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PJ Kilgallon

The Effect of Sulphate Reducing Bacteria on the Hydrogen
Absorption of Cathodically Protected High Strength
Low Alloy Steel

Supervisor: Dr MJ Robinson

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ABSTRACT

The hydrogen embrittlement of two HSLA steels was studied in conditions typical of the marine environment. Double cantilever beam specimens, heat treated to produce the microstructure in the heat affected zone of a weld, were tested in seawater containing sulphate reducing bacteria (SRB) over a range of cathodic protection (CP) potentials and the threshold stress intensities (K_{th}) were recorded. The hydrogen concentration absorbed by the steel (C_o) was measured and shown to be higher at more negative CP potentials and significantly increased when SRB were present. An inverse relationship was established between $\log K_{th}$ and C_o . It was concluded that crack propagation occurs by a single mechanism whether or not SRB are present. Three point bend specimens of both steels were machined from welded plate. Corrosion fatigue tests were carried out in seawater with and without SRB. The presence of active SRB caused increased crack growth rates.

Sediment samples were collected from the River Mersey and the base of a North Sea platform. In addition, SRB were added as an inoculum to artificial seawater. SRB numbers were enumerated and their activities assessed by measuring the concentrations of sulphide generated. Hydrogen permeation tests were performed on steel held at a range of CP potentials and exposed to each environment. Measurements were also carried out in seawater containing chemically prepared sulphides.

Hydrogen absorption was shown to be enhanced when SRB were present and to be related to the total sulphide (TS) concentration in the environment. High hydrogen

concentrations were produced by chemically prepared sulphides and the nature and thickness of the sulphide film appeared to be important in determining the extent of hydrogen absorption. Chemically produced sulphide gave sustained levels of absorbed hydrogen, but those generated biogenically decayed rapidly unless the TS concentration was maintained in the solution.

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ABSTRACT

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FIGURE 2

APPENDIX C : Anaerobic Jars

1. Death

2. Change

3. No change

4. Skin

5. Fat

6. Bone

7. Muscle

8. Blood

9. Hair

10. Nails

11. Teeth

12. Bones

13. Skin

14. Fat

15. Bone

16. Muscle

17. Blood

18. Hair

19. Nails

20. Teeth

21. Bones

22. Skin

23. Fat

24. Bone

25. Muscle

26. Blood

27. Hair

28. Nails

29. Teeth

30. Bones

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34. Muscle

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NOTATION

a	- CRACK LENGTH
a_c	- CRITICAL CRACKLENGTH
A	- CONSTANT
A_c	- CONSTANT
AC	- ALTERNATING CURRENT
$ACPD$	- ALTERNATING CURRENT POTENTIAL DROP
AE	- AUXILLIARY ELECTRODE
B	- DCB SPECIMEN WIDTH (UNGROOVED)
B_F	- FATIGUE SPECIMEN THICKNESS
BOP	- BEAD ON PLATE
B_n	- GROOVED DCB SPECIMEN WIDTH
C	- CONSTANT
C_σ	- HYDROGEN CONTENT IN MATERIAL UNDER TENSILE STRESS σ
C_I	- MOLAR IODINE CONCENTRATION
C_L	- EFFLUX HYDROGEN CONCENTRATION
C_O	- SURFACE HYDROGEN CONCENTRATION
CP	- CATHODIC PROTECTION
C_s	- MOLAR TOTAL SULPHIDE (ACID SOLUBLE) CONCENTRATION
CS	- CONDITIONING SUBSTRATUM
C_T	- MOLAR THIOSULPHATE CONCENTRATION
D	- APPARENT DIFFUSION COEFFICIENT
d_{COM}	- COMMON CONNECTION TO MICROGAUGE
d_{CRACK}	- CRACK CONNECTION TO MICROGAUGE
d_{REF}	- REFERENCE CONNECTION TO MICROGAUGE
DC	- DIRECT CURRENT
DCB	- DOUBLE CANTILEVER BEAM
δ	- DCB LOAD LINE DISPLACEMENT
ΔK	- STRESS INTENSITY RANGE
E	- YOUNG'S MODULUS
E_{corr}	- CORROSION POTENTIAL

EPS	- EXTRACELLULAR POLYMERIC SUBSTANCE
F	- FARADAY'S CONSTANT
G	- CONSTANT
G_I	- STRAIN ENERGY RELEASE RATE
h	- DCB SPECIMEN HALF HEIGHT
HAC	- HYDROGEN ASSISTED CRACKING
HAR	- HYDROGEN ABSORPTION REACTION
HAZ	- HEAT AFFECTED ZONE
HE	- HYDROGEN EMBRITTLEMENT
HER	- HYDROGEN EVOLUTION REACTION
HIC	- HYDROGEN INDUCED CRACKING
i_a	- CURRENT DENSITY
J_∞	- HYDROGEN FLUX EQUILIBRIUM VALUE
K	- CRACK TIP STRESS INTENSITY
K_I	- CRACK TIP STRESS INTENSITY (MODE I)
K_b	- CRITICAL K FOR MACROBRANCHING
K_m	- CRITICAL K FOR MICROBRANCHING
K_p	- K THAT CORRESPONDS TO ONSET OF PLATEAU REGION
K_{Isc}	- SCC THRESHOLD STRESS INTENSITY
K_{th}	- THRESHOLD STRESS INTENSITY
l	- SPECIMEN HALF DISTANCE
L	- MEMBRANE DISTANCE
M_A	- ATOMIC WEIGHT
M_k	- FRONT FREE-SURFACE CORRECTION
MPN	- MOST PROBABLE NUMBER
n	- VALENCE
N	- NUMBER OF FATIGUE CYCLES
NHE	- NORMAL HYDROGEN ELECTRODE
P	- HYDROGEN GAS PRESSURE
P_H	- HYDROGEN GAS PRESSURE
Q	- CONSTANT
Q_c	- CONSTANT

Q_c	- FLAW SHAPE PARAMETER
R	- STRESS RATIO (S_{min}/S_{max})
RE	- REFERENCE ELECTRODE
R_U	- UNIVERSAL GAS CONSTANT
ρ	- DENSITY
S_{max}	- MAXIMUM STRESS IN FATIGUE CYCLE
S_{min}	- MINIMUM STRESS IN FATIGUE CYCLE
SCC	- STRESS CORROSION CRACKING
SCE	- SATURATED CALOMEL ELECTRODE
σ	- STRESS
σ_H	- HYDROSTATIC STRESS
σ_y	- YIELD STRESS
σ_{ys}	- YIELD STRESS
σ_1	- GREATEST PRINCIPAL STRESS
σ_3	- SMALLEST PRINCIPAL STRESS
SRB	- SULPHATE REDUCING BACTERIA
t	- TIME
T	- TEMPERATURE
t_b	- BREAKTHROUGH TIME
τ_1	- SHEAR STRESS
θ_H	- HYDROGEN ATOM SURFACE CONCENTRATION
TS	- TOTAL SULPHIDE
t-SRB	- THERMOPHILIC SRB
TTF	- TIME-TO-FAILURE
UTS	- ULTIMATE TENSILE STRENGTH
v	- CRACK VELOCITY
V	- CRACK VELOCITY
V_H	- PARTIAL MOLAR VOLUME OF HYDROGEN
ν	- POISSONS RATIO
W	- FATIGUE SPECIMEN WIDTH
WE	- WORKING ELECTRODE
X	- PROMOTING ELEMENT

1.0 INTRODUCTION

During 1988, the Department of Energy became aware of cracking found in the spudcans and lower leg chord sections of two designs of jack-up drilling rigs. Investigation indicated that fatigue may have caused the failure in some instances, but in other cases where fatigue was unlikely, hydrogen embrittlement (HE) was suspected⁽¹⁾.

In assessing a materials susceptibility to HE the most important material properties are yield strength and hardness. British Standards BS4360⁽²⁾ and BS7191⁽³⁾ both specify steels up to a minimum yield strength of 450MPa for offshore use, steels with yield strengths below 550MPa are known to be more resistant to HE⁽⁴⁾. Legs and footings/spudcans of jack-ups are now increasingly being constructed using high strength steels¹ (450+MPa) to obtain adequate strength to weight ratios required when drilling in 100+m water depths⁽¹⁾. Even higher strength steels (up to 750MPa yield) are being used for leg chords and lower bracing members as well as jackhouses⁽¹⁾.

A steels susceptibility to HE also increases with increasing hardness, therefore, the effects of welding are of concern. The welding thermal cycle can promote hardening in and around the heat affected zone (HAZ). Maximum hardness values to avoid HE at welds have been proposed which range from 250 to 325 Hv⁽⁵⁾. No abrupt change in material susceptibility to HE is seen as hardness increases so these values are based solely on engineering decisions.

Take steel

¹ Relative to offshore constructional steels, 450+ MPa is considered high strength.

Obviously, in addition to a hard susceptible microstructure there has to be a source of hydrogen for HE to be a problem. The two main sources of hydrogen offshore are corrosion by sulphate reducing bacteria (SRB) and cathodic protection (CP). Ideally, a correctly working CP system should prevent corrosion whilst not producing significant concentrations of hydrogen at the metal surface. Therein lies a problem in deciding what is the correct level of CP for a given environment, whilst knowing no HE will result.

The main factor that decides the level of protection required is whether or not active SRB are present. If so, then an increase in CP levels is recommended. The increase is necessary as SRB produce sulphides which cause the local environment to become more corrosive (causing sulphide stress corrosion cracking and pitting corrosion), but increasing CP levels cause more hydrogen to be produced. To add to the problem, the sulphides produced by the SRB have the effect of increasing the amount of hydrogen absorbed by the steel by poisoning the hydrogen recombination reaction. It is also thought that the SRB or/and the sulphides they produce can depolarise the cathodic reaction.

On offshore structures SRB can be found in the bottom sediments, under marine fouling, stagnant seawater storage tanks and in heat exchangers. They require an aqueous anaerobic environment with a supply of sulphate and suitable organic material for growth and subsequent production of hydrogen sulphide.

It is not clear whether the combination of SRB and CP will cause an unacceptable level of hydrogen uptake in susceptible steels. Gooch⁽⁵⁾ considered the problems arising from hydrogen entry into cathodically protected steels, and identified the need for more work to be carried out with SRB. Also, as higher strength steels are now being used the relationships between yield strength (hardness), CP level and SRB needs to be studied.

In this work, these factors have been addressed by measuring the hydrogen absorption of cathodically protected steel membranes together with the cracking of two steels in the same environment. Two mechanical tests were used, firstly, HE tests employing double cantilever beam specimens and secondly, fatigue tests with three point bend specimens. Both types of test were carried out in sterile seawater and in a seawater based solution containing a mixed culture of marine bacteria which included SRB. Hydrogen absorption measurements were also carried out in two different marine sediments and with prepared sulphide solutions. The SRB containing solution was monitored for bacterial numbers and total sulphide solution during the tests.

The aims of the work were to:-

1. To assess the risk of corrosion fatigue and HE occurring within the HAZ in welded offshore steels as a result of the application of CP.
2. Determine the relationships between the susceptibility to cracking and the hardness, microstructure and diffusible lattice hydrogen content of the steel.
3. Study the effects of SRB on the corrosion fatigue and hydrogen assisted cracking of freely corroding and cathodically protected offshore steels.

4. Establish the optimum level of CP that is required in the presence of SRB to both control pitting corrosion and minimise hydrogen absorption by the steel.

2.0 LITERATURE SURVEY

2.1 HYDROGEN EMBRITTLEMENT

2.1.1 INTRODUCTION

Hydrogen embrittlement (HE) of a metal, can be defined in terms of hydrogen causing a reduction in the ability of the metal to bear loads and/or absorb mechanical energy⁽⁶⁾. The fact that hydrogen can severely embrittle steel is well documented⁽⁷⁾, and it is now established that hydrogen can degrade, in varying degrees, the mechanical properties of most metals and alloys under specific conditions⁽⁶⁾. Therefore, if after a steel has been exposed to a hydrogen containing environment, a loss in macroscopic ductility or cracking is observed in the steel, then HE of the steel is said to have occurred.

Steels with yield strengths below 550Mpa are generally regarded as being immune to this type of hydrogen degradation⁽⁴⁾, but higher strength steels can be particularly susceptible. Relatively small hydrogen concentrations within a steel can greatly affect its mechanical properties. In low, medium and high strength steels, hydrogen has little effect on the yield strength but reduces ductility and the threshold stress intensity (K_{th}) required for crack propagation⁽⁸⁾. Conditions which favour temper embrittlement also favour hydrogen embrittlement⁽⁹⁾. Cracking tends to initiate internally and propagate in a mode I manner⁽¹⁰⁾. Crack propagation can occur intergranularly, along prior austenite grain boundaries, or transgranularly⁽⁹⁾.

Microstructurally, the susceptibility to hydrogen degradation increases in the following

order: (1) lower bainite (2) quenched and tempered martensite (3) pearlite or spheroidized structures and (4) martensite. Fine grain and carbide sizes are beneficial with susceptibility increasing with increasing carbon content of the steel⁽⁸⁾.

Hydrogen absorption can occur during a metals processing/fabrication processes or during service in hydrogen containing environments. Processing and fabrication processes that cause introduction of hydrogen include electroplating, solidification forgings and welding⁽¹¹⁾. Service conditions that cause hydrogen absorption, in particular offshore conditions, include corrosion and cathodic protection.

Embrittlement is enhanced by slow strain rates and moderately elevated temperatures, suggesting that the phenomenon and its rate is controlled by the diffusion of hydrogen⁽¹¹⁾. For low carbon and austenitic steels it has been found that there is a temperature at which embrittlement is at a maximum. As the temperature increases or decreases from this temperature then HE decreases in both cases. The position of this maximum is dependent on metallurgical condition, strain rate and hydrogen content⁽¹²⁾. Several authors have shown that so called external and internal hydrogen embrittlement are distinguished by hydrogen being present uniformly or as a gradient from the surface⁽⁸⁾.

The fractographic features typical of hydrogen embrittled specimens include microvoid coalescence, isolated dimples, tear ridges, intergranular fracture and quasi-cleavage⁽¹²⁾. Lynch⁽¹³⁾ carried out sustained load cracking of steel in a hydrogen environment and observed gradual changes in fracture surface appearance with gradually changing stress

intensity. At low stress intensities ($20-30\text{MNm}^{-3/2}$) fairly flat intercrystalline facets were produced. With intermediate stress intensities ($40-50\text{MNm}^{-3/2}$) many intercrystalline facets exhibited tear ridges and dimples, and at high stress intensities ($65-75\text{MNm}^{-3/2}$) predominantly dimpled transcrystalline fractures were observed.

Basically, there are three main types of hydrogen damage that occur in metals and alloys. The first type of damage results in internal pores, cracks, blisters or other flaws in the material. This damage is caused by hydrogen bubbles being trapped in the material during solidification or by diffusion of hydrogen through the metal which accumulates at the flaws. The trapped gas then creates a pressure which can cause growth of cracks or voids (mechanism (4) section 2.1.2). A second form of damage is caused by hydrogen forming hydrides at flaws and thus deleteriously altering the mechanical properties (mechanism (3) section 2.1.2). The third form of damage covers the rest of the hydrogen related failures and occurs particularly in the presence of sustained loads. The form of damage has been identified by several different names, one of the most common being hydrogen assisted cracking (HAC)⁽¹⁴⁾.

The term HAC was suggested by Beachem in 1972⁽¹⁵⁾ to describe HE behaviour, which has been referred to previously as sustained load cracking, hydrogen stress cracking, static fatigue and hydrogen cracking. Beachem introduced the term because he felt that embrittlement wrongly described the phenomena. He argued that the fracture paths available in ordinary fracture were also produced in cathodically charged steels, hence hydrogen 'assisted' the ordinary fracture mode⁽¹⁴⁾.

In recent years, much work has been carried out addressing HE (HAC), both in terms of systems studied and also the diversity of materials investigated^(8,16-18). In spite of this volume of work there is still uncertainty about the mechanisms involved. There has been no shortage of proposed mechanisms with evidence strongly suggesting that there are in fact several HE mechanisms and not just one dominant mechanism⁽¹⁹⁾. The proposed mechanisms are reviewed in section 2.1.2.

2.1.2 PROPOSED MECHANISMS

(1) Brittle Crack Tip

This is a thermodynamic theory⁽⁸⁾ which states that segregation of any element to an arbitrary interface necessarily embrittles that interface. Thomson⁽²⁰⁾ and others^(21,22) have demonstrated that plastic flow can 'screen' a crack tip from intense stress concentrations whilst still allowing the crack tip to propagate in a brittle manner. The screened concentrated stress need only reach the yield stress at a defect site (dislocation source, sub-boundary, etc.) at a given distance from the crack tip. Thus, with a screened crack tip, cracking can occur in a locally irreversible brittle manner by thermal or athermal activation over the lattice trapping barrier associated with the periodic arrangement at an atomically sharp crack tip.

Oriani⁽²³⁾ has suggested that kinetic laws favour an irreversible rather than a reversible process, but local flow processes can be so complex that a sufficiently accurate kinetic model is not yet available. Gilman⁽²⁴⁾ proposed that strong chemisorption would tend to prevent dislocation emission at crack tips and thus favour brittle cracking.

