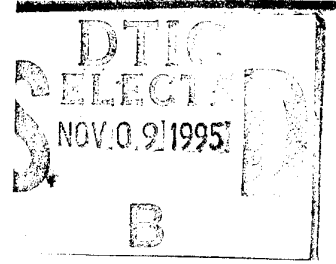AR-009-181

DSTO-GD-0035

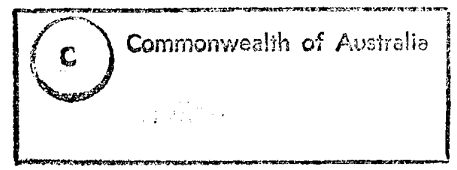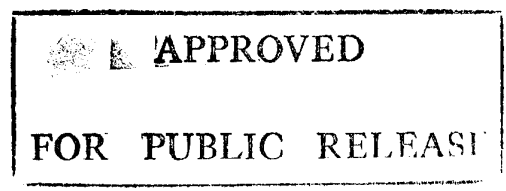# Cathodic Protection Criterion for a New Hull Steel

B.T. Moore and B.S. Smith

19951108 098

DEPARTMENT ◆ OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

Cathodic Protection Criterion for a New Hull Steel

B.T. Moore and B.S. Smith

**Ship Structures and Materials Division
Aeronautical and Maritime Research Laboratory**

DSTO-GD-0035

ABSTRACT

The minimum potential required for complete cathodic protection has been determined for BIS 812 EMA steel which is being used for the main pressure hull of the Royal Australian Navy's Collins class submarine. The experimental method provided plots of weight loss versus applied potential for both BIS 812 EMA steel and the traditional HY80 steel over appropriate potential ranges. These were decided from determinations of the corrosion potentials of the two steels. The minimum protective potential determined was -740 mV, compared with -710 mV for HY80 and -790 mV previously determined for mild steel.

RELEASE LIMITATION

Approved for public release

APPROVED FOR PUBLIC RELEASE

Cathodic Protection Criterion for a New Hull Steel

Executive Summary

The main pressure hull of the Royal Australian Navy's new Collins class submarine is being constructed from a newly developed high strength low alloy (HSLA) steel, designated BIS 812 EMA.

The submarine is to be fitted with a sacrificial anode cathodic protection system to prevent corrosion of the underwater hull. The RAN's reference manual on cathodic protection (ABR 5023) requires that the normal steel hulls of the present fleet be maintained at a potential at least as negative as -820 mV (with respect to a silver/silver chloride reference electrode). The work described in this report was undertaken to ensure that this criterion would also apply satisfactorily to the new BIS 812 EMA steel.

The experiments were designed, firstly, to define the potential of freely corroding BIS steel in seawater (its corrosion potential) and, secondly, to determine the minimum level of cathodic protection required to completely prevent corrosion. The latter was achieved by determining the corrosion rate of BIS steel specimens in seawater at increasingly more negative potentials, starting at the corrosion potential, until a potential was reached at which the corrosion rate was zero. This was designated the minimum protective potential for BIS steel.

The opportunity was taken to conduct a similar set of experiments on HY80 steel, an older HSLA steel, which is present in sections of many hulls of the RAN's present fleet.

The minimum protective potential for complete cathodic protection of BIS 812 EMA steel in seawater was found to be -740 mV. For HY80 the value was -710 mV.

These values are less negative than the generally accepted value of -790 mV for mild steel, and show that the new BIS steel (and HY80) will be adequately protected against corrosion at the RAN's normal protective potential requirement of -820 mV.

Contents

1. Introduction

A new high strength low alloy (HSLA) steel, designated BIS 812 EMA, has been developed in Sweden and Australia for the main pressure hull of the Royal Australian Navy's new Collins class submarines.

To prevent external corrosion of the underwater hull and appendages during service, the submarines are to be fitted with a galvanic (or sacrificial) anode cathodic protection system. The criterion for complete cathodic protection of RAN ships stated in the RAN's reference manual (ABR 5023) requires the underwater hull to be maintained at a potential of -820 mV, or more negative, to a silver/silver chloride reference electrode*. This has been quite satisfactory for the range of steels so far used in hull construction for RAN ships. The present work was undertaken to ensure that this criterion would also apply satisfactorily to this new steel.

The specific aim of the work was to determine, for aerated natural seawater conditions, the electrochemical potential to which the steel surface must be cathodically polarised from its corrosion potential before complete cathodic protection is achieved. This is the minimum potential shift necessary for the hull of the submarine to achieve complete immunity to corrosion. This potential, termed the anodic potential, is theoretically defined as the potential of the most anodic sites on the metal surface and its value is dependent on the particular metal or alloy and the electrolyte in which the metal is immersed. Its value for mild steel has been determined previously by the authors (unpublished work) to be -790 mV vs the saturated calomel reference electrode (SCE).

