstructure and the hull, respectively. Aluminium flake is also a constituent in the primer applied to the keel up to the waterline and iron is a minor constituent in the alkyd resin topcoats. Galvanic corrosion of the aluminium in preference to the iron hull would cause significant increases in the levels of aluminium with a corresponding plateau or only very slight increases in the concentration of iron in the sediment. Hence, the increases in the aluminium and iron levels measured in the sediment over the one year monitoring period support the initial corrosion survey results, which indicate that minimal cathodic protection is being afforded by the aluminium superstructure to the steel hull after twelve months in an aerobic seawater environment.

Chromium and nickel are alloying metals in stainless steel however, corrosion of stainless steel occurs predominantly under anaerobic conditions and since both vessels lie essentially proud of the seabed in aerobic seawater this would be only a minor source of contamination. More likely the chromium has originated from the original yellow zinc chromate primer that is commonly used on aluminium alloys. Although some or all of the original coatings were replaced in the 1980's and despite recent coating formulations that did not contain chromium salts, the extent to which the original coatings were stripped prior to repainting is unknown. The copper, zinc and tin in the sediment would originate from the corrosion of copper and copper alloy components

on the vessel however, much of this material was removed prior to scuttling. Copper linear flex shaped charge explosives were used to scuttle the *Perth* and may have also contributed to the contamination however, if the explosives were the major source of the contamination then increases in the sediment copper levels over time would not be expected. It is more probable that the major source of copper and tin would be from the copper oxide and organotin, which are the major constituents of the recent anti-foul.

The anti-foul is a one pack, organotin based antifouling, self polishing copolymer (Intersmooth Hisol) used for vessels larger than 25m. The coating contains tributyltin and the dry copolymer film contains 2.2% tin. The biologically toxic organotin and copper compounds leach into the water column and prevent marine organisms attaching to the external immersed hull sections. The TBTO leaches into the water column and degrades slowly in the marine environment to the tributyl, dibutyl and monobutyl species and finally to inorganic tin. The environmental degradation of TBT is principally biologically mediated and closely follows first order kinetics. The speciation products of organotin degradation are complicated by accumulation and degradation processes, which occur at different rates depending on the environmental compartment. Hence, the relatively low levels of tin in the sediment after one year of monitoring suggests that the surrounding sediment is not significantly contaminated with organotin species at this stage.

The degradation of the original zinc chromate primer could account for some of the zinc enrichment but the major source would be from the zinc salts, such as zinc phosphates and zinc powder added to the more recent primers as corrosion inhibitors. Lead was used as ballast in these vessels but due to its biological toxicity it was all removed during the preparation process prior to the scuttling in accordance with the EMPs. No lead oxides were present in the most recent paint formulations however, they may have been used in some of the original coatings and could possibly be a source of the lead contamination. During the scuttling of the *Swan*, the explosives used were lead linear flex shaped charges, which would have contributed some lead to the surrounding environment and presumably to the seabed sediments. The elevated levels of lead found in sediments near the *Swan* may have resulted from the explosive charges. As a result, lead linear flex shaped charges are no longer used for scuttling vessels.

The sediment results indicate that after the first twelve months of immersion in an aerobic marine environment the metal components on the *Perth* and the *Swan* are corroding but minimal cathodic protection is being afforded to the vessels and the protective paint coatings are deteriorating albeit at a relatively slow rate. Overall, the results indicate that the scuttling of the *Swan* and *Perth* has had no adverse environmental impacts on sediments and it is unlikely the enrichment at these levels will impact significantly on marine life. However, the gradual increase in metals and TBT concentrations near the vessels should continue to be monitored and the sediment chemistry included as an integral part of the corrosion monitoring programmes over the next ten years as the corrosion rates of the vessels will probably increase significantly over this time period.

## 5. Conclusion

The results of the corrosion and sediment monitoring programmes have shown that the corrosion behaviour of the three vessels are very similar over the first twelve months of immersion and corrosion rates increase over time, especially after the first year. However, the vessels are still corroding at a slow rate even after four years exposed to a typical open circulation, aerobic marine environment. There is evidence of aluminium and iron corrosion on all vessels indicating pitting corrosion of the superstructure and steel hull but the anti-corrosive paint system, albeit failing in some areas, is still providing considerable protection to the vessels. The vessels are still in the initial stages of corrosion without encapsulation by concretion, although there has been considerable secondary colonisation of the metal surfaces. However, the corrosion mechanisms are slowly changing over time. The effects of galvanic corrosion are beginning to be discerned after four years, but the effect is not significant at this stage. The wrecks are successful dive sites and artificial reefs and the impact on local environments has been minimal after one year of submersion. Complex corrosion behaviour is being exhibited by these vessels and it is still too early in the monitoring programmes to make any definitive statements regarding the long-term stability of the vessels and their effect on the marine environment. Therefore, it is of paramount importance that these monitoring programmes continue so as much information as possible regarding the corrosion processes and the long-term environmental effects of these vessels is obtained.

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