(2) Decohesion Theory

This is one of the oldest and most commonly referred to mechanisms of HE. The Decohesion Model is related to the Surface Energy Model (6) as both employ the hypothesis that hydrogen reduces the cohesive strength of iron. The models differ in the proposed site of embrittlement, one favouring the surface (Surface Energy) and the other

the bulk lattice (Decohesion). The theory, first proposed for high strength steels by Troiano⁽⁷⁾, suggested that absorbed hydrogen caused the true fracture strength of the lattice to be lowered, causing a loss in lattice cohesion, or in other words 'perfect' cleavage (absence of any ductile tearing) was made easier. This occurred because electrons associated with the hydrogen atoms could enter the d bands of the metallic cores as shown in figure 1. The resulting increase in the electron concentration of these bands produces an increase in repulsive forces between metallic cores, or in effect, the reduction in the cohesive strength of the lattice. This electrostatic repulsive force reduces the additional stress required for atomic separation by processes which are supposed to be 'perfect' cleavage. It is assumed that hydrogen migrates to positions of highest triaxial stress via stress induced migration to produce the large local concentration of hydrogen. There is now experimental evidence for this proposed hydrogen accumulation⁽²⁵⁾ from autoradiography work using tritium. In addition, Rice⁽²⁶⁾ has related the mobility of hydrogen in the metal to the energy needed for 'brittle' cleavage.

Troiano⁽⁷⁾ suggested that when this local hydrogen concentration reached some critical value the resulting reduction in cohesive strength caused crack nucleation. The brittle crack produced would then propagate out of the region of high hydrogen concentration and become arrested by plastic deformation (figure 2). The process would then repeat itself, thus resulting in discontinuous propagation.

Oriani^(27,28) further elaborated on the lattice decohesion theory when postulating that

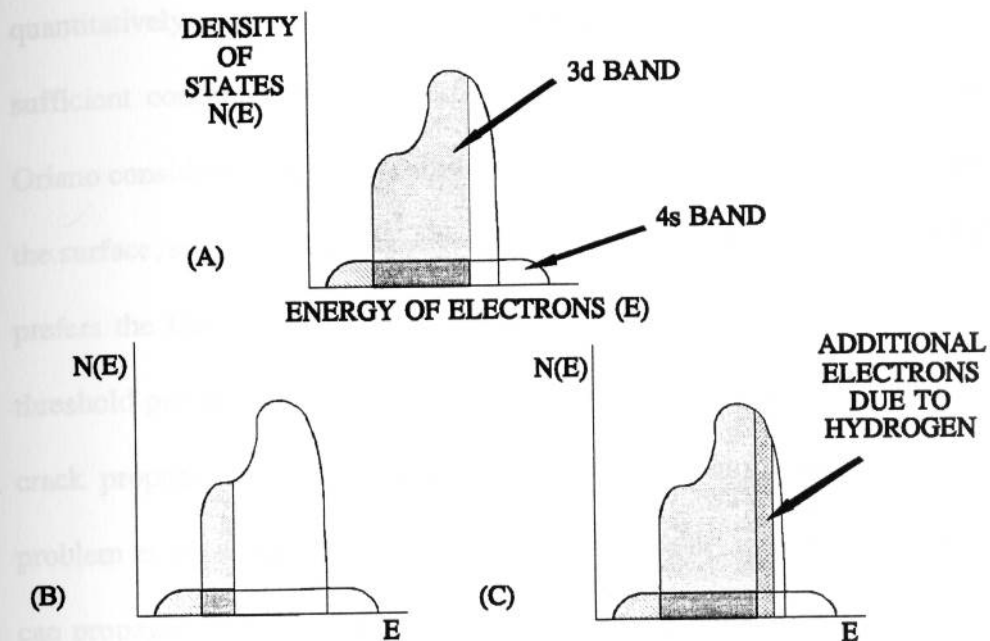


Figure 1. Density of States in Hydrogen-Free and Hydrogenated Nickel and Nickel Base-Chromium-Iron Alloys (7).

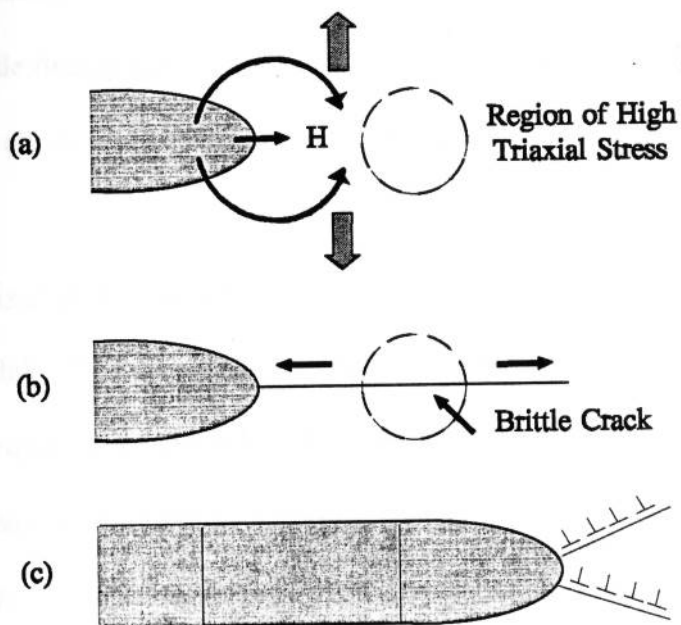


Figure 2. Schematic Illustration of the Decohesion Model For Hydrogen Embrittlement (29).

hydrogen lowers the 'maximum resistive cohesive force'. Oriani modified the model by quantitatively considering the magnitude of the elastic stresses required to create sufficient concentrations of hydrogen to accumulate at the sites of crack nucleation. Oriani considered that the embrittlement would occur 'within a few atomic distances' of the surface, so the model only slightly differs from the Surface Energy Model⁽²⁹⁾. Oriani prefers the Decohesion Model as it better explains the observed isotope effect on the threshold pressure for crack nucleation in gaseous hydrogen⁽²⁸⁾. Oriani considers that crack propagation is continuous (opposite to Troiano), and therefore has the same problem as encountered by the Surface Energy Model in explaining how a brittle crack can propagate at low velocities without becoming blunted by plastic deformation.

While the detailed crack tip behaviour is still not understood, the concept of lattice decohesion has emerged as a valid qualitative model. This is because second phase particle decohesion, crack nucleation and crack propagation at low hydrogen fugacities must all involve atomic bonds being broken at a crack tip.

(3) Hydride Formation

Westlake⁽³⁰⁾ proposed this mechanism, in which cracking occurred due to formation and subsequent cracking of a hydride near the crack tip. A number of metallic systems have demonstrated hydrogen embrittlement by the formation and cracking of the hydride⁽³⁰⁻³⁵⁾ but this model has not been considered for iron and steel⁽⁸⁾, due to the lack of stability of the hydride below hydrogen pressures of 2GPa⁽³⁶⁾. Hydrides are also thought to be involved in the SCC of several nonferrous alloys such as titanium alloys⁽³⁷⁾ and refractory

metals⁽¹⁶⁾. Their action is thought to be either by acting as barriers to dislocation motion and therefore promoting brittle fracture of the matrix, or by providing paths for brittle fracture through the hydride phase. Gilman⁽²⁴⁾ has proposed a model involving a surface hydride which he applied to ferrous materials. In addition, the formation of stress induced hydrides cannot be ruled out as it has been demonstrated that the hydrostatic stress field around a stressed crack tip can stabilize a hydride which is otherwise unstable without stress.

(4) Internal Hydrogen Pressure Theory

This mechanism, also known as the planar pressure theory, was discussed in a paper by Zapffe and Sims⁽³⁸⁾. They suggested that the growth of voids or internal cracks, is caused by hydrogen gas at large internal pressures in the voids. Atomic hydrogen diffusing through the metal can combine to form molecular hydrogen and thus create the high pressure. The stress caused by this pressure, they argue, is triaxial and such stressing does not allow plastic flow. The failure mode resulting was described as 'rupture' and they suggest that this explains the flat, bright fracture surfaces they obtained. Beachem⁽¹⁴⁾ argues that they misinterpreted the meaning of triaxiality of the pressurized gas, as the state of stress at the surface of a crack is biaxial, that rupture was meant to be 'perfect cleavage' and rupture may itself be a plastic flow process. De Kazinczy's⁽³⁹⁾ proposed a similar theory which again utilized internal pressures, but differed in that the approach was via elastic energy release rates.

Tetelman and Robertson⁽⁴⁰⁾ supported the concept that recombined hydrogen gas

pressures in internal cracks cause embrittlement. They also addressed the plasticity of the cracking process, found the cracking plane to be the [001] in iron-silicon and concluded that internal pressures and stresses from applied loads are additive and combine to propagate cracks. The theory does not explain the embrittlement of high strength steels in low pressure hydrogen gas, or the absence of embrittlement of steel exposed to He gas which dissolves into the steel⁽⁴¹⁾. But the theory is still partially valid, as it is known that internal pressures can cause crack growth and blister formation is a known hydrogen damage problem. It has been suggested that the hydrogen gas in blisters can cause HE by one of the two atomic mechanisms⁽¹⁴⁾.

(5) Slip Softening Models

Beachem⁽¹⁵⁾ first suggested, on the basis of observations of varying degrees of plasticity in material degraded by hydrogen, a theory in which the role of hydrogen is to cause locally enhanced plasticity at the crack tip. The model suggests that the existence of a sufficient concentration of dissolved hydrogen just ahead of the crack tip will aid whatever deformation processes the microstructure allows. Thus instead of hydrogen locking dislocations in place, it unlocks them and allows them to multiply or move at reduced stresses. Beachem argues that microvoid coalescence found in lower strength steels may not be possible in the higher yield strength steels. It is suggested that the model still applies to the HAC of these steels in the form of aiding crack tip plasticity during intergranular or quasicleavage cracking (figure 3). In recent years the theory has been supported by work^(6,42-45) on a variety of systems. It has clearly been shown that the mechanism is a viable failure mechanism for a large number of systems⁽⁷⁾ including

iron alloys^(46,47).

While the concept of enhanced plasticity appears to be at odds with embrittlement, the distribution of hydrogen can be highly non-uniform under an applied stress. Thus locally the flow stress can be reduced, resulting in localized deformation which leads to highly localized failure by ductile processes, while the total macroscopic deformation remains small. However, hardening effects also occur, so the idea of softening is not a general one. Moreover taking the view that hydrogen and dislocations are required to nucleate a crack at an inclusion, for example, enhanced dislocation motion is not a model itself, but a contributing factor to an overall degradation mechanism, analogous to the transport factors described below.

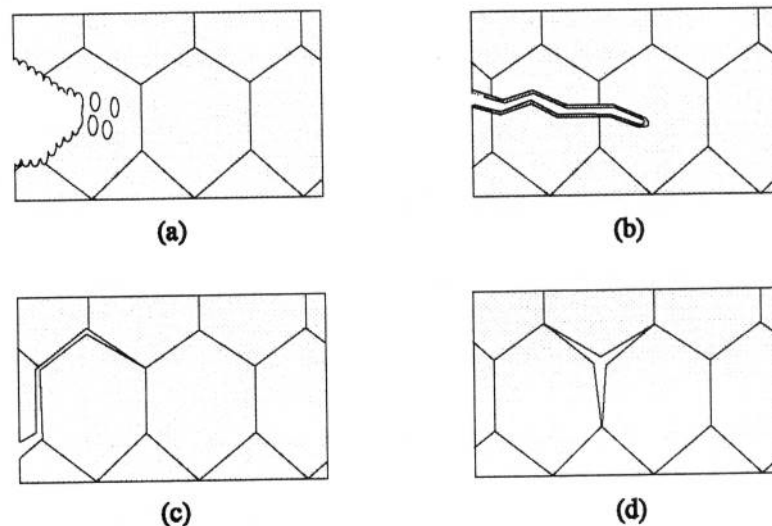


Figure 3. Sketches of Microscopic Fracture Modes Observed in Experiments as a Function of Decreasing Stress Intensity Factor and Concomitant Decreasing Cracking Rate (a) High K, Microvoid Coalescence (b) Intermediate K, Quasi Cleavage (c) Low K, Intergranular Cracking (d) Intergranular Cracking With an Assist From Hydrogen Pressure (15).

Oriani⁽²⁸⁾ has criticised the concept of hydrogen causing cracking by increasing plasticity, in that it would seem to suggest that any other method of increasing plasticity would also cause cracking, and this has not been observed. He also questions the atomic mechanism by which the alleged enhancement of plasticity could be caused by hydrogen, suggesting that enhancement of nucleation of kinks on dislocations is the only possibility, but states that evidence from strain aging and internal friction work is contrary in that hydrogen actually impedes dislocation movement.

(6) Surface Energy (Adsorption Model)

Griffith cracks and their mathematical treatment have been incorporated into HE and SCC theory. Petch and Stables⁽⁴⁸⁾ suggested that hydrogen already in the lattice might diffuse to the crack tip where adsorption of hydrogen on to the crack surfaces, created during crack propagation, lowers their surface energy and thus lowers the work of fracture, thus promoting cracking. Viewed atomically, it proposes that hydrogen will be adsorbed by strained bonds at the crack tip, and this interaction causes a reduction in bond strength, as demonstrated in figure 4⁽²⁹⁾. Beachem⁽¹⁴⁾ has pointed out that this would require hydrogen to diffuse through the hydrogen trapping plastic zone at the crack tip to get to the surface. The theory is based on energy considerations, taking no account of plasticity effects, and assuming that the fracture path and material microstructure were of little importance.

Uhlig⁽⁴⁹⁾ introduced the phrase 'stress sorption cracking' when suggesting that adsorbing monolayers of chemical species reduce the surface energy, thus lowering the metals

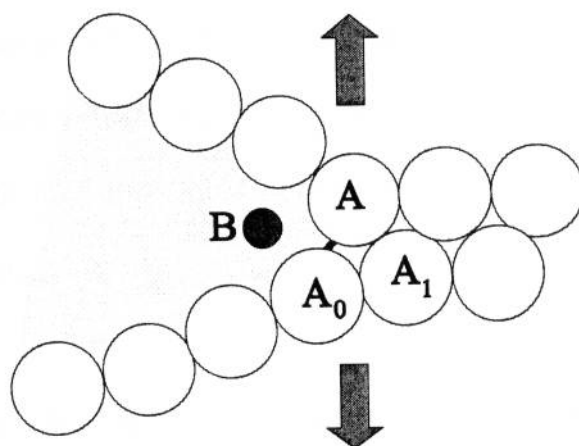


Figure 4. Schematic Illustration of the Adsorption Model (29). The Model Requires That a Specific Ion From the Environment, B, Interacts and Reduces the Cohesive Strength of Strained Bond A-A₀ at the Tip of a Brittle Crack.

resistance to cracking. Although Uhlig was concerned with SCC, and did not mention hydrogen in particular as the adsorbing species, it has consequently been shown that in at least some systems SCC is a form of hydrogen damage⁽¹⁴⁾. More recently, Uhlig⁽⁵⁰⁾ has made several additions to the theory. Instead of considering the adsorption to take place at the strained bonds at the elastic crack tip, as in figure 4, it was suggested that adsorption occurred at dislocations or other mobile imperfections in the vicinity of the crack tip. It has been suggested⁽²⁹⁾ that this modification was made to account for the contention that pure metals are immune to cracking⁽⁵¹⁾. Thus, the interstitials C and N are considered to interact with the defects in iron, prolonging the surface half-life and allowing adsorption to occur, whereas in pure iron, the defects are thought to be too mobile for adsorption to take place. Uhlig⁽⁵⁰⁾ also proposes that a sharply defined

potential exists below which the adsorption of damaging ions, and hence cracking, does not occur (assuming that the applied potential does not cause hydrogen damage). Bockris⁽⁵²⁾ has pointed out that there is no potential at which ions become suddenly adsorbed. Rather adsorption begins at the potential of zero charge and increases gradually with shift in potential. Bockris also disputed that adsorption would occur at specific imperfections.

This model involves purely brittle fracture and therefore is consistent with cleavage like transgranular fractures observed in austenitic stainless steels. Crack propagation would be controlled by the rate of transport of the damaging ions to the crack tip. Pugh⁽²⁹⁾ has expressed difficulty in the concept that an atomically sharp crack can remain stable in a ductile fcc alloy at such low crack velocities. Also, there is no way, in terms of this model, that the crack can propagate independently of the environment, nor does it specify a means of inhibiting plastic flow in material ahead of the crack.

Hancock⁽⁵³⁾ stated that the source of embrittlement must be adsorbed hydrogen. It was demonstrated that hydrogen gas at 1 atm was sufficient to cause cracking in high strength steel. This provided evidence that the Planar Pressure Theory (number 4) was not sufficient to explain HE. It was also demonstrated that oxygen layers can have an inhibiting effect on crack growth in steel. It was found that when oxygen was removed from the external environment that previously growing cracks usually restarted. This observation shifts attention away from the triaxial state ahead of the crack to the crack tip surfaces, and suggests that incubation times (and diffusion) are not needed for this

type of damage. This indicates, also, that cracking is basically a continuous rather than a discontinuous process.

Arguments against the theory are that it (1) greatly underestimates the work of fracture⁽⁵⁴⁾ (2) cannot account for discontinuous cracking as indicated by sonic emissions⁽⁸⁾ (3) cannot explain why the tendency for delayed failure can be reversed on stress removal⁽⁸⁾ (4) cannot demonstrate why oxygen not only fails to promote cracking but stops the hydrogen effect⁽⁵³⁾.