2. Experimental

The approach taken followed that used previously [1] . The corrosion potential of the new BIS steel in seawater was first determined, then specimens of the steel were held at several potentials on either side of this value and their weight losses at each potential were determined. As the potentials were made more negative, the weight losses became smaller. The potential at which the weight loss first became negligible was accepted as the minimum protective potential. The anodic potential in deaerated seawater (i.e. the potential of the most anodic sites on the metal surface) was also determined, as this should theoretically coincide with, or experimentally be similar to, the minimum protective potential.

---

*Note: All potentials in this report are quoted with respect to the saturated calomel reference electrode (SCE). For practical purposes this electrode has the same potential as the silver/silver chloride/seawater electrode.

At the same time, parallel experiments were conducted with HY80, a steel which has been widely used for submarine and ship hull construction, but for which potential data have not been available.

Three sets of experiments were undertaken as described hereunder. Typical compositions of the BIS 812 EMA and HY80 steels used in the experiments are shown in Table 1.

Table 1: Chemical Compositions (%) of BIS 812 EMA and HY80

Element	BIS 812 EMA	HY80
C	0.13	0.15
Si	0.24	0.25
Mn	0.93	0.25
Ni	1.30	2.50
Cr	0.48	1.40
Mo	0.40	0.40
Cu	0.21	0.25
S	0.012	0.02
P	0.010	0.02
V	0.02	0.02
Ti	0.01	0.01

2.1 Determination of the Corrosion Potential

Triplicate specimens of both steels (dimensions 100 x 50 x 5 mm) were abraded to a P100 aluminium oxide abrasive finish, vapour degreased in toluene, swabbed with acetone, dried and weighed. A steel rod was screwed into the centre of the top edge of each specimen. The rods, covered with heat-shrinkable pvc and sealed at the specimen junction with a neutral-cure silicone sealant, were used to suspend the specimens in the seawater and to provide electrical connection.

The specimens were immersed in aerated natural seawater and allowed to corrode freely for 30 days. The aeration also provided gentle water movement. After an initial period of equilibration, potentials were measured daily against a saturated calomel reference electrode using a high impedance Tacussel millivoltmeter. For each steel, the corrosion potential was taken as the average of all these measurements.

At the end of the exposure period, corrosion products were removed from the specimens by scrubbing in hot water followed by pickling in concentrated hydrochloric acid for 10 s. The specimens were then rinsed in distilled water, dried and

weighed. The corrosion rates, quoted as mm/a, were calculated from the weight losses assuming uniform corrosion over the whole exposed surface of each specimen.

2.2 Determination of the Anodic Potential in Deaerated Seawater

Specimens were either solid cylinders (11 mm diam. x 10 mm) mounted on steel rods attached and sealed as described in Section 1 above, or small button specimens (10 mm diam.) mounted in crevice-free bakelite mounts according to the method of Turnbull [2]. They were finished on 400 grit, or finer, silicon carbide paper, washed in distilled water, rinsed in acetone and dried .

Two button specimens cut from standard welds in BIS 812 EMA were also included in this experiment. These were also mounted using Turnbull's method.

The experiments were conducted in seawater of 19,000 mg/l chloride ion, with temperatures in the range 20-24°C. The seawater was deaerated by bubbling high purity nitrogen through it for about 2 hours before the specimens were introduced. The specimens were then held in this environment for up to three days, with potentials being recorded hourly on a Data Electronics DT100I data logger.

2.3 Controlled Potential Trials

Test specimens were prepared and weighed in an identical manner to that of the freely corroding specimens described in section 1 above. Nine sets of triplicate specimens were tested for each alloy. Each set of specimens was held at a selected potential in aerated seawater for 14 days, using an Amel 551 potentiostat to control the potential. For each experiment the auxiliary electrodes were two carbon rods, and the reference electrode an SCE in a glass Luggin capillary, with its tip close to the centre specimen. The selected potentials were spaced at 10 mV intervals.

The potential range covered for BIS 812 EMA was from -660 mV to -740 mV, while that for HY80 was from -630 mV to -710 mV. These ranges were decided from the results of the corrosion potential determinations.

It was found that, even at the most reactive (positive) potentials, both alloys had a strong tendency to passivate if placed under potentiostatic control immediately after immersion. In an attempt to overcome this problem and activate the steel surfaces, all specimens were allowed to corrode freely for an initial period of 20 hours before potentiostatic control was applied. An average weight loss was determined for each alloy for these initial activation periods. These "blank" losses were later deducted from the overall weight losses of the specimens before corrosion rates were calculated.