(7) Transport Models

Evidently, in order to cause subsurface cracking hydrogen must be transported to the surface, adsorbed, absorbed, transported internally by diffusion or by dislocation motion and then contribute to crack nucleation/propagation. These processes contribute as part of the degradation but are not themselves mechanisms but rather part of an overall mechanism.

Summary

The general failure mechanism by which high strength steels crack in aqueous environments, especially in the presence of promoters such as sulphide, is now widely accepted as hydrogen embrittlement. For iron-base alloys, the Surface Energy Model and the Decohesion Model appear to be the most popular. Both of these models are based on the hypothesis that hydrogen reduces the cohesive strength of iron, but differ in respect to where the embrittlement takes place (and mode of propagation in the early

decohesion model). These models still have some drawbacks, and as there is no general agreement on any system, new models and modifications to old theories are still being proposed.

As Pugh⁽²⁹⁾ has pointed out, there are still many questions arising about the characteristics and experimental observations of failure as yet unexplained; 'Why do cracks in martensitic steels generally follow prior austenitic grain boundaries?', 'Why is the occurrence of cracking related to the strength of the steel?', 'Is cracking continuous or discontinuous and does hydrogen diffusion in the lattice play a significant role in the cracking involving external sources of hydrogen?' and 'Does the metallurgical structure play a critical role or is it simply related to the necessity of sustaining high stresses?'

2.1.3 CRACK PROPAGATION AND BRANCHING

The propagation of a crack in a material subjected to sustained loading, has a plot of log crack velocity (V or da/dt) against stress intensity (K) of the form shown in figure 5. Three distinct regions, I, II and III are ascribed to the curve, but studies of crack propagation usually focus on regions I and/or II. The slope of region I is normally so steep that it is taken as a measure of the threshold stress intensity (K_{th} or K_{Isc}). This region is generally characterized by intergranular cracking⁽⁸⁾. K_{th} is discussed in more detail in the next section. Region II is characterized by mixed mode tearing and quasi-cleavage and sometimes by crack branching and tortuosity, and region III by transgranular ductile rupture by void growth⁽⁸⁾.

The effect of pH and 'poisons' on crack propagation due to hydrogen embrittlement results from their effect on the volume of hydrogen that is produced and absorbed into the material. Therefore, lowering the pH or adding a 'poison' (such as H_2S) will increase the hydrogen absorption (section 2.4.2) and enhance crack propagation. The presence of several percent of sodium chloride in a hydrogen sulphide solution generally has no additional effect on embrittlement⁽⁵⁵⁾.

Crack branching in region II has been observed in some materials⁽⁵⁶⁾, including high strength steels⁽⁵⁷⁾ and 4340 steel in 3.5%NaCl solutions⁽⁵⁸⁾. Failures due to SCC under specific conditions has led Speidel⁽⁵⁶⁾ to classify two specific types of branching;

1. Microbranching - crack front splits into several local cracks with separation

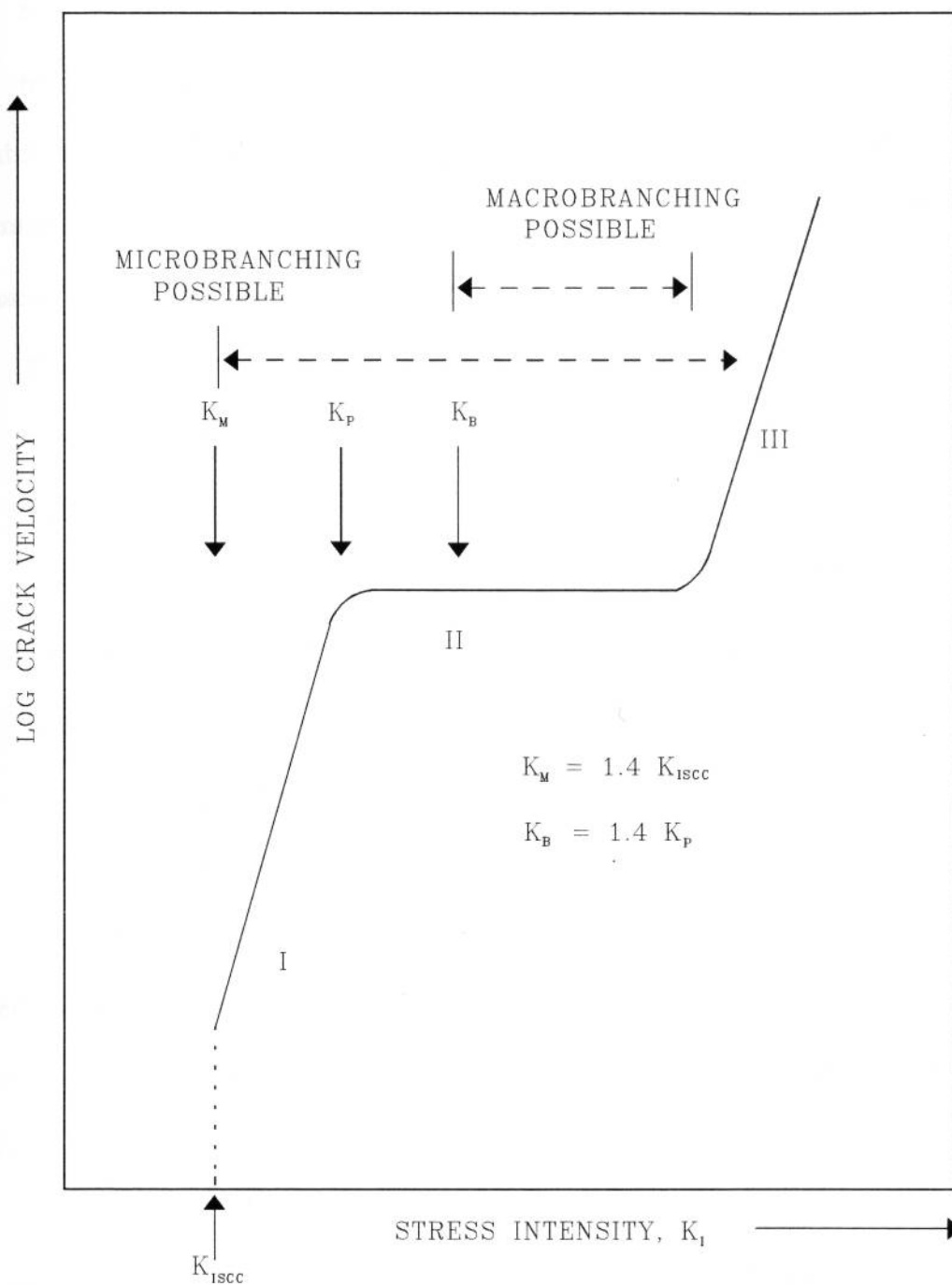


Figure 5. Schematic Representation of the Dependence of Stress Corrosion Crack Growth Rate, Microbranching and Macrobranching on the Crack Tip Stress Intensity (after Speidel).

distances of the order of a grain diameter.

2. Macrobranching - crack separates into two or more macroscopic components that tend to diverge.

In addition, Speidel⁽⁵⁶⁾ has used his wide experience of SCC to propose some rules governing the branching behaviour. These conditions are necessary (but not sufficient) for macrobranching to occur;

1. The crack velocity (V) must be independent of the crack tip stress intensity (K_I) (in other words, the V versus K_I curve must exhibit a plateau region II as in figure 5).
2. The crack tip stress intensity (K_b) (above which macrobranching can occur) must be equal or larger than 1.4 times the stress intensity K_p (above which the V versus K_I curve shows a plateau) as shown in figure 5.
3. The fracture path must be relatively isotropic (SCC should not follow exclusively microstructural features such as grain boundaries or cleavage planes with a strongly preferred orientation).

Carter⁽⁵⁹⁾ found the ratio $K_b / K_{Isc} = (2n)^{1/2}$ was in the range of 1.5 to 4.2 which implies that n would have a value in the range 1.13 to 9. Other work⁽⁶⁰⁾ has given a value of 1.2 for K_b / K_p .

Microbranching can occur under less restrictive conditions⁽⁵⁶⁾. V does not have to be stress independent, but the stress intensity limit for microbranching is a certain multiple of K_{Isc} (if such a threshold for SCC exists). At extremely low stress intensities no microbranching is observed.

Experiments testing for K_{Isc} (K_{th}) can be seriously affected by crack branching⁽⁵⁶⁾. Too high a K_{Isc} will be reported for crack arrest if it is assumed that there is only one crack to stop while in reality there are two (if only on a microscale). This problem can be avoided in K_{Isc} testing if the applied K_I is maintained below $1.4K_{Isc}$ during the entire test⁽⁵⁶⁾.

Speidel⁽⁵⁶⁾ offered a theoretical model to explain the rules listed earlier in this section, in which the strain energy release rate (crack driving force), G_I , is related to K_I in the following way;

$$K_I^2 = (EG_I) / (1 - \nu^2) \quad (1)$$

where E is the modulus of elasticity and ν is poissons ratio. It was argued that propagation of two cracks instead of one, requires twice the G_I . Therefore, the required stress intensity for crack bifurcation should be at least $\sqrt{2}$ times the stress intensity required to propagate a single crack. This would appear to explain why microbranching is observed at stress intensities above $1.4K_{Isc}$. Congleton⁽⁶⁰⁾ warns that a factor of $\sqrt{2}$ can easily be introduced into crack branching calculations and that too much faith in the agreement between a simple theory and experimental observations maybe unwarranted. A more detailed approach⁽⁶⁰⁾ than that above considered the dependence of K_b on the angular separation of the branches for a bifurcating crack loaded in anti-plane strain. Calculations gave a value of 1.23 times the K value required for a single crack to propagate.

For macrobranching, the extra condition of a stress independent velocity was considered

as follows⁽⁵⁶⁾. To stop one crack from outrunning the second, both should propagate with approximately the same velocity. This requires both cracks to be in the plateau region, as only in this region do minor differences in crack length (and thus stress intensity) not result in major differences in crack growth rate. From the explanation above, bifurcation should reduce the stress intensity at each newly generated branch to $1/\sqrt{2}$ times the stress intensity of a single growing crack. Therefore, for both branches to be in the plateau region, K_b has to be at least $\sqrt{2}$ times the lowest stress intensity (K_p) at which plateau behaviour is observed.

In region II, studies⁽⁶²⁾ have shown that the relationship between velocity and temperature is of the form shown in figure 6. At low temperatures, in region A, the velocity is proportional to $P^{1/2}$, consistent with rate control by diffusion of hydrogen into the region ahead of the crack. In region C, velocity is proportional to $P^{3/2}$ and rate control by the dissociative chemisorption step at the surface is suggested.

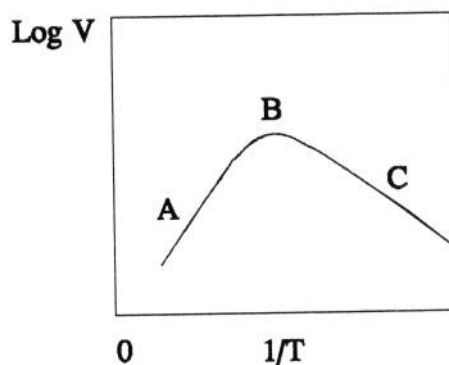


Figure 6. Form of the Crack Velocity-Temperature Relationship For Crack Propagation in Region II of Figure 5 (8).

It has been demonstrated^(54,62), that crack propagation can occur in dry hydrogen gas at atmospheric pressure or lower (down to ~ 200 Pa). Hancock⁽⁵⁴⁾, in addition, showed that small amounts of oxygen would stop cracking, but crack propagation would restart when the oxygen was removed from the environment. Work^(23,62) has shown that the velocity of cracks in high strength steels respond immediately (within the experimental resolution of ~ 1 second) to changes in stress intensity. Previously⁽²⁷⁾ it was assumed that this indicated that the effect of hydrogen on crack propagation occurred well within the plastic zone, where microstructural effects are important. Other work^(21,22) has demonstrated that the plastic zone could be well within a distance of ~ 10 μm , thus allowing diffusion of hydrogen within 1 second, so that internal effects are possible and must be considered.

2.1.4 CRACK ARREST

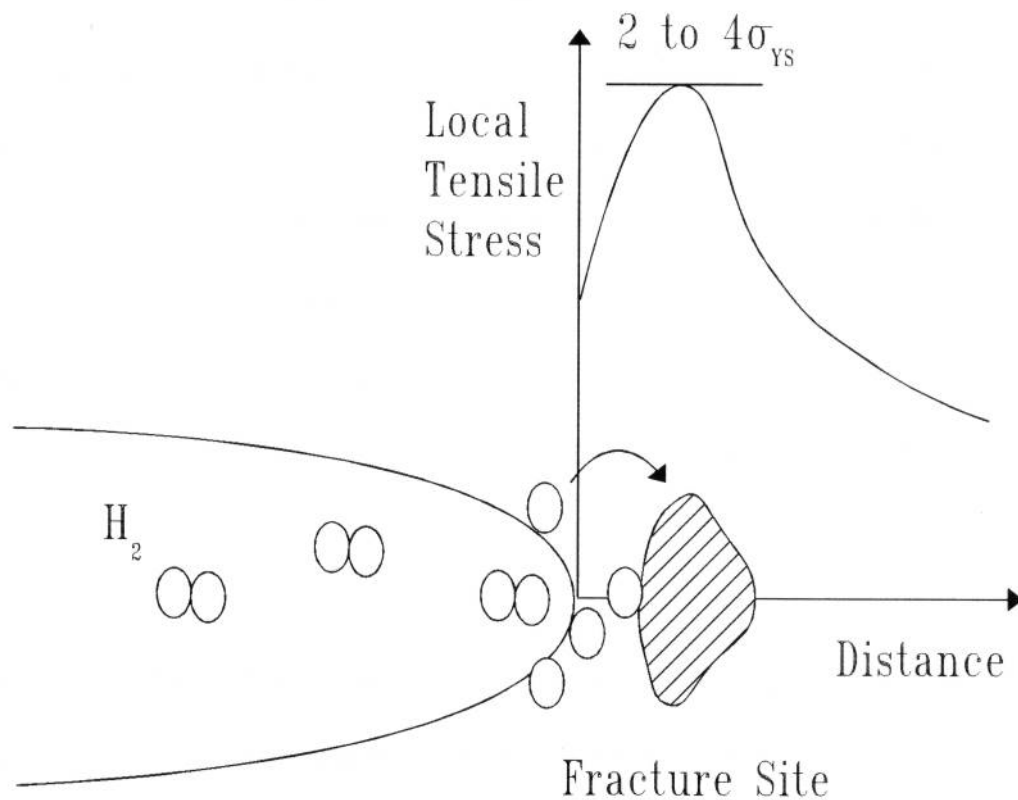
In the previous section it was noted that stage I of figure 5 was usually taken as a measure of the threshold stress intensity, K_{th} . K_{th} can be considered as the highest stress intensity achievable without resolvable crack growth for a material in a given environment⁽⁶³⁾. Typical values of K_{th} are between 10 and 75% of the inert fracture toughness, K_{ISCC} , and are dependent on alloy strength, impurity content, loading rate, electrode potential and environment composition⁽⁶⁴⁾. In some work⁽⁶⁵⁾, the K_{th} value has been taken when stage I propagation is occurring at a velocity of 10^{-10} ms^{-1} , which is taken as the point where the crack is moving so slowly it can be assumed to have stopped.

Experimental factors can have an effect on the fracture threshold values obtained. Incubation periods ranging between minutes and months can precede crack growth for K levels above K_{th} ⁽⁶⁶⁾. Erroneously high threshold values can be obtained if the rate of the applied K increase occurs too rapidly or in the case of decreasing K methods, there is poor crack length resolution and a requirement for rapid testing. Finally, factors such as specimen thickness, crack depth and remaining ligament size can influence K_{th} through chemical mechanisms⁽⁶³⁾.

Gangloff⁽⁶³⁾ has given a theoretical description of the processes which occur during crack propagation caused by hydrogen. At the propagation threshold, the crack tip stresses equal the materials cohesive strength which has been reduced by hydrogen. Increasing

the hydrogen concentration causes the material resistance to further decrease and therefore the K_{th} for HE is lowered. The precise location for nucleation of the brittle crack in relation to the preexisting crack tip is unknown. As previously described, models have been developed for surface adsorbed HE^(48,49) and for cracking in the bulk lattice, in the order of 2 μ m ahead of the crack tip^(7,27,28). The model described by Gangloff, shown in figure 7, is based on the latter. Cracking is controlled by the maximum crack tip tensile stress and the enhanced hydrogen concentrations (enhanced concentrations are caused by hydrostatic lattice dilation and microstructural trap sites). K_{th} depends on a complex function of material yield strength and environment chemistry. Any comparisons of steels with differing compositions or the effect of microstructure on embrittlement must be developed at constant yield strength⁽⁶³⁾. The K_{th} - σ_{ys} relationship has been shown to vary as a function of the surface hydrogen concentration, C_o . The source of hydrogen (electrochemical, gaseous or internally dissolved) affects the magnitude of C_o , but the basic mechanism of HE is unchanged, provided that the site of crack nucleation does not change with differing hydrogen sources⁽⁶⁷⁾.

K_{th} depends inversely on steel yield strength as demonstrated in figure 8⁽⁶³⁾. Work⁽⁶⁸⁾ with AISI 4130 steel in NACE sulphide SCC solution (<5wt% NaCl, Sat. H_2S , pH 2-4) have given K_{th} values below $10\text{MNm}^{-3/2}$ for hardness values above R_c35 (corresponding to σ_{ys} above 1050MPa). For steels of hardness equal to R_c20 (σ_{ys} of about 600MPa), K_{th} levels near $30\text{MNm}^{-3/2}$ have been measured. Often dramatic increases in K_{th} are observed with decreasing σ_{ys} for a given material and environment. This strength effect can be very significant, in some cases embrittlement can be eliminated by moderate



- AT THE THRESHOLD OF CRACK PROPAGATION:-
- THERMODYNAMIC CONDITION WHERE $K_{APPLIED} = K_{TH}$ (MATERIAL-ENVIRONMENT PROPERTY)

LOCAL CRACK TIP STRESS AT FRACTURE SITE	=	INHERENT MATERIAL STRENGTH AT FRACTURE SITE
	=	EFFECT OF METALLOID IMPURITIES PROPORTIONAL TO FRACTURE SITE COVERAGE
	=	EFFECT OF HYDROGEN PROPORTIONAL TO FRACTURE SITE COVERAGE

Figure 7. Theoretical Description of the Threshold Stress Intensity For Hydrogen Embrittlement (65)

strength reductions, for environments which produce relatively low levels of adsorbed hydrogen (for example aqueous NaCl or low pressure H_2)⁽⁶³⁾. As the environments ability to produce adsorbed hydrogen increases, the yield strength effect becomes less pronounced, with severe HE observed over a wide range of σ_{ys} . The interaction between yield strength and the environments activity is expected, based on the complex relationship between K_{th} , σ_{ys} and C_o predicted by modelling (figure 7)⁽⁶³⁾. K_{th} decreases with increasing cathodic polarisation. K_{th} has been shown to increase proportionally to temperatureⁿ, where $n = 1.4$ to 2.0 ⁽⁵⁶⁾, and to be related to the log of the hydrogen gas pressure (P).

It has been proposed that for any constant yield strength, a unifying approach to hydrogen environment embrittlement is based on the relationship between K_{th} and C_o . Models of HE are based on an estimate of the hydrogen concentration, C_T , at the fracture nucleation site near to the crack tip⁽⁶⁹⁾. C_T is related to C_o through analysis of microstructural trapping and hydrostatic stress enhancements of hydrogen solubility, and ultimately to K_{th} based on a hydrogen fracture criterion. Hirth⁽⁸⁾ cites a typical example;

$$K_{th} = \alpha - \beta \log C_o \quad (2)$$

where α and β are constants.

For environments where the hydrogen activity is constant, C_o is determined from permeation measurements with analysis of hydrogen diffusion through a membrane, and correlated with fracture mechanics data for equivalent bulk gases or liquids. The chemical mechanism for the production of hydrogen is complex for aqueous chloride

environments, owing to the occluded nature of the crack. Considering a fracture mechanics specimen, embrittling hydrogen may be produced electrochemically on crack walls and on external surfaces in the bulk solution. The dominant hydrogen source depends on environment chemistry. Therefore, for such electrolytes, localized crack chemistry must be modeled in terms of mass transport and reaction to define the extent to which crack tip hydrogen production differs from bulk charging. In some cases where crack hydrogen production dominates, the local crack C_O must be correlated to K_{th} .

Gangloff⁽⁶³⁾ has summarised work where crack tip hydrogen localization was ignored and K_{th} was related to C_O (defined from bulk solution permeation measurements) for steel in a variety of aqueous chloride electrolytes. Regression analysis yielded;

$$K_{th} = 16.1 C_O^{-0.102} \quad (3)$$

Work⁽⁶⁴⁾ with 50D steel with a hardness of 405 ± 25 VPN in aqueous chloride environments gave the relationship;

$$K_{th} = 91.2 e^{-0.49C_O} \quad (4)$$

Work⁽⁷⁰⁾ with AISI 4135 steel with a strength range of 1480 to 1800MPa, tested in various solutions with and without cathodic polarization, gave the following relationship;

$$K_{th} = 17.0 C_H^{-0.16} \quad (5)$$

Table 1. Reported Hydrogen Concentrations For Onset of Hydrogen Embrittlement

MATERIAL	CONDITION	HYDROGEN CONC. (PPM)	REF
Steel	UTS = 886 to 1860 MPa	0.1	71
Steel	σ_{ys} = 880 to 1275 MPa	0.1	72
4340 Steel	UTS = 1780 MPa	1	73
4340 Steel	Notch Tensile Strength 1650 MPa - 15% Load	0.25	74
4340 Steel	Notch Tensile Strength 1650 MPa - 40% Load	0.007	74
Armco Iron	-	2.5	73
Mild Steel	σ_{ys} = 275MPa	1.8	75

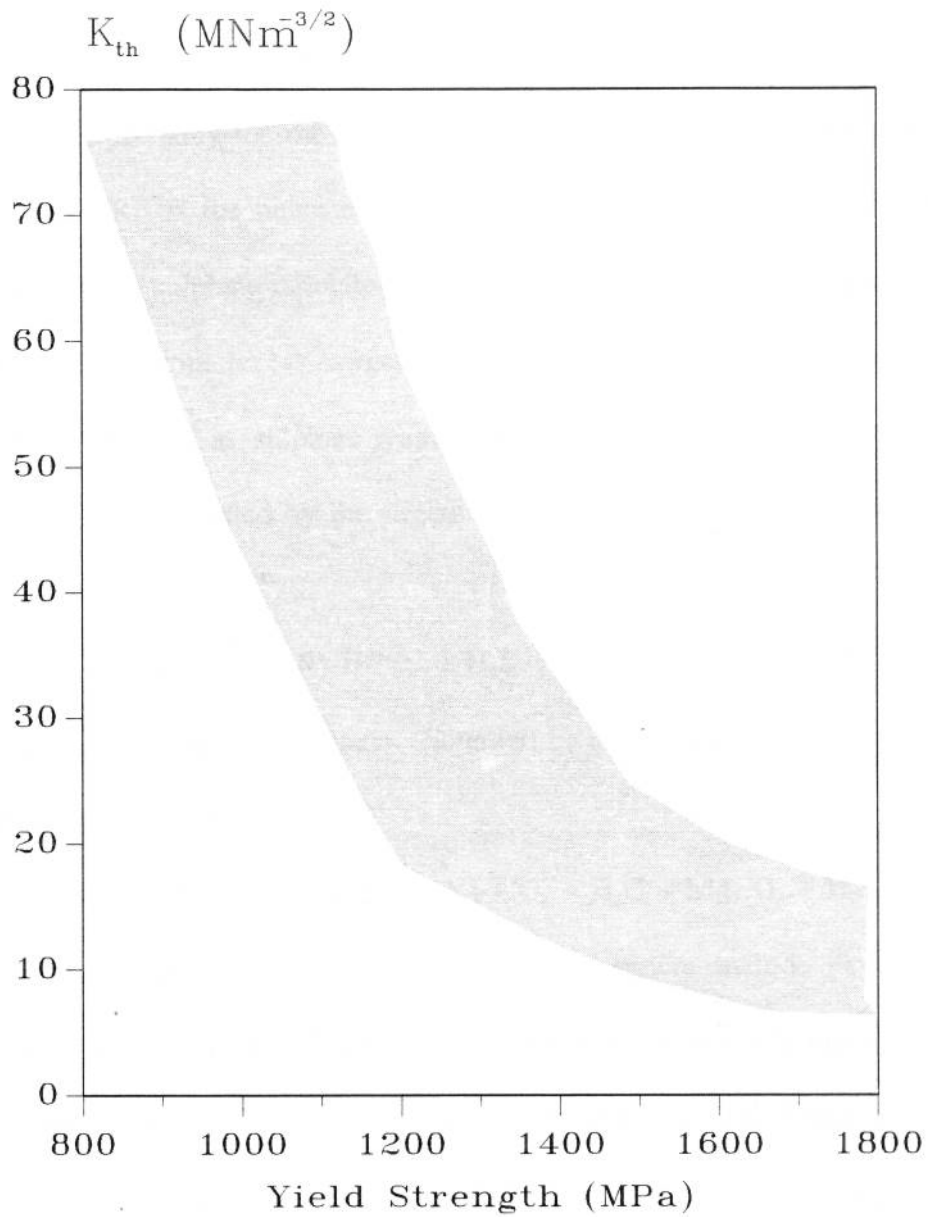
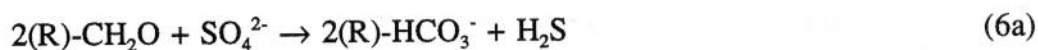


Figure 8. Relationship Between K_{th} and Yield Strength For Low Alloy Steels Freely Corroding at -625mV(SCE) in 3.5% NaCl. Shaded Area is Region Between Upper and Lower Bound Data. (After Gangloff)

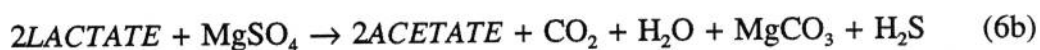
2.2 SULPHATE REDUCING BACTERIA

2.2.1 INTRODUCTION

Sulphate reducing bacteria (SRB) were discovered by Beijerinck in 1895⁽⁷⁶⁾, and have been described as probably the most troublesome bacteria in causing corrosion in the environment⁽⁷⁷⁾. SRB is the name reserved for the diverse class of microbes which conduct dissimilatory sulphate reduction. Sulphate ions act as oxidising agents for the dissimilation of organic matter (as oxygen does in conventional respiration), the process is sometimes referred to as sulphate respiration (equation 6a). A small amount of reduced sulphur is assimilated by the organism, but virtually all is released into the external environment as H_2S ⁽⁷⁸⁾.



where (R) refers to an organic molecule. Equation 6a can be written more specifically for a lactate containing medium;



SRB are obligate anaerobes (see Appendix A), the genera include psychrophilic, mesophilic, thermophilic (t-SRB), barophilic and halophilic strains. The range of organic matter that can be utilized is limited to lactate, pyruvate, cholin, fumarate, malate, ethanol and occasionally glucose, sucrose, glycerol and citrate. Inorganic sulphate is the usual terminal electron acceptor in the dissimilation of organic material but sulphite, thiosulphate and tetrathionate can also be used. For growth they require, in addition to the organic substrate and electron acceptor, an aqueous environment with a redox potential around $-100mV$ ^(78,79), which means that the mere exclusion of air is not sufficient to ensure growth.

SRB have a remarkable capacity for survival in terrestrial and aquatic environments. In aerobic environments the bacteria exist in a dormant biologically inactive form. Where access to oxygen is limited, aerobic bacteria or corrosion may consume the oxygen and modify the environment to one which is conducive to growth of SRB. Conditions of limited aeration can be found on offshore structures, for example, in internally stored volumes of seawater, under external marine fouling, under drill muds which have settled on and around the platform structure, and in bottom sediments.

Temperatures between 25-44°C are best for growth of mesophilic SRB⁽⁸⁰⁾ and above 50°C they are rapidly killed⁽⁷⁸⁾. However t-SRB are able to exist at higher temperatures (up to 100-120°C) often in high pressure conditions (500-1000 bar)⁽⁸¹⁾. The optimum pH range for growth is 7.2 to 7.8⁽⁸²⁾ but good growth is seen between pH values of 5.5 and 9⁽⁸⁰⁾.

Mesophilic SRB grow relatively slowly compared to common soil and aquatic organisms, often showing linear growth and not exponential growth rates. One reason for slow growth is due to the H₂S formed as a by-product of SRB respiration. It can decrease the growth rate, and at high concentrations can even halt growth. It is dangerous to specify doubling times for SRB numbers when growth is often non-exponential, but doubling times quoted in cases of exponential growth vary from 3-6 hours (30°C) to >20 hours⁽⁷⁸⁾. Once growth of the bacteria has started then production of H₂S occurs. Concentrations of the gas can rapidly be produced, typically with a

doubling of concentration approximately every 10-15 hours⁽⁸³⁾. Concentrations of biogenic sulphide quoted in the literature are given in Table 2.

Table 2 Literature Values of Biogenic Hydrogen Sulphide
Concentrations in Marine Environments

H_2S (mg l ⁻¹)	SOURCE / LOCATION	REF. NO.
5	Anaerobic seawater storage tank (offshore platform)	84
50	2% decomposing marine fouling in seawater	85
50-60	In water	83
80-100	Anaerobic seawater storage tank (offshore platform)	84
150	10% decomposing marine fouling in seawater	85
300-600	Mixed culture in ASTM seawater enhanced to Postgate medium	85
500	10% decomposing algae in seawater	86
2000+	Ideal laboratory conditions (gas phase)	87

Certain strains of SRB (hydrogenase positive) produce the enzyme hydrogenase, an organic substance which catalyses the oxidation of hydrogen. Recent work⁽⁸⁸⁾ has shown that the bacteria possess two hydrogenase enzymes, one associated with the outer membrane (periplasmic), the other an intercellular (cytoplasmic) enzyme. It has been suggested that a high molecular weight hydrogenase produces hydrogen during early growth, and that a lower molecular weight hydrogenase oxidises this hydrogen, thus

preventing the waste of reducing power. This hydrogen cycling has been termed vectorial electron transfer, and in effect is hydrogen production by the periplasmic enzyme and hydrogen consumption by the cytoplasmic. Such an arrangement would provide SRB with a versatile metabolism able to match certain changes in their environment. With sulphate present, SRB could gain an advantage by reoxidation of the hydrogen produced in the cytoplasm. When sulphate is limited, substrate phosphorylation would be promoted by transfer of excess hydrogen to other types of hydrogen consuming bacteria⁽⁸⁸⁾. The periplasmic enzyme appears to be the enzyme involved with hydrogen uptake when the bacteria are grown on hydrogen⁽⁸⁹⁾, with some evidence suggesting that the periplasmic enzyme constitutes a greater proportion of the total hydrogenase found in SRB grown on hydrogen than of the hydrogenase in SRB grown on lactate⁽⁸⁹⁾. In addition, the bacterial periplasmic hydrogenase activity can be varied, for certain bacteria growth with an acetate medium rather than a lactate one can create such a difference⁽⁹⁰⁾. This means that the type of energy source available during growth could be critical when carrying out research work with SRB. Depolarisation studies could be influenced by the SRBs ability to use cathodic hydrogen⁽⁸⁹⁾. On the basis of the metal content of the enzyme, broadly three types of hydrogenases have been identified⁽⁹¹⁾:

1. A nickel containing iron-sulphur protein with low activity in the hydrogen evolution assay that consists of two subunits.
2. Exclusively a non-heme iron hydrogenase with high specific activity in the hydrogen evolution assay, consisting of a single polypeptide chain.
3. Hydrogenase containing selenium in addition to nickel and non-heme iron.

The fact that some SRB have hydrogenase has led to the belief that there was autotrophic strains of this bacteria. These bacteria can use gaseous hydrogen for the reduction of sulphate (equation 7). If the energy yielded by this reaction could be coupled to the assimilation of CO₂, the bacteria would be able to grow in a purely inorganic environment (true autotrophs). This belief was backed up by some early experimental work^(92,93), but later investigations^(94,95) showed that the apparent autotrophy was not real. Certain SRB, are in fact, capable of a coupled assimilation of acetate and CO₂ together. This reaction is termed mixotrophy and verges upon autotrophy⁽⁷⁸⁾.



2.2.2 ECOLOGY AND DISTRIBUTION

Ecology is the science of an organisms interaction with its environment. When applied to bacteria, ecology and distribution do not necessarily correspond owing to the capacity of bacteria to remain dormant. A very good example of this is provided by SRB, due to their wide distribution in hostile environments (aerobic) on which they do not seem to be having any effect..

Once growth of SRB starts in a given anaerobic environment, the chemical and physical nature of that environment changes. It has already been mentioned in section 2.2.1 that SRB activity causes the removal of organic material and sulphate and the production of the sulphide ion. In this reducing environment, created by the SRBs sulphide production, free oxygen can only exist transiently except at extremely low concentrations. The aerobic micro-flora of the environment will tend to be replaced by anaerobes, and organic material will be fermented rather than oxidised. Besides suppressing the multiplication of aerobes, the produced sulphide is toxic to most aerobes, higher animals and plants, and they will be killed off and putrefaction of their cells will augment organic material available to the SRB.

The alkali and alkaline earth sulphides dissociate in solution to yield free H_2S as well as HS^- and OH^- ions. Since H_2S is volatile the pH of the environment tends to become alkaline. Over a long period of time this alkalinity is neutralised by atmospheric CO_2 causing carbonate and bicarbonate to accumulate. Heavy metal ions will precipitate as

the metal sulphide. Iron is common in most soils and waters, so blackening due to formation of FeS is a characteristic of SRB activity. This blackening is used in many of the bacterial enumeration techniques employed with SRB.

Removal of hydrogen is a characteristic product of anaerobic fermentation, and the presence of the enzyme hydrogenase in the majority of the acetate producing SRB enables them to utilise H_2 for sulphate reduction. Scavenging of H_2 has been suggested as one interpretation of the apparent incompatibility of SRB and methane producing bacteria. Methanogens have been shown to be able to tolerate fairly high levels of sulphide, so sulphide toxicity does not seem to be a likely cause. SRB would, in any natural eco-system, out compete methanogens for hydrogen and acetate unless their ability to oxidise hydrogen was limited, as would be the case if sulphate was deficient⁽⁷⁹⁾.