The post-trial cleaning treatment was the same as that described above for the freely corroding specimens.

3. Results and Discussion

3.1 Corrosion Potentials

The corrosion potential measured for BIS 812 EMA steel in these experiments was -680 ± 10 mV and the average corrosion rate was 0.11 mm/a (Table 1). For HY80 steel the comparable values were -660 ±10 mV and 0.08 mm/a respectively.

In other experiments with these steels, but with specimens of different geometric shape, the potential values were found to be marginally different at -660 ±15 mV for BIS 812 EMA and -650 ±10 mV for HY80.

These potentials are all considerably more noble than the -750 mV determined for bare mild steel in the same environment [1].

3.2 Anodic Potentials in Deaerated Seawater

The anodic potentials of the two steels measured in deaerated sea water were -745 ± 7 mV for BIS 812 EMA, -742 ± 3 mV for the weld, and -735 ±5 mV for HY80 (Table 2). The former two values were in good agreement with the potentials determined for the minimum protective potential for each steel; however, the agreement between HY80 values was only fair. A possible explanation is that the difference in shape between the two sets of HY80 specimens caused more end grain to be exposed in the cylindrical specimens, thereby generating more anodic potentials. That this did not happen with the other two steels may be attributable to their lower alloy content and different microstructures.

All potentials were more noble than that determined for mild steel under the same conditions.

Table 2: Measured Potentials of the Two Steels Compared With Mild Steel (mV)

	BIS 812 EMA	HY80	Mild Steel
Freely corroding in seawater	-680	-660	-750
First complete cathodic protection	-740	-710	-790
Deaerated seawater (most anodic)	-745	-735	-790
Minimum potential shift required to achieve complete cathodic protection	60	50	40

3.3 Controlled Potential Trials

Despite the initial activation period, most specimens (including the anodically polarised ones) corroded very unevenly, often with large passive regions remaining on their surfaces. This effect has been observed on all other freely corroding specimens of these steels in seawater.

Weight losses often varied considerably within triplicate sets of specimens and it was considered that there were two main reasons for this: (i) the inhomogeneity of surface oxide films as noted above resulted in non-uniform corrosion and hence variability in weight loss, since the specimens were under potential control rather than current control, and (ii) because the potential/corrosion-rate relationship was critical in the experimental potential ranges, small differences in potential on surfaces distant from the Luggin capillary's controlling point could have had a significant effect on the corrosion rate. However, as the main objective of the exercise was to determine the potential at which the weight loss was reduced to zero, these variations were not deemed detrimental to the aim.

The average weight losses which occurred during the initial 20 hour activation period were 50 mg for BIS 812 EMA and 60 mg for the HY80 steel. After these "blank" losses had been deducted from the primary weight losses, the average corrosion rate of each specimen was calculated in mm/a. Experimental errors were significant at very low weight losses, tending to mask the exact point at which complete protection was achieved. However, the effect of this was, if anything, for the chosen minimum protective potential values to err on the conservative side.

The corrosion rate of BIS 812 EMA at various potentiostatically controlled potentials is shown in Table 3. The corrosion rate was reduced from a high 0.36 mm/a at -660 mV to a low 0.02 mm/a at -710 mV. Complete protection was achieved unequivocally at -740 mV (arrow, Fig.1).