Seawater would be expected to contain 1-10 SRB/ml (most likely dormant), this population comprising bacteria disturbed from their natural habitat (because the bacteria are sessile and anaerobic their natural habitat would not be expected to be in bulk seawater). SRB numbers in marine sediments will depend on various factors such as redox potential, organic content, temperature and sulphate concentration but would normally be in the range 10^2 - 10^5 bacteria/g. In drilling muds settled on horizontal jacket members of the North Sea Thistle rig 10^2 SRB/g have been reported⁽⁹⁶⁾. Within the drill leg of the Brent Bravo platform, entrained seawater which had stagnated contained 10^3 cells/l, whilst the surrounding walls had much higher bacterial concentrations of 10^8 cells/m² ⁽⁹⁶⁾. Investigation of the spud can environment of a jack-up rig gave values of

up to 10^6 SRB/ml in the silt phase and up to 10^2 in the water phase⁽¹⁾. The above findings emphasise the important point that bacterial numbers measured in the bulk solution can be much lower than the surface concentration.

In work⁽⁹⁷⁾ similar to that of Efird and Lee⁽⁸⁵⁾, the corrosion of mild steel in putrid seawater (created by decomposition of marine algae) was studied. The maximum sulphide concentration and SRB numbers measured were 125ppm and 3.6×10^6 cells ml⁻¹. SRB numbers were found to be directly proportional to the sulphide concentration. Sulphide concentrations are normally used as a measure of bacterial activity and usually are not a reflection of the bacterial numbers. Comparisons of bacterial numbers from different sources can be complicated due to the results obtained being related to the counting method employed.

Fouling refers to the undesirable formation of deposits on equipment surfaces, which significantly decrease equipment performance and/or its useful life. Several types of fouling and their combinations may occur, including biological, corrosion, particulate and precipitation fouling. In many cases more than one type of fouling will be occurring simultaneously⁽⁹⁸⁾.

SRB (and other bacteria) on solid surfaces in the marine environments are attached in the form of a biofilm. When solid surfaces are exposed to natural waters they are rapidly conditioned by adsorbing organic matter and become populated with bacteria in a few hours⁽⁹⁹⁾. The conditioning film is composed mainly of high molecular weight

polymeric substances such as polysaccharide⁽¹⁰⁰⁻¹⁰⁵⁾ or glycoproteins^(103,106) contributed from two main sources⁽¹⁰⁰⁾:

1. Spontaneous adsorption of biological macromolecules or more often their oxidised end-products, such as humic matter and gelbstoffe, which were originally in solution or suspension in the seawater.
2. Bacterial secretion of extracellular polymeric substances (EPS) such as protein-polysaccharide slimes by pioneer attaching microbial organisms.

These bacterial polymers act as strong adhesives and guarantee that the pioneer bacteria will be permanently attached to the material surface⁽¹⁰³⁾. When viewed under an electron microscope the extracellular polysaccharide polymers appearance varies from flocculose or filamentous growths to barely discernable discrete gelatinous slimes⁽¹⁰⁴⁾. The sticky stringy consistency of these polymers is due to uronic acids giving the polymers a polyanionic charge⁽¹⁰⁵⁾. Whether the resulting organic film is glycoprotein or humic in nature, its presence affects surface charge⁽⁹⁹⁾ and surface wettability⁽¹⁰⁷⁾. These factors play a vital part in the ensuing attachment of bacteria to the conditioned surface. Typical values of bacterial numbers for a mature biofilm (110 days) have been quoted as $10^6/\text{cm}^2$ for SRB and $10^8/\text{cm}^2$ for heterotrophic bacteria⁽¹⁰⁸⁾.

Biofilms may include many components such as bacteria, algae, cellular extrudates, organic and inorganic matter coming from the bulk of the solution and trapped in the mucilage⁽¹⁰⁹⁾. Biofilm accumulation is the net result of the following physical, chemical and biological processes⁽⁹⁸⁾.

1. Transport of organic molecules from bulk liquid to the substratum, attachment

creates a conditioning substratum (CS).

2. Transport from bulk solution of a fraction of planktonic microbial cells to CS.
3. A fraction of the cells that strike the CS adsorb to it for a finite time then desorb (reversible adsorption). Desorption may result from fluid shear forces or other physical chemical or biological factors.
4. A fraction of the reversibly adsorbed cells remain immobilized beyond a critical residence time and become irreversibly adsorbed.
5. Irreversibly adsorbed cells grow at the expense of substrate and nutrients in the bulk solution, increasing biofilm cell numbers. The cells may also form a significant number of products, some of which may be excreted (such as EPS). Thus, biofilm accumulation increases through microbial metabolism at the expense of substrate energy in the bulk solution.
6. Cells and particulate matter attach to the biofilm, increasing biofilm accumulation.
7. Portions of the biofilm detach and are re-entrained in the bulk solution.

Microfouling films can act as physical barriers for the inward diffusion of both oxygen (or other cathodic reactants) to the cathodic sites and aggressive anions to the anodic sites, whilst also obstructing the outward diffusion of corrosion products. Corrosion of the metal surface may be caused simply by the non-uniform blanketing of the surface leading to the development of differential aeration cells⁽¹⁰⁴⁾. If the aerobic respiration rate within the biofilm exceeds the oxygen diffusion rate through the film, a change in the cathodic reaction (oxygen reduction to hydrogen evolution) might occur. Such an

environment would allow anaerobic metabolism by microorganisms, such as SRB, at the metal surface⁽¹⁰⁶⁾. It has variously been estimated that this effect is evident with biofilms of between 25-100µm thickness⁽¹¹⁰⁾. Once SRB activity has been initiated the production of sulphide will lead to more extensive anaerobic zones allowing further SRB activity.

The spontaneous adsorption of organic material from the aqueous phase alters the interfacial free energy of the solid as well as the corrosion potential of the metal surfaces⁽¹¹¹⁾. To identify which component of the biofilm caused the change in potential, Scotto⁽¹¹²⁾ added sodium azide to kill the lifeforms present without causing detachment of the biofilm. Elimination of the living part of the biofilm brought the potential back to that measured in sterile water.

Obviously SRB are not found in isolation from other bacteria in the environment, but are found to be in close physical and metabolic contact⁽¹¹⁰⁻¹¹⁴⁾. Relationships between anaerobic heterotrophs, SRB and facultative aerobic bacteria is very common in natural and industrial systems⁽¹¹⁵⁾. In cases such as marine fouling, SRB are found to be associated not only with other bacteria but with higher forms as well. These communities of organisms are referred to as consortia or biofilms, thus SRB in biofilms can be considered a component organism within a complex consortia. These consortia are not always complex, but can be simple, as in the case with marine sediment⁽¹¹⁶⁾. Aerobic organisms in the top few centimetres of the sediment produce reducing conditions which favour SRB activity. SRB can utilise only a limited range of organic substrates, this does not include methane and higher petroleum hydrocarbons, but the

consortia can be capable of hydrolytic and fermentable metabolism of primary nutrients such as carbohydrate and proteins, organic detritus and hydrocarbons. Therefore, the SRBs carbon and energy requirements can be met by the reduced metabolic products (such as acids, alcohols, acetate, hydrogen, etc.) of other organisms in the community. In considering the complete degradation of organic material (including hydrocarbons) in anaerobic environments it has been suggested that the involvement of three broad groups of organisms^(110,113):

1. Heterotrophs, either aerobic or facultative, (including higher forms) giving rise to a range of fermentation products. The activity of the heterotrophs generally leads to the formation of the conditions required for activity of the acetogenic and SRB.
2. Hydrogen producing acetogenic bacteria.
3. SRBs (or methanogens in sulphate limited environments)

2.2.3 EFFECTS ON CORROSION

In anaerobic environments the reduction of dissolved oxygen (equation 8) is obviously not a feasible cathodic reaction. Other possible cathodic reactions are the reduction of hydrogen ions (equation 9) and the water reduction reaction (equation 10). Reaction 9 occurs very slowly in near neutral solutions such as seawater. Significant corrosion of steel, therefore, would not be expected in anaerobic, near neutral solutions.

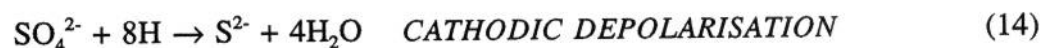
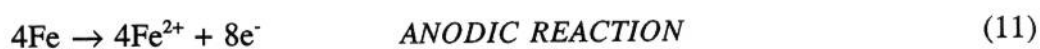


In reality, high rates of corrosion often occur, which can be several orders of magnitude higher than would be predicted for an aerobic environment⁽¹¹⁷⁾, this increased corrosion rate has been ascribed to the presence of SRB.

The role of SRB in inducing or accelerating electrochemical corrosion processes has been interpreted on the basis of different mechanisms, which can be conveniently classified as follows;

1. Stimulation of the cathodic reaction in the absence of oxygen by SRB, either directly by removal of atomic hydrogen or indirectly by the formation of iron sulphide or hydrogen sulphide.
2. Acceleration of the anodic reaction by the action of sulphide ions or other sulphur species produced by the SRB.
3. A combination of both effects.

At the start of the century, it was suspected that bacteria might be involved in the degradation of buried ferrous metals. In 1934, Kuhr and Vlugt⁽¹¹⁸⁾ conducted studies which indicated that SRB were associated with the corrosion occurring in wet, anaerobic polder clay. They proposed, what is now known as the 'classical theory', a corrosion mechanism in which the bacteria depolarised the cathode by utilising cathodic hydrogen, by way of their enzyme hydrogenase, for the dissimilatory reduction of sulphate to sulphide. The proposed mechanism can be summarised by the following equations;



The overall reaction being,



Most of the work subsequent to the above has either supported or challenged the classical theory, with no clear mechanism emerging to date. The main criticism of the above theory is that the ratio of corroded iron to iron sulphide should, in theory, be 4:1 but is actually found to vary between 0.9:1 and 50:1⁽¹¹⁷⁾. Also, the mechanism does not consider the effects of hydrogen sulphide, iron sulphide or corrosion products, and suggests that only hydrogenase positive bacteria are involved.

The cathodic depolarisation step (14) in the above sequence was based on the findings

of Stephenson⁽¹¹⁹⁾, who first suggested the biological activation of hydrogen and termed the enzyme involved as hydrogenase. The charge transfer step for the cathodic reaction leads to the formation of adsorbed hydrogen atoms (equation 18);



Miller⁽¹²⁰⁾ has questioned how an intact bacterium can remove adsorbed hydrogen atoms from a metal surface as distinct from the uptake of molecular hydrogen dissolved in water. Furthermore, the two alternative steps for completion of the hydrogen evolution reaction are either chemical recombination (equation 40, section 2.4.1) or electrochemical desorption (equation 41, section 2.4.1), for transition metals there are conflicting views about the rate determining step⁽¹²¹⁾, plus the presence of HS^- modifies the path of the charge transfer reaction. Doubt has also been expressed⁽¹¹⁹⁾ to whether the bacterial uptake of hydrogen (as related to the hydrogenase activity) would accelerate these reactions because the desorption of molecular hydrogen does not control the reaction rate.

In 1939, Bunker⁽¹²²⁾ carried out tests on steel in neutral, deaerated solutions with and without bacteria. The samples remained bright in solutions without bacteria, but corroded by way of pitting in their presence, thus further indicating their role in anaerobic corrosion.

Booth^(123,124) employed cathodic polarisation techniques to iron in two cultures of *Desulfovibrio*. It was shown that growing strains of hydrogenase positive bacteria (*D. vulgaris*) could depolarise a cathode, while hydrogenase negative bacteria

(*Desulfotomaculum orientis*) did not affect the depolarisation. After one week both strains of bacteria had induced the formation of a partially protective iron sulphide film. These results were taken as confirmation of the classical theory even though the corrosion rates found were significantly lower than those encountered in the field⁽¹¹⁹⁾.

In later work, Booth⁽¹²⁵⁾ found that semi-protective sulphide films became detached after 20-30 weeks exposure to a bacterial environment causing the corrosion rates to increase significantly, even in the case of *Dt. orientis*. The direct correlation between corrosion and bacterial hydrogenase activity (one of the basic assumptions of the classical theory) became doubtful.

Booth⁽¹²⁶⁾ observed that the addition of high Fe^{2+} concentrations to the culture medium caused very high corrosion rates (comparable to field measurements). It was suggested that ferrous iron reacted with the bacterially produced sulphide to prevent formation of the semi-protective sulphide film. A completely unprotective loose mass of corrosion products consisting of iron sulphide and ferrous carbonate was observed to form.

Booth⁽¹²⁷⁾ attempted to clarify the situation by conducting polarisation studies in sulphate free conditions, thus avoiding any effects sulphide might have. Benzyl viologen, a redox dye, was used as an alternative to sulphate. Depolarisation of the cathode was independent of hydrogenase activity when a reducible substrate was absent, but when present, depolarisation was increased. Hydrogenase negative bacteria were found to be completely inactive. Thus it was suggested that within a limited experimental range, the

rate of corrosion was a function of the extent of hydrogen utilisation.

Booth⁽¹²⁸⁾ again carried out cathodic polarisations with SRB environments absent of sulphate. In this study, tests were carried out with and without additions of chemically prepared suspensions of ferrous sulphide in 1% NaCl solution. Two mechanisms of depolarisation were seen, one involving hydrogenase, the other involving solid ferrous sulphide. It has been shown^(129,130) that different iron sulphides can lead to accelerated corrosion of mild steel, indicating that the action of SRB is due to the formation of fresh iron sulphides. Miller⁽¹²⁰⁾ has suggested that all iron sulphides are cathodic towards iron. Recognising that iron sulphides in bacteria-free systems do not act as permanent cathodes, it was claimed that the role of SRB could be either to regenerate the iron sulphide enabling it to remain cathodic, or to produce fresh iron sulphide or bring fresh iron sulphide surfaces into contact with the steel due to cell movement. Recent studies⁽¹³¹⁾ have found that the bacteria often have iron sulphide adhering to their cell walls.

Experiments⁽¹²⁶⁾ carried out with growing strains of different types of bacteria, have indicated that corrosion rates are independent of hydrogenase activity as hydrogenase negative and positive bacteria both gave high rates of corrosion. These results again tend to suggest that hydrogenase is less important than originally thought and indicates that other factors may be involved, such as sulphide films or sulphide species.

Results of other studies⁽¹³²⁾ have also implied the nature of the sulphide formed is of

importance. In low iron media, the primary corrosion product was found to be a protective iron sulphide film, but due to sulphidation, there was a change in its nature, resulting in an increase in volume. Rupture of the film caused high rates of corrosion and it was suggested that the iron sulphide formed a galvanic cell with the underlying metal.

Costello⁽¹³³⁾ measured cathodic polarisation curves of mild steel in cultures of *D. vulgaris* and two other strains of the genus *Desulfovibrio* at pH 6.5 and compared the results with those obtained in the presence of 0.01M H₂S at the same pH. He concluded that cathodic polarisation in cultures of SRB may be attributed to the cathodic activity of dissolved hydrogen sulphide produced by the microorganisms. Togano⁽¹³⁴⁾ measured corrosion rates of mild steel exposed to biogenic H₂S as a function of time whilst monitoring E_{corr} , H₂S formation rate/concentration and numbers of viable SRB. The relationship established indicated that the corrosion rate was proportional to the instantaneous concentration of H₂S produced by the bacteria, although the picture was complicated by sulphide film formation. It was also claimed that the accelerating effect of the H₂S was greater on the anodic reaction than on the cathodic reaction, an opinion previously expressed by Wanklyn⁽¹³²⁾ in the 1950's.

King and Miller⁽¹³⁵⁾ demonstrated that the stimulation of corrosion by chemically prepared sulphides decreased with time. The decrease was attributed to hydrogen being bound up within the sulphide lattice. Sustained corrosion rates could be achieved by removal of this hydrogen. Bacterial hydrogenase could do this and so an alternative

mechanism was proposed. The two mechanisms are compared in Figure 9.

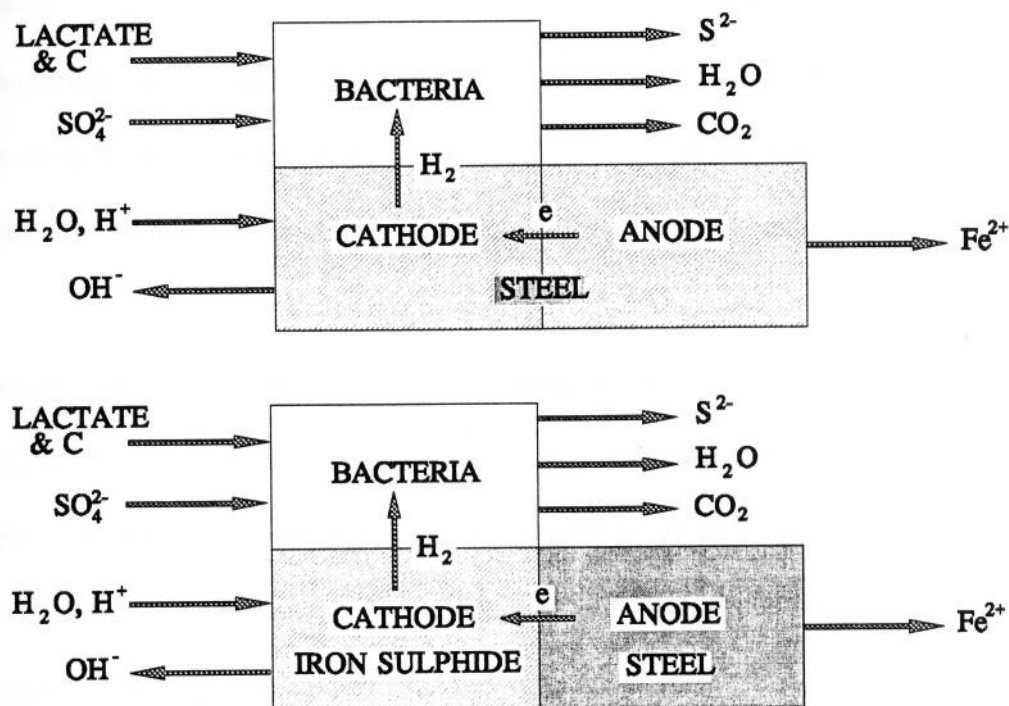


Figure 9. Schematic Representation of the Classical Mechanism (top) and Alternative Mechanism (bottom). (After King & Miller)

Herbert et al⁽¹³⁶⁾ studied the effect of temperature and pressure on SRB. They showed that hydrogenase activity reduced with increasing pressure and stopped at 400 bar. The corrosion rate increased however, due to sulphide and therefore highlighted the importance of sulphide in the corrosion process.