Table 3: Corrosion Rate versus Potential for BIS 812 EMA Steel in Seawater

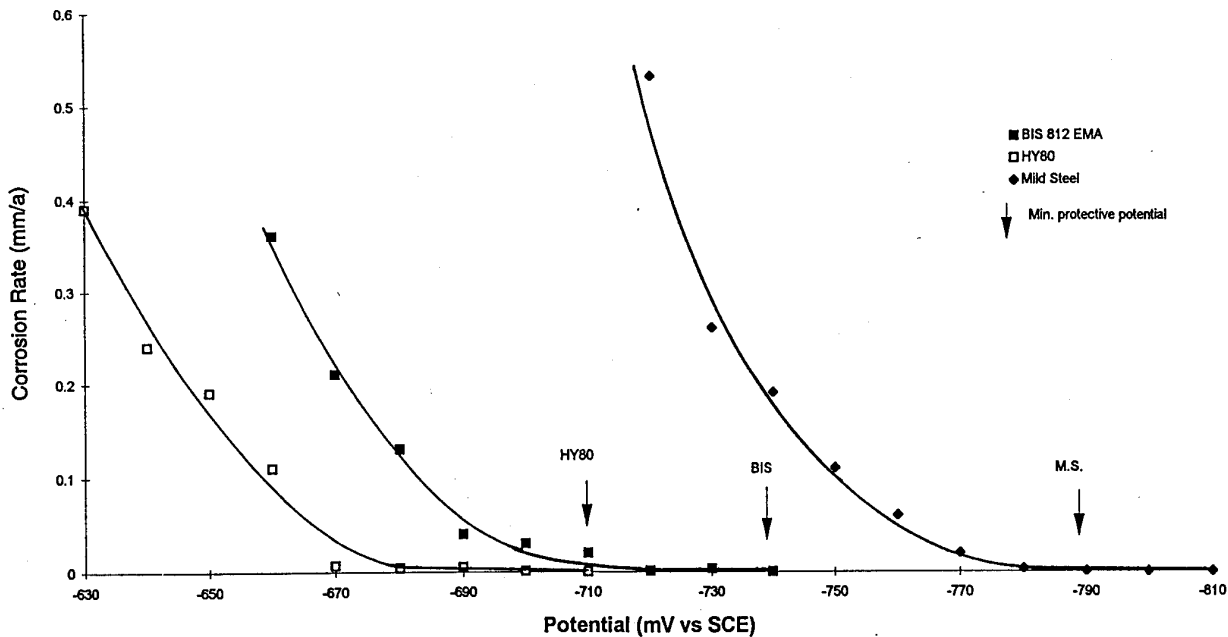| Potential (mV)	Average weight loss (g)	Corrosion rate (mm/a)
-660	1.145	0.36
-670	0.695	0.21
-680	0.432	0.13
-690	0.124	0.04
-700	0.080	0.03
-710	0.052	0.02
-720	0.004	0.001
-730	0.012	0.003
-740	<0.001	<0.001

Figure 1:   Corrosion Rate vs Potential for Three Steels.

A similar effect for HY80 steel can be seen in Table 4. The corrosion rate diminished rapidly from a high 0.39 mm/a at -630 mV to a low 0.01 mm/a at -670 mV. Complete protection was achieved at -710 mV (arrow, Fig.1).

Figure 1 shows graphically the effect of cathodic polarisation on the corrosion rates of BIS 812 EMA, HY80 and mild steel in aerated natural seawater. All three steels show a similar rapid decline in corrosion rate over a cathodic shift in potential of about 50 mV from their corrosion potentials. The corrosion potential of each steel determines the position of each curve along the potential axis. BIS 812 EMA (and HY80) steel will therefore be completely protected against corrosion at any potential more negative than -740 mV. With impressed current cathodic protection systems controlling at -820 mV, the necessary potential shift will be well exceeded, ensuring the steel will receive more than adequate protection under all circumstances. With sacrificial anode cathodic protection systems, where potentials under way can become significantly less negative than -820 mV, BIS 812 EMA steel will not suffer underprotection (i.e. onset of corrosion) until its potential becomes less negative than -740 mV.

Table 4: Corrosion Rate versus Potential for HY80 Steel in Seawater

Potential (mV)	Average weight loss (g)	Corrosion rate (mm/a)
-630	1.324	0.39
-640	0.822	0.24
-650	0.644	0.19
-660	0.385	0.11
-670	0.022	0.007
-680	0.014	0.004
-690	0.018	0.005
-700	0.005	0.001
-710	<0.001	<0.001

The potentials in Table 2 indicate that HY80 is slightly more noble than BIS 812 EMA and that both are significantly cathodic to mild steel. This is consistent with the gradation in alloying content between the three, particularly with respect to the ennobling elements Cr and Ni. In any galvanic couple situation, mild steel would be expected to provide a degree of cathodic protection to either of these steels. This has been confirmed in another series of experiments (to be published) where the galvanic effects of other alloys coupled to BIS 812 EMA steel have been investigated.

4. Conclusions

1. For BIS 812 EMA steel in seawater, the potential at which complete cathodic protection is first achieved was found to be -740 mV. For HY80 steel the value was -710 mV.

2. These values are respectively 50 and 80 mV less negative than the accepted minimum protective potential of -790 mV for mild steel.

3. BIS 812 EMA steel will be adequately protected against corrosion when polarised to the RAN's normal cathodic protection potential requirement of -820 mV.

4. BIS 812 EMA steel should remain completely protected against corrosion in sea water at all potentials more negative than -740 mV, effectively a broader potential region of protection than that for conventional mild steels.

5. References

1. Moore, B. T. and Knuckey, P.J. (1978). Minimum Protective Potential of Mild Steel in Seawater. Corrosion Australasia, **3** (3), 4.