Hardy⁽¹³⁷⁾ placed steel samples into an anaerobic environment containing SRB and obtained low corrosion rates (1.45mg/dm²/day). Once good growth had been established, the systems were aerated, producing a large increase in observed corrosion rate

(1.29mg/dm²/day). The film on the steel surface was found to be a crucial component of the air driven corrosion process. It was composed of a hard tarnish overlaid by a glutinous black precipitate, mainly composed of mackinawite (Fe_(1+x)S). The film differentiated into small discrete anodic and cathodic areas. It was proposed that film rupture arose from sulphidation of the mackinawite tarnish as proposed by Mara and Williams⁽¹³⁸⁾. This exposed anodic sites, resulting in rapid pitting attack.

Low corrosion rates of steel in SRB containing environments have been found by other workers^(80,97,139,140). Reduced rates of corrosion following oxygen depletion and rapid sulphide production were explained by Eashwer et al⁽⁹⁷⁾ using the potential/time observations made by Togano⁽¹³⁴⁾ and Salverezza⁽¹⁴¹⁾ who found that high sulphide levels in anaerobic seawater tended to shift the potential of steel from the active state back to the open circuit potential. This does not happen in the presence of oxygen. Eashwer et al⁽⁹⁷⁾ concluded that O₂-H₂S interactions are important in the corrosion process with maximum corrosion rates occurring before complete oxygen depletion during the early stages of putrefaction.

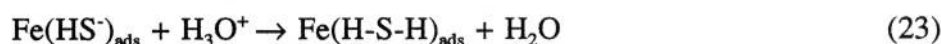
There is very little quantitative data available related to the rate and extent of microbial sulphide production in biofilms⁽¹⁴⁰⁾. Nielson⁽¹⁴²⁾ reported kinetic data from a continuous flow SRB biofilm reactor which indicated that sulphate diffusion in the biofilm was rate limiting for SRB activity and that corrosion of mild steel was insignificant in the presence of the active SRB biofilm. However, the combination of the SRB biofilm with dissolved oxygen, iron ions and iron sulphide caused enhanced corrosion. There was

no cathodic depolarisation and no correlation between corrosion and SRB activity in the absence of ferrous ion in a biofilm reactor at pH 8. When the formation of an iron sulphide film was prevented until after biofilm formation there was no significant corrosion. If the sulphide film was allowed to form before the biofilm then pitting attack was observed.

It is well established that some sulphur compounds (such as H_2S and SO_2 and their respective anions) enhance the dissolution rate of iron and steels in acidic solutions⁽¹¹⁹⁾. It has been suggested that the catalytic effect of sulphide ions on the anodic reaction can be explained by the formation of intermediate adsorbed sulphide species as opposed to hydroxide species as follows⁽¹¹⁹⁾:



The acceleration of the cathodic reaction in the presence of H_2S has been explained by the following equations:



in which the autocatalytic active species $\text{Fe}(\text{H-S-H})_{\text{ads}}$ is readily reduced to adsorbed H atoms. The anodic behaviour in alkaline sulphide solutions has been interpreted⁽¹⁴³⁾ in terms of the competitive adsorption of H_2O , OH^- and HS^- . Processes like the formation

of mackinawite, development of pitting or passivation of the metal surface by an oxide layer are suggested to depend on the HS^-/OH^- concentration ratio.

There is no doubt that H_2S can accelerate both the anodic and cathodic reaction. The complexity of the systems associated with the growth of SRB makes it more difficult, compared with sterile environments, to define the precise role of H_2S in the corrosion kinetics. The participation of other metastable sulphur species in the acceleration of the anodic reaction cannot be excluded. Iverson⁽¹⁴⁴⁾ suggested, on the basis of experiments in which high corrosion rates were observed, that in addition to H_2S , SRB produce a highly corrosive substance, possibly a soluble compound containing phosphorus, which enhances the dissolution of iron under anaerobic conditions at a neutral pH. He emphasized that the enhanced corrosion can be expected only when the substance comes in contact with iron before sulphide film formation takes place. Otherwise corrosion is stifled, although the subsequent breakdown of the film could result in further increase of the corrosion rate.

On the other hand, Schaschl⁽¹⁴⁵⁾ showed that elemental sulphur, dissolved in the presence of sulphide ions, promotes the accelerated corrosion of mild steel in contaminated brines by a concentration cell mechanism similar to that of differential aeration. He claimed that dissolved sulphur acts as a cathodic reactant (equation 27), indicating that bacteria may provide the shielding action needed to promote concentration cell action. Bates⁽¹⁴⁶⁾ reinterpreted the action of sulphur, proposing that polysulphides (S_x^{2-}) are the cathodic reactants (equation 26). Elemental sulphur dissolves in neutral or alkaline sulphide

solutions forming a polysulphide:



The overall reaction being:



A basic requirement for localised corrosion is a physical separation of anodic and cathodic sites. General corrosion takes place when such a physical separation does not exist. Often, localisation of anodic sites arises from areas of the metal surface being occluded, causing some areas to be less oxygenated than others. All types of microbes can colonise surfaces and produce a mass of 'slime', thereby establishing a differential aeration cell (section 2.2.2). Active growth of the microorganisms uses available oxygen and thus further decreases the concentration. Death of organisms within the colony does not prevent the development of the cell as a physical barrier still prevents oxygen influx. The anaerobic conditions produced are conducive to the development of SRB. In the case of cast iron the preferential dissolution of iron leads to the well known phenomenon of graphitization. With carbon steels, the attack manifests itself as pitting corrosion. Due to the relatively poor protective properties of the passive film the attack tends to be shallow, but extended over a large area. In the more corrosion resistant alloys pits are normally smaller in diameter, but can be extremely deep. Concern has been

expressed⁽¹⁴⁷⁾ about the replacement of carbon steels by stainless steels, which may produce greater corrosion problems if the mechanism of the bacterial action are not well understood.

Up to the end of the 1970s, only two genera of SRB were recognised (*Desulfovibrio* and *Desulfotomaculum*), both were isolated using lactate based media. However, since 1979 a whole new range of SRB have been identified which are capable of utilizing alternative substrates⁽⁷⁹⁾. These new genera are found occupying the same habitats as the classical lactate utilizing SRB and it has been suggested that they vastly outnumber the latter in the natural environment⁽¹⁴⁸⁾. Laboratory media and conditions required for the isolation and growth of the new SRB genera are complex and exacting⁽⁷⁹⁾, which probably explains the reason why SRB related corrosion studies still centre around lactate based media⁽¹⁴⁹⁾. There is a possibility that the inability to detect non-lactate utilising SRB may lead to the misidentification of some types of corrosion as non-biological⁽¹⁴⁹⁾.

Gaylarde⁽¹⁴⁹⁾ has carried out work, which has addressed these issues, in which two new genera of SRB (*Desulfobacter postgatei* and *Desulfobulbus propionicus*) are compared to a lactate utilising SRB, *Desulfovibrio vulgaris*. Results indicated that *Desulfobacter postgatei* and *Desulfobulbus propionicus* do not significantly influence the corrosion rate of mild steel whilst *D. vulgaris* enhanced corrosion. Both of the new genera produce sulphide during growth, so the lack of enhanced corrosion may indicate that sulphides are of less importance than currently thought, but as the production of sulphide was not

measured it could be that the two genera produce little H_2S compared to *Desulfovibrio vulgaris*. It was reported that the lack of odour of H_2S associated with these cultures would indicate this. It has been suggested that the two most important characteristics of SRB involved with corrosion are sulphide production and hydrogenase activity⁽¹⁵⁰⁾. As *D. postgatei* has no hydrogenase activity, it may be, as suggested by Bryant⁽¹⁵¹⁾, that the activity of the hydrogenase enzyme is crucial in determining the corrosive nature of SRB species. Levels of corrosion observed with *D. vulgaris* were lower than those reported in previous publications. Previous work used media which was not prepared and incubated in anaerobic cabinets, so it has been suggested that the higher corrosion rates reported could be due to traces of O_2 ⁽¹⁴⁹⁾.

In summary, it is obvious that even after extensive research it is still unclear what role SRB take in the corrosion process. The classical theory in which hydrogen is utilised via hydrogenase has been challenged and alternative mechanisms proposed. These involve the action of one or more of the following: hydrogen sulphide, sulphide species, sulphur, iron ions and other bacterial metabolites such as a volatile phosphorus compounds. Even the ability of SRB to enhance corrosion in totally anaerobic conditions has been questioned by the suggestion that dissolved oxygen is required to be present to cause enhanced corrosion.

2.3 CATHODIC PROTECTION

2.3.1 CATHODIC PROTECTION THEORY

Corrosion is the spontaneous chemical reaction of a metal with its environment. If this environment is an aqueous solution, then corrosion proceeds by an electrochemical mechanism involving oxidation of the metal (anodic reaction) and simultaneous reduction of species in the aqueous phase (cathodic reaction). Taking iron in water for example, the anodic reaction would be,



and possible cathodic reactions could be,



It would seem logical that an electrochemical method should be employed to reduce or stop corrosion. Cathodic protection (CP) is such a method, in which the corroding metal is made the cathode in the electrochemical cell by displacing its electrode potential, E_A , below the corrosion potential, E_{corr} (figure 10). This is achieved by either attaching an anode made of a baser metal (sacrificial anode) or application of a current through an external source (impressed current) or a hybrid of the two systems.

The principal method of corrosion protection for the submerged parts of offshore platforms is CP. A 1988 survey⁽¹⁵²⁾ of 58 platforms in UK waters showed that 46 operated sacrificial anode CP systems, 5 used impressed current (2 later being converted to sacrificial anode due to failures) and 7 employed hybrid systems. The majority of the

operating potentials reported had maximum values in the range -950 to -1050mV(Ag/AgCl) but the most negative reported was -1270mV(Ag/AgCl).

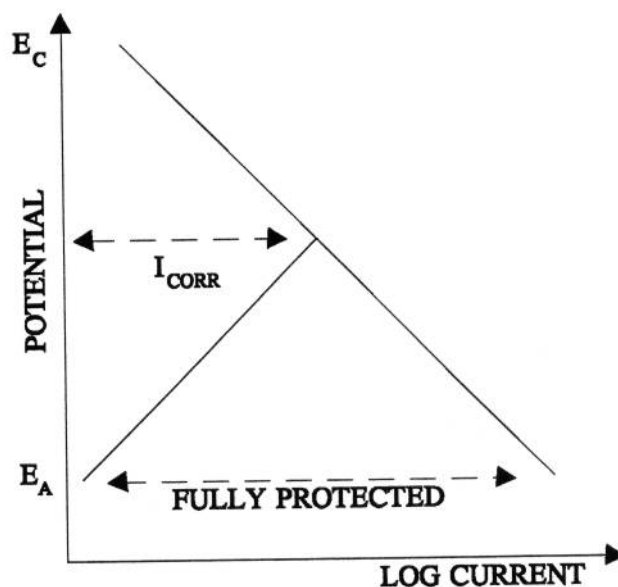


Figure 10. Evans Diagram Illustrating Principles of Cathodic Protection

The E_{corr} of steel in seawater is approximately -650mV(SCE) and the range of recommended applied potentials for total CP is -770 to -850mV(SCE)⁽¹⁵³⁾. The potential of a pure zinc sacrificial anode in seawater will lie in the range -950 to -1030mV(Ag/AgCl)⁽¹⁵⁴⁾. Only one factor consistently takes the criterion outside the above recommended range, and this is the presence of SRB and/or heavy pollution, for which a further depression of the potential by about 100mV is usually advised^(155,156). In practical terms, results from the 1988 survey⁽¹⁵²⁾ show that -950mV is a standard level of protection, with many structures receiving more negative potentials.

The use of CP to protect steels can have the detrimental effect of producing quantities

of hydrogen (equation 32) high enough to cause hydrogen embrittlement in susceptible materials. The hydrogen equilibrium potential is dependent on pH and temperature, but would be of the order of $-710\text{mV}(\text{Ag}/\text{AgCl})$ for North Sea seawater at pH 8.3 and $10^\circ\text{C}^{(157)}$. This means that no significant hydrogen is produced until the potential exceeds this value. As the CP potential, applied to a steel, becomes more negative the amount of hydrogen evolved and absorbed increases^(158,159). The increase in entry rate was found to be a linear function of the steels surface potential by Thomason⁽¹⁵⁶⁾ using hydrogen permeation measurements. This is the overriding reason why overprotection should be avoided when protecting high strength steels which are known to be susceptible to HE.

2.3.2 PRODUCTION, NATURE AND EFFECTS OF CALCAREOUS DEPOSITS

Metals being cathodically protected in aqueous solutions can support either oxygen reduction or hydrogen evolution reactions (equations 8 & 32) at the metal surface. All these reactions cause the pH to increase close to the metal surface (Figure 11) as they generate hydroxyl ions. Kobayashi⁽¹⁶⁰⁾ applied a cathodic current of 0.938 mA/cm² to a static 3% sodium chloride solution of pH 8. At a distance of 0.1 mm from the surface the pH was measured at 11.5. Engell and Forchhammer⁽¹⁶¹⁾ proposed from their model that the pH at the surface of a cathodically protected steel would be 10.9. Values ranging from 10.75 to 11.25 were calculated by Wolfson and Hartt⁽¹⁶²⁾ from their model. These models do not, however, take into account the buffering capacity and ionic strength of seawater. This has been included in the model by Dexter and Lin⁽¹⁶³⁾ who measured a pH of 10.2 at 50-100µm from the metal surface protected at a CP potential of -970mV(SCE).

In seawater the pH is buffered, to a value in the range 7.5 to 8.3⁽¹⁵⁴⁾, by the carbonate/bicarbonate equilibrium reaction (equation 34). This is due to carbon dioxide dissolving in water to form carbonic acid (equation 33). Increasing pH will shift the equilibrium towards the right and cause an increase in the carbonate species.



Seawater contains calcium and magnesium ions and therefore the deposition of calcium carbonate (equation 35) occurs in the region where the pH increases above 8.3. The

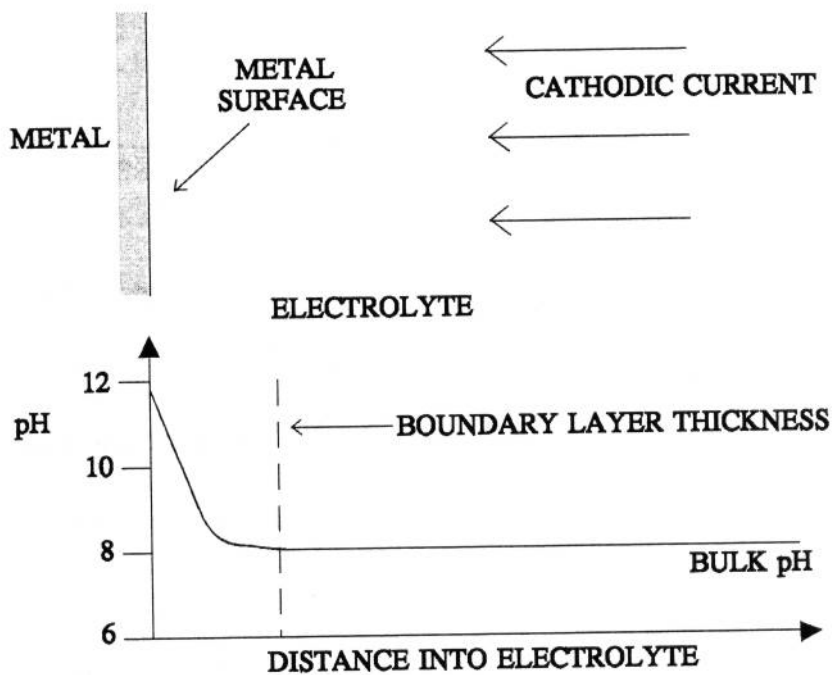


Figure 11. Schematic Illustration of the pH Profile of the Electrolyte Adjacent to a Cathodically Protected Metal Surface (162).

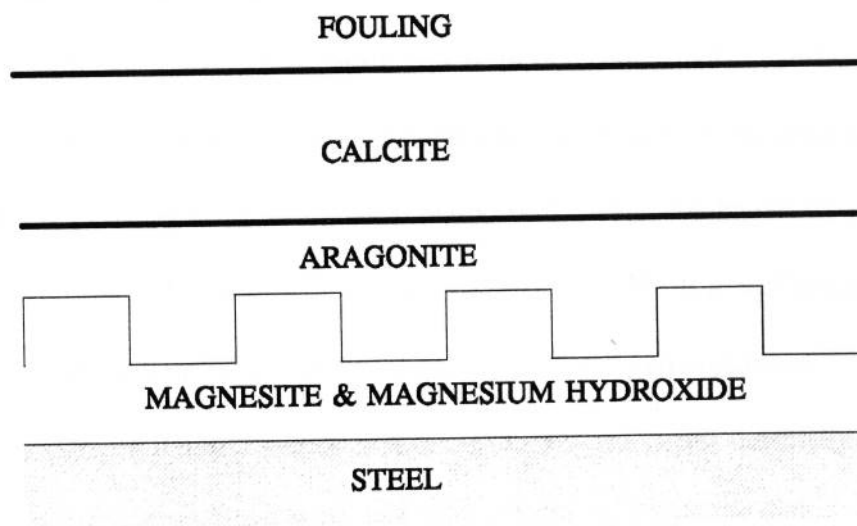


Figure 12. Composition of scale formed on a Protected Steel Surface (165).

calcium carbonate can occur in two forms, calcite and aragonite^(164,165). Also, magnesium carbonate (magnesite) and the mixed magnesium/calcium carbonate (dolomite) can form (equations 36 and 37).



At higher currents (more negative potentials) the pH is raised even higher. When the pH exceeds 9.3⁽¹⁵⁴⁾ to 9.5⁽¹⁶⁴⁾ a deposit of magnesium hydroxide can be formed in addition to the dominant calcium carbonate.



The chemistry of the deposit may be complex and variable depending on the conditions of formation. The most influential factors on scale formation are cathodic current density/potential^(162,166) (and resulting pH), temperature^(166,167), pressure⁽¹⁶⁴⁾, water chemistry⁽¹⁶⁴⁾, seawater velocity^(166,168) and the nature of the substrate^(164,168). Figure 12 shows schematically the composition of a scale formed on steel protected at -950mV(SCE) after immersion in a continuous flow seawater tank⁽¹⁶⁷⁾. Scales comprised of a relatively thin magnesium rich inner layer covered by a more voluminous calcium rich outer layer have been found by other workers⁽¹⁶⁹⁾. The thickness of such scales, initially, is related to the current density and exposure time⁽¹⁶²⁾. It is well established that scaling rates increase with increasing temperature. It has been suggested⁽¹⁶⁴⁾ that this is due to increased precipitation kinetics as the rate controlling step is thermally controlled. Once formed the scale is virtually insoluble at normal seawater pH values⁽¹⁶⁷⁾.

The formation of calcareous deposits has a beneficial effect by reducing the current requirements of the CP system. This has been described as the calcareous scale acting as an additional ohmic resistance in the electrolytic part of the current path. However, work has shown that the calcareous scale alters the position and shape of the cathodic protection curve in a way that is not compatible with just the simple insertion of an ohmic resistance. Mechanistically, the appropriate picture is probably that of a surface with an active area reduced by partly impervious scale, with oxygen arriving at a diffusion limited rate through pores⁽¹⁵³⁾. The current density at the base may in fact be high enough to bring the potential into the range for hydrogen evolution⁽¹⁶²⁾, this reaction being little influenced by the deposits⁽¹⁶⁶⁾.

Several authors have reported that the protective value of scales does not increase with more negative potentials. Above a certain potential the scales become more porous and less adherent⁽¹⁷⁰⁾. This is usually attributed to increasing hydrogen evolution within the porous deposits^(153,154,170). Humble⁽¹⁷¹⁾ noticed that deposits formed at lower current densities were more stable than those created at higher current densities. It was suggested that the reason for this was the lower solubility of the calcium ion relative to the magnesium ion. Alternatively the reduced protection of the deposits formed at current densities greater than 0.3 mA/cm^2 has been explained by the poor coating properties of magnesium hydroxide.

It is well established that correctly applied levels of CP improve the fatigue life of offshore structural steel by reducing corrosion and crack initiation^(157,172), and can reduce

crack growth rates to values approaching those found in air⁽¹⁷²⁾. This additional benefit of CP has been ascribed to calcareous deposit formation within fatigue cracks and thus contributing to crack closure⁽¹⁷²⁻¹⁷⁵⁾, in some cases deposits may even fill the cracks. The crack closure caused by the deposits is in fact a wedging effect which reduces the stress intensity range at the crack tip during the fatigue cycle. The effect has been used to explain why crack growth rates in C-Mn steels in seawater are lower than those in 3% sodium chloride solutions, and also why plateau behaviour is seen in seawater tests and not in the 3% sodium chloride solution⁽¹⁷⁵⁾.

As previously mentioned, the scale forms a protective barrier and reduces current demand, its alteration can influence the performance and economics of the CP system⁽¹⁶⁵⁾. It is suggested that the differences in corrosion⁽¹⁷⁶⁾ and calcareous scale deposition⁽¹⁶⁷⁾ between artificial seawater and natural seawater are largely due to the organic content of the water^(177,178). Recent work⁽¹⁶⁵⁾ has found that differences in seawater composition affect the composition of the scale formed as demonstrated in table 3.

Table 3 Carbonate Minerals Observed in Deposits
on Cathodically Protected Steel⁽¹⁶⁵⁾

ENVIRONMENT	A (%)	C (%)	D (%)	M (%)
Artificial Seawater	25	40	30	5
Natural Seawater	0	80	0	20
High Organic Seawater	0	60	35	5

where A=Aragonite, C=Calcite, D=Dolomite, M=Magnetite

2.3.3 EFFECTS OF SULPHATE REDUCING BACTERIA AND BIOFILMS

As previously mentioned, for complete CP of steel in seawater a potential of $-780\text{mV}(\text{SCE})$ is recommended^(179,180). It is well known that in anaerobic environments, where SRB are present, a more negative potential is required to stop corrosion. Deciding on the potential required for successful CP in SRB containing environments can be a problem. This difficulty arises due to the fact that a large number of SRB genera exist, and parameters used may be specific to each anaerobic environment.

Horvath and Novak⁽¹⁸¹⁾ calculated that a CP potential of $-800\text{mV}(\text{SCE})$ was required for complete protection when sulphides were present, although they also showed that the more negative potentials could be required in some instances. Most of the microbiological work supports the widely accepted value of $-880\text{mV}(\text{SCE})$ for anaerobic environments, but some results have indicated that corrosion can occur at lower potentials. Booth⁽¹²⁷⁾ conducted polarisation studies on mild steel in sulphate free solutions containing SRB. Under these anaerobic conditions no sulphides were produced but corrosion was found at applied potentials of $-1095\text{mV}(\text{SCE})$.

For North Sea anaerobic clay, thermodynamic considerations gave a theoretical potential of $-950\text{mV}(\text{SCE})$ to stop corrosion⁽¹⁸²⁾. Fischer⁽¹⁸³⁾ found that CP applied at $-880\text{mV}(\text{SCE})$ was sufficient to protect steel in saline, SRB containing, clay sediment. Residual corrosion was found to be about 5 to 6 microns/year at this potential, in the temperature range $5\text{-}30^{\circ}\text{C}$.

The application of a more negative CP potential causes an increase in the alkalinity at the metal surface, and it has been suggested that this will suppress the growth of SRB⁽¹⁸⁴⁾. Sanders and Hamilton⁽¹⁸⁵⁾ found that efficiently applied CP minimised corrosion caused by SRB, but the activity of the SRB was not significantly reduced. This suggests that the more negative potential is required because of the more aggressive environment caused by the production of sulphides by the SRB, and that the increased potential has little effect on SRB activity. The fact that sulphide deposits have been found under marine biofouling on offshore structures protected at -950mV(SCE) ⁽¹⁸⁶⁾ adds weight to this argument. Maxwell⁽¹⁸⁶⁾ found that when compared to freely corroding specimens, the application of CP had inhibited heterotrophic and sulphate reducing bacteria. He argues that the freely corroding specimen is providing a more suitable environment in terms of surface area (corrosion product) and anaerobic zones (sulphide trapping by iron ions). This argument is partly backed up, as the work indicates that CP does not directly inhibit SRB and biofilm formation.

Jack and Worthington⁽¹⁸⁷⁾ studied the corrosion of cathodically protected steel in SRB containing soils. CP levels of -880mV(SCE) were found to stop corrosion, over extended periods of semi-continuous growth of the bacteria. They suggested that under protection could possibly enhance SRB activity, and therefore the microbial corrosion taking place, by supplying cathodic hydrogen, which can be utilised as an energy source. Hardy⁽⁸⁹⁾ had found that SRB were capable of utilising hydrogen generated at cathodic sites.

Dexter⁽¹⁸⁸⁾ has shown that marine biofilms change the morphology of calcareous scales formed on a stainless alloy, giving a more uniform film. It was also shown that a marine biofilm can either enhance or reduce the effectiveness of a CP system. The deciding factor was the applied cathodic current. If this was too low the resulting surface pH may be too low to inactivate the biofilm which could then cause problems. The high pH generated by some algae during photosynthesis may enhance formation⁽¹⁸⁹⁾ whereas the low pH values found under some animals such as sea anemones⁽¹⁹⁰⁾ could have the opposite effect.

Organic material has been shown to effect the structure of calcium carbonate precipitation⁽¹⁹¹⁾. Wilkins⁽¹⁷⁰⁾ has noted that polysaccharides (produced by biofilms) in seawater may influence the structure and form of the calcareous scale, as long chain molecules are used to control the thermal deposition of calcium carbonate and magnesium hydroxide scales on heat exchanger surfaces. Recent work⁽¹⁶⁷⁾ also has suggested that organic material produced by microfouling organisms can alter the physical characteristics of the calcareous scale, and thus possibly effect the protection afforded by the scale. Cathodically protected steel in seawater appears to be colonised faster by bacteria and microalgae compared to unprotected steel⁽¹⁹²⁾, and significant microfouling activity can occur at the same time as calcareous scale deposition, especially over long time scales (weeks).

The production of hydrogen by CP has been discussed in section 2.3.1, and it was noted that increasing the level of CP increased the hydrogen production. In SRB containing

environments an increase in CP levels is recommended, so increased hydrogen absorption would be expected. But in SRB containing environments, active SRB would produce sulphides which are known to poison the hydrogen recombination reaction and therefore would increase the volume of hydrogen absorbed. The combination of CP and SRB (sulphides) have been shown to be synergic⁽¹⁵⁹⁾ in relation to hydrogen absorption. Effects of hydrogen sulphide and sulphides in general on hydrogen entry are discussed in more detail in section 2.4.3.

2.4 HYDROGEN EVOLUTION AND ENTRY

2.4.1 MECHANISM OF THE CATHODIC EVOLUTION OF HYDROGEN FROM ALKALINE AQUEOUS ENVIRONMENTS.

The entry of hydrogen into steel is usually undesirable due to the damage that may result to the physical and mechanical properties. It has been stated in section 2.3.1 that the application of CP causes the production of hydrogen at the metal surface. Because of the extreme variation of the exchange current density found for the hydrogen evolution reaction (HER) on various metals, considerable changes in the reaction mechanism and energies are thought to occur from one metal to another⁽¹⁹³⁾. This cathodic evolution of hydrogen from alkaline electrolytes, such as seawater, is known to proceed in several successive stages, McCright⁽¹⁹³⁾ described them as follows;

- (1) transport of a hydrated proton (H_3O^+) to the double layer.
- (2) loss of the water of hydration shield in the vicinity of the double layer.
- (3) adsorption of the proton to the electrode surface.
- (4) discharge (electronation) of the proton to an adsorbed hydrogen atom.
- (5a) chemical combination of two adjacent hydrogen adatoms to form a hydrogen molecule, possibility of surface migration between site of discharge and site of recombination.
- (5b) electrodic combination of an adatom and a proton to form a hydrogen molecule.
- (6) desorption of H_2 .
- (7) bubble formation as H_2 molecules coalesce, and evolution of bubbles.

This is shown schematically in figure 13. The overall hydrogen evolution reaction

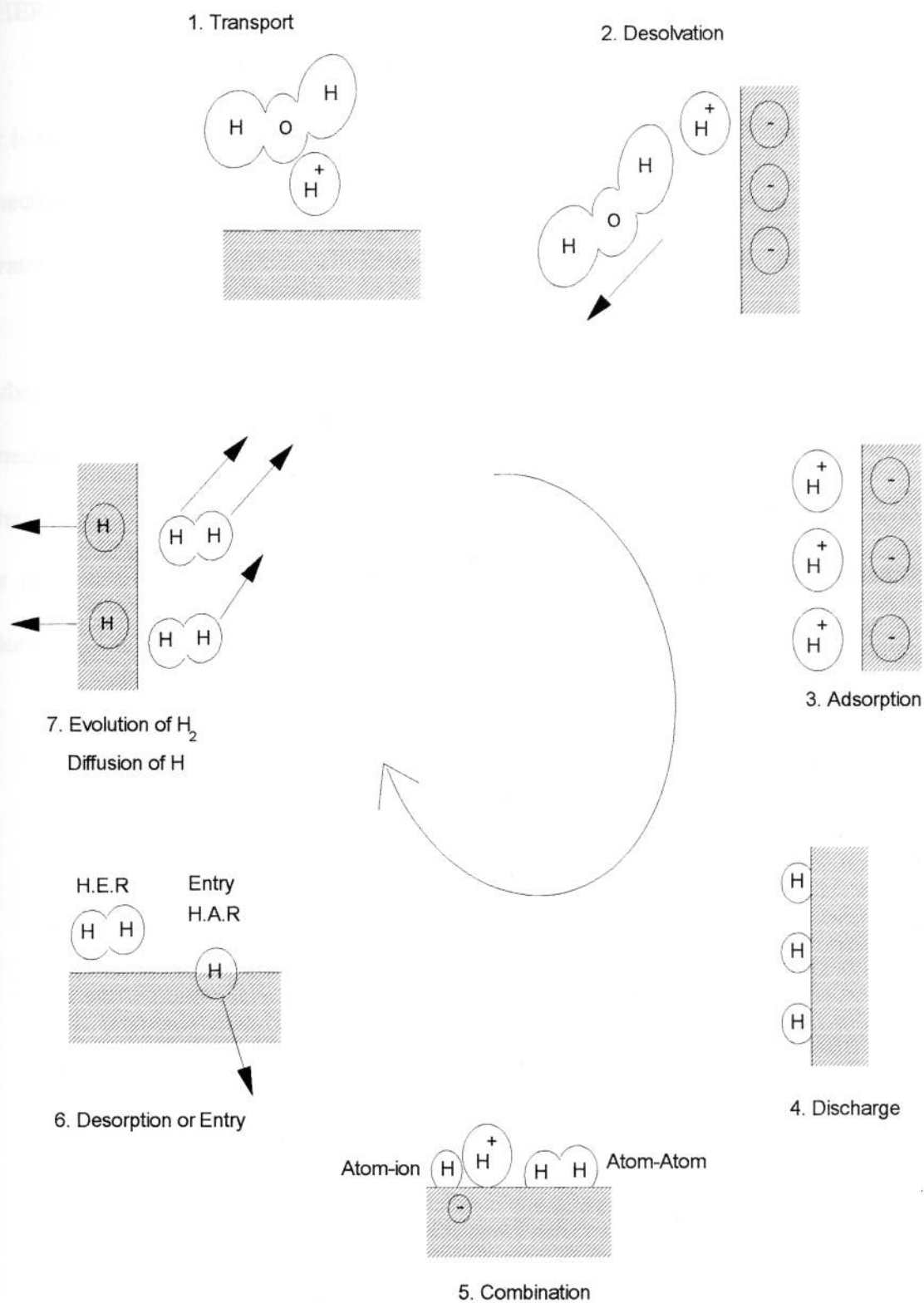


Figure 13. Schematic of Processes of Hydrogen Evolution and Absorption (after McCright)

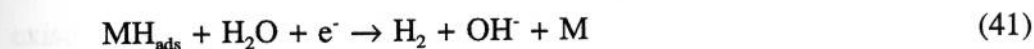
(HER) can be written,



It is now generally accepted that two successive steps are essential to the overall HER mechanism. The first step which is common to all metals, consists of reduction of water,



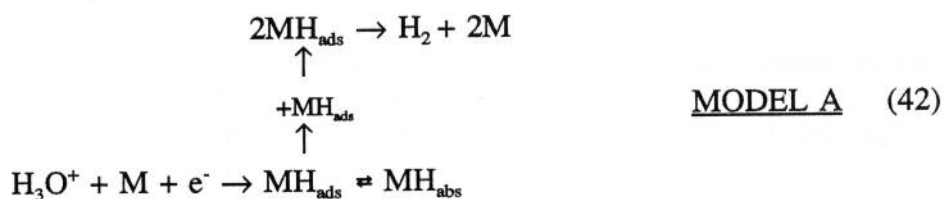
where MH_{ads} represents a hydrogen atom adsorbed on the metal surface. The presumed mechanism of the next step of HER depends on the nature of the electrode metal and the cathodic current density. The detachment of hydrogen atoms from the metal surface is thought to occur by either chemical desorption (equation 40) or electrochemical desorption (equation 41),



2.4.2 ENTRY OF HYDROGEN INTO METALS

In the case of metals which have the ability to absorb hydrogen, such as steel, both the HER and the hydrogen absorption reaction (HAR) occur simultaneously. This absorption provides an alternative reaction path to the chemical or electrochemical desorption of hydrogen atoms (reactions 39 & 40). Usually only a small portion of the hydrogen liberated at the cathode enters into the metal. The rate of hydrogen entry depends on many variables but certain compounds, such as hydrogen sulphide, promote hydrogen entry.