2. Turnbull, B.W. (1985). The Corrosion Resistance of Stainless Steel. Part 1 - Pitting Resistance. Corrosion Australasia, **10** (1), 4.

REPORT NO. DSTO-GD-0035	AR NO. AR-009-181	REPORT SECURITY CLASSIFICATION UNCLASSIFIED

TITLE

Cathodic protection criterion for a new hull steel

AUTHOR(S) B.T. Moore and B.S. Smith	CORPORATE AUTHOR DSTO Aeronautical and Maritime Research Laboratory PO Box 4331 Melbourne Victoria 3001

REPORT DATE July 1995	TASK NO. NAV 92/337	SPONSOR

FILE NO. G6/4/8-4609	REFERENCES 2	PAGES 14

CLASSIFICATION/LIMITATION REVIEW DATE	CLASSIFICATION/RELEASE AUTHORITY Chief, Ship Structures and Materials Division

SECONDARY DISTRIBUTION

Approved for public release

ANNOUNCEMENT

Announcement of this report is unlimited

KEYWORDS

Collins class submarines Cathodic protection	HSLA 100 steel HY-80 steel	Submarine hulls Sea water

ABSTRACT

The minimum potential required for complete cathodic protection has been determined for BIS 812 EMA steel which is being used for the main pressure hull of the Royal Australian Navy's Collins class submarine. The experimental method provided plots of weight loss versus applied potential for both BIS 812 EMA steel and the traditional HY80 steel over appropriate potential ranges. These were decided from determinations of the corrosion potentials of the two steels. The minimum protective potential determined was -740 mV, compared with -710 mV for HY80 and -790 mV previously determined for mild steel.

Cathodic Protection Criterion for a New Hull Steel

B.T. Moore and B.S. Smith

(DSTO-GD-0035)

DISTRIBUTION LIST

Director, AMRL
Chief, Ship Structures and Materials Division
Dr J.C. Ritter
Dr B.F. Dixon
Mr B.T. Moore
Mr B.S. Smith
Library, AMRL Maribyrnong
Library, AMRL Fishermens Bend

Chief Defence Scientist (for CDS, FASSP, ASSCM)   1 copy only
Head, Information Centre, Defence Intelligence Organisation
OIC Technical Reports Centre, Defence Central Library
Officer in Charge, Document Exchange Centre   8 copies
Air Force Scientific Adviser, Russell Offices
Navy Scientific Adviser
Senior Defence Scientific Adviser / Scientific Adviser - Policy and Command   1 copy
Senior Librarian, Main Library DSTOS
Librarian, DSD, Kingston ACT
Serials Section (M List), Deakin University Library, Deakin University, Geelong 3217
NAPOC QWG Engineer NBCD c/- DENGRS-A, HQ Engineer Centre, Liverpool
   Military Area, NSW 2174
ABCA, Russell Offices, Canberra ACT 2600   4 copies
Librarian, Australian Defence Force Academy
Head of Staff, British Defence Research and Supply Staff (Australia)
NASA Senior Scientific Representative in Australia
INSPEC: Acquisitions Section Institution of Electrical Engineers
Head Librarian, Australian Nuclear Science and Technology Organisation
Senior Librarian, Hargrave Library, Monash University
Library - Exchange Desk, National Institute of Standards and Technology, US
Acquisition Unit (DSC-EO/GO), British Library, Boston Spa, Wetherby, Yorkshire LS23 7BQ, England
Library, Chemical Abstracts Reference Service
Engineering Societies Library, US
Documents Librarian, The Center for Research Libraries, US
Army Scientific Adviser, Russell Offices - data sheet only
Director General Force Development (Land) - data sheet only
ASSTASS PD, CP3-4-12, Campbell Park Offices, Canberra ACT - data sheet only
SO (Science), HQ 1 Division, Milpo, Enoggera, Qld 4057 - data sheet only
Librarian - AMRL Sydney - data sheet only
Counsellor, Defence Science, Embassy of Australia - data sheet only
Counsellor, Defence Science, Australian High Commission - data sheet only
Scientific Adviser to DSTC Malaysia, c/- Defence Adviser - data sheet only
Scientific Adviser to MRDC Thailand, c/- Defence Attache - data sheet only

Capt K. Greig, DNER-SM, Campbell Park Offices, CP2-6-04, Canberra ACT 2600
Mr G. Stuart, SP-PEM, Department of Defence (Navy), PO Box E33,
   Queen Victoria Tce, Canberra ACT 2601
DNA
ADNA-Mat. CP1-5-16
DME, CP1-3-12
Engineering Services Manager, SPDO, Adelaide, SA
Mr G. Stuart, SPD-PEM, APW1-5-38
DNA, CP1-5-05