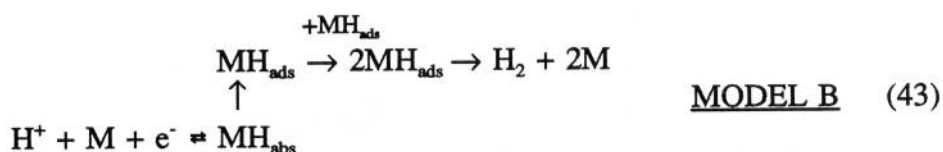
Two models for explaining hydrogen entry into the metal have been proposed. The first, model A^(194,195), considers that the hydrogen enters in the same elementary form as it exists on the surface (atomic hydrogen). Thus, the intermediate stage through which electrolytic hydrogen passes on entry to the metal substrate is the adsorbed state and is identical to that which leads to hydrogen evolution. The reaction sequence at the cathode surface is as follows (in acid).



Where MH_{ads} refers to adsorbed hydrogen on the surface, MH_{abs} refers to absorbed hydrogen directly beneath the metal surface. In this model the absorption step and recombination (chemical desorption) are competing. According to this model the entry rate should be proportional to the surface coverage of the metal surface by adsorbed

hydrogen atoms, Θ_H .

Bagotskaya⁽¹⁹⁶⁾ and Frumkin⁽¹⁹⁷⁾ have postulated that hydrogen enters the metal in the same elementary form in which it is discharged, that is, as a proton. Thus the intermediate state through which hydrogen enters the metal lattice is not identical with the adsorbed intermediate state which leads to hydrogen evolution. In this model B the HAR and the HER occur independently, and would compete for the same discharged proton. The reaction sequence at the cathode surface can be summarised as follows,



Horiuti⁽¹⁹⁸⁾ proposed two models of chemisorption that can be related to models A and B. The first model, called r-type adsorption, is shown schematically in figure 14. Hydrogen atoms are positioned outside the electronic cloud of the metal but are directly over a corresponding metal atom. The metal-hydrogen bond is about 0.25nm in length, is largely covalent, and the hydrogen is the negative part of the dipole. The second model, called s-type adsorption, is shown in figure 15. Hydrogen atoms are slightly within the metals electronic cloud and thus behave more like protons dissolved in the surface layer of the metal. The bonding is more ionic with hydrogen this time being positive. This second condition represents an energy state that is higher than the r-type adsorption. Lattice defects and any other surface imperfections will significantly reduce this energy and therefore s-type adsorption would be favoured. These adsorption variations affect the electrical resistivity of films. Results from resistivity measurements carried out on nickel and platinum, show r-type adsorption dominating at low hydrogen

coverages and the s-type at higher coverages. The model based on entry from adsorbed atoms (model A) is comparable to r-type adsorption, while entry from protons (model B) corresponds to s-type adsorption.

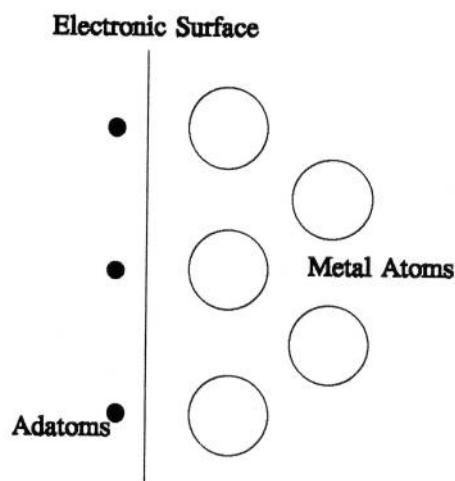


Figure 14. *r-Type Adsorption* (198)

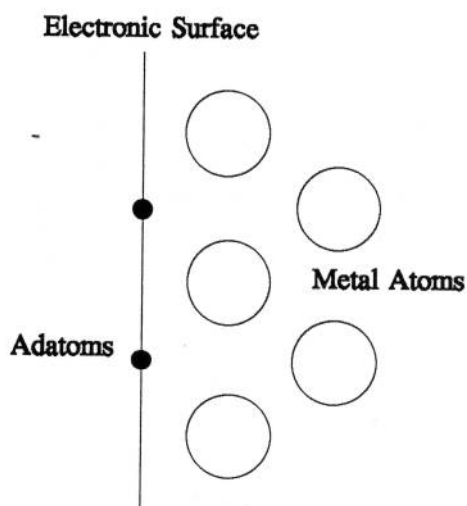


Figure 15. *s-Type Adsorption* (198)

Factors which control the rate of the HAR⁽¹⁶⁹⁾ are as follows;

(1) Metal potential/current density

The potential/current density has a major influence on the HER and consequently the HAR. From a thermodynamic point of view the activity of the hydrogen at the solution/metal interface establishes the boundary condition that determine the dissolved hydrogen concentration within the metal.

(2) Solution pH and Composition

In alkaline conditions a cathodic potential is required for the entry of hydrogen into the metal. This is due to the corrosion potential (E_{cor}) in alkaline solutions being above the reversible potential for hydrogen evolution. In general the lower the pH the higher the hydrogen entry rate. Anions can sometimes alter the HAR.

(3) Promoters

There are a number of species which can increase the kinetics of hydrogen entry into iron, steel and other ferritic alloys. In many cases, very small additions of these substances bring about a substantial increase in the hydrogen kinetics. The generic terms cathodic 'poison' and cathodic 'promoter' are often applied to these species as they are said to poison the HER and therefore promote hydrogen absorption.

Among the species which are known to promote hydrogen entry are certain compounds and elemental forms of Group V-A and VI-A elements of the periodic table. They are phosphorus, arsenic, antimony, bismuth, sulphur, selenium and tellurium. Other species which can increase hydrogen permeation are the halide ions, cyanide ions and the aromatic hydrocarbon naphthalene. Under some conditions salts of heavy metals such as mercury, tin and lead have been reported as enhancing hydrogen entry. Many of the

promoters mentioned form stable hydrides, for example, H_2S , H_2Te , H_2Se , PH_3 , AsH_3 and SbH_3 . The effect of hydrogen sulphide on hydrogen entry is discussed in more detail in section 2.4.3.

(4) Temperature

Available data indicate that the tendency for sulphide cracking in susceptible steels decreases markedly with increasing temperature. A maximum susceptibility is observed in the vicinity of room temperature. Treseder⁽⁵⁶⁾ has noted, however, that this beneficial effect of increased temperature is observed in all systems where the hydrogen charging is introduced by any common method: corrosion, cathodic charging, and exposure to hydrogen gas. Therefore he concluded that the temperature effect is related to effects within the metal rather than to a surface reaction effect.

(5) Stress

The effect of applying uniaxial tensile stresses to an iron specimen during cathodic hydrogen charging has been investigated by Beck⁽⁷³⁾. The effect of tensile strain increases the concentration of absorbed hydrogen because of dilation of the interstitial lattices sites where hydrogen lodges. The diffusivity of hydrogen did not change from the unstressed to the stressed condition so that the increase in permeability measured by these authors was due to the increase in solubility. With regard to the promoter species, the presence or absence of these substances seems to be less important during dynamic straining.

2.4.3 EFFECTS OF HYDROGEN SULPHIDE.

Several types of compounds have been found to promote the entry of hydrogen into metals from both liquids and gaseous environments. One such compound is hydrogen sulphide which as previously mentioned is a by-product of SRB activity. It is known to accelerate not only general corrosion but also stress corrosion cracking of steel. The embrittlement phenomena observed in hydrogen sulphide containing environments have been termed sulphide stress cracking or sulphide corrosion cracking, but it is generally accepted that this type of failure occurs as a result of hydrogen embrittlement.

These promoters often show their full effect at relatively low concentrations, and sometimes the promoting action decreases with increasing concentration. The decrease in promoting action has been explained by co-deposition of metallic compounds occurring as the promoter concentration increases. In the case of sulphide there is no corresponding sulphur formation, so the hydrogenation enhancement occurs over a much wider concentration range and generally increases monotonically with concentration of the concentration of the promoter species⁽¹⁹³⁾.

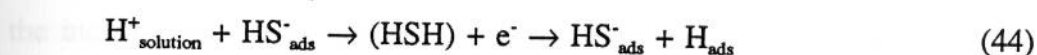
In spite of numerous investigations, the influence of hydrogen sulphide on the HER and HAR is neither well established nor understood. This is due mainly to the metal-water-hydrogen sulphide system being very complicated. Hydrogen sulphide can be adsorbed on the metal surface as H_2S or HS^- in competition with H_2O and OH^- . Although the mechanistic role of hydrogen sulphide in promoting the entry of hydrogen into iron

based alloys has not been determined with certainty, the fact that hydrogen embrittlement occurs in sulphide containing environments is unquestioned. Thermodynamic data predict that iron sulphide films will tend to form in preference to oxide films, because the equilibrium potential for the Fe/FeS reaction is more negative than that for the Fe/Fe₃O₄ reaction.

Smialowski⁽¹⁹⁹⁾ measured the elongation of iron wires charged with hydrogen in the presence of promoters. Tests were carried out with the group V-A and VI-A elements. Because the form of the element appearing to cause the hydrogenation of the coil was either the hydride or a compound easily reduced to the hydride, these investigators concluded that the hydride form of the poison was a necessary condition for hydrogenation.

Newman and Shreir⁽²⁰⁰⁾ have confirmed previous findings that the hydride of these promoters is the most significant species in the mechanism of hydrogen entry into steel during cathodic polarization, and that the amount of hydrogen absorbed is related to the bond strength of the hydride. They also showed that a promoter is only effective in the pH range in which the hydride is stable. The paramount role of hydrides in promoting entry into iron and steel has further been confirmed by a series of investigations conducted with a rotating disc electrode⁽²⁰¹⁾. This technique has permitted a comparison to be made of the effects of different compounds over a wide range of pH and electrode potential.

Addition of H_2S to an aqueous solution containing an iron specimen causes the metals E_{corr} to become less noble and the current density (at a given potential) to increase⁽¹²⁰²⁾. Explanations given for enhancement of the HER by H_2S are as follows. The first theory⁽²⁰²⁾ assumes that H_2S is adsorbed on the iron surface, as HS^- ions, which modify the activation energy of the HER. The adsorbed HS^- ions then act as proton transfer centres as shown in equation 44:



The above mechanism could be formulated with H_2S as the proton transferring species instead, noting the far higher bulk concentration of H_2S compared to HS^- in acid solutions (figure 16).

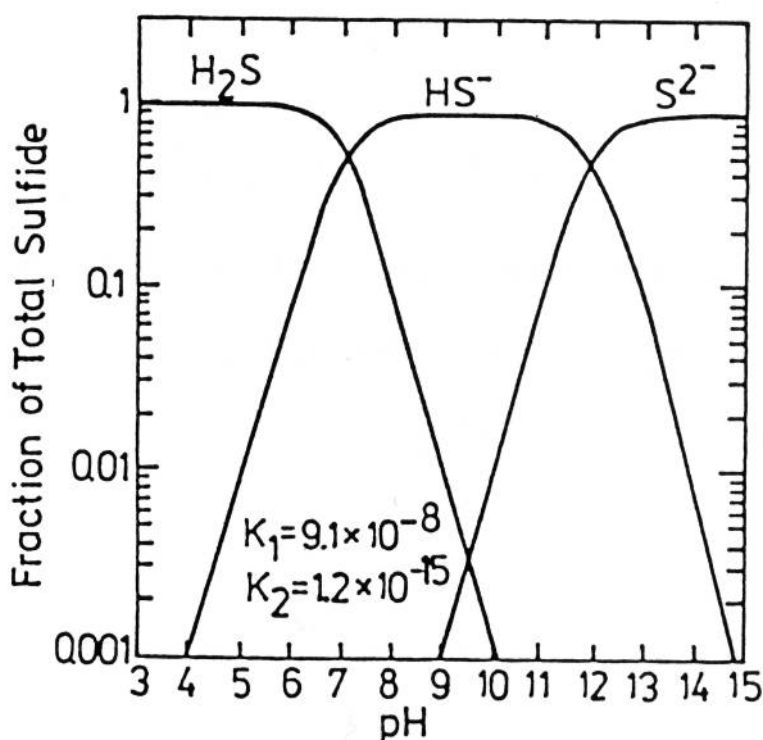


Figure 16. Relative Abundance of H_2S , HS^- and S^{2-} as a Function of pH.

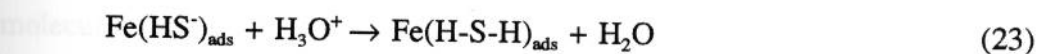
Bolmer⁽²⁰³⁾ postulated that in the presence of H₂S, hydrogen evolution may be represented by the following overall reaction;



which is limited by diffusion of H₂S to the electrode surface. The diffusion current appeared to be dependent on the partial pressure of H₂S. Above the diffusion current the electrode reaction is decomposition of either HS⁻ or H₂O. Kaesche⁽²⁰⁴⁾ interpreted the increase of cathodic current in the presence of H₂S on the basis of the favoured reaction (46) which is also characterised by a limiting current.



From work⁽²⁰²⁾ using a rotating disc electrode, it was concluded that H₂S does not directly participate in the cathodic reactions, but HS⁻ accelerates the discharge of hydrogen ions by the following reactions;



In this model, reactions (19) and (23) are quasi-reversible and the last reaction (24) is the rate determining step. The interpretations from the work were incomplete in the sense that the reaction parameters remained unknown. Also, as figure 16 demonstrates, in acid solutions there is a far higher concentration of H₂S relative to HS⁻.

Other investigators⁽²⁰⁵⁾ have expressed differing views concerning the mechanism of the HER in acidic H₂S solutions. They suggest that the elementary reactions of the HER are proton discharge and recombination of adsorbed hydrogen atoms, with the rate

determining step being proton discharge. The mechanism of the HER does not change in the presence of H_2S , but undissociated molecular H_2S adsorbed on the steel surface accelerates the proton discharge by the following reactions;



It was demonstrated that H_2S did not change the Tafel slope, but decreased the cathodic overpotential in acid solutions. Therefore, the molecular H_2S adsorbed on the steel surface acts as a bridge-forming ligand for the proton discharge.

As previously mentioned, the mechanisms by which promoters enhance hydrogen entry (HAR) into metals has not yet been satisfactorily explained. Previously, this was often attributed to 'poisoning' of the recombination reaction of adsorbed hydrogen atoms into molecules (equation 52):



This 'poisoning' was thought to either increase the coverage of the metal surface by hydrogen atoms, (θ_{H}) ,⁽²⁰⁷⁾ or to decrease the M-H_{ads} bond energy^(196,200). Lowering of this bond energy would increase the activation energy required for the discharge process of the HER. Therefore, it would be expected, that the hydrogen overvoltage would increase with increasing poison concentration. But it is well established that H_2S actually

decreases the hydrogen overpotential, so the poisoning model does not apply in this case⁽²⁰²⁾.

It has been proposed⁽²⁰⁶⁾ that when H₂S is present, competition for adsorption sites occurs between the respective molecules and reactions similar to 50 and 51 occur for H₂S:



reactions 51 and 52 are kinetically fast whereas reaction 55 is slow, hence in solutions containing H₂S the formation of H₂ is slowed, increasing the amount of hydrogen absorbed into the metal.

Another theory⁽²⁰²⁾ based on competition for adsorption sites argues that volatile hydrides of the elements belonging to the V-A and VI-A groups are strongly chemisorbed by clean metal surfaces. Thus their catalytic action has been assumed to be connected with the so called dissociative chemisorption of their molecules. Chemisorption of water and other hydrides have been described as occurring according to the following reactions⁽²⁰²⁾;



where M is a surface metal atom and X is the promoting element of valence n. One radical of the XH_(n-1) type of OH is assumed to cover two sites in chemisorption, while the detached H atom occupies another single site on the metal surface. When such a film is attacked by more hydride molecules, these attempt to dislodge the H atoms from their positions, and this might facilitate their entry into the bulk metal phase.

The force constant of water molecules is greater than that of either H_2 or $H_nX^{(202)}$. It is thought, therefore, that compared to water, the H_nX molecules chemisorbed dissociatively have a more pronounced ability to transmit hydrogen atoms by producing a larger number of transmission sites. The possibility that the water molecule itself can promote hydrogen entry was suggested by Newman and Shreir⁽²⁰⁰⁾. Wei and Simmons⁽²⁰⁸⁾ similarly suggested that absorption of hydrogen into a high strength steel, in amounts to cause HE, may result from the dissociative chemisorption of water molecules.

2.5 IRON SULPHIDES

Corrosion mechanisms involving SRB have been suggested where iron sulphides play a major role (section 2.2.3). An important feature of the mechanisms involve the nature of the iron sulphide formed, in particular whether it is protective or non-protective. There are six naturally occurring iron sulphide minerals that can be classified as single species^(209,210). All the naturally occurring iron sulphides except marcasite have been found singly or in mixtures in laboratory cultures of SRB, adjacent to corroding buried steel⁽²¹⁰⁾, in sour gas corrosion products or soil environments⁽¹³⁵⁾. Most iron sulphides have been shown to be potentially corrosive to steel by polarisation techniques^(128,210). Their corrosiveness has been further demonstrated using weight-loss techniques⁽¹³⁵⁾. The various iron sulphides are described below:

Mackinawite

The chemical formula for mackinawite is $\text{Fe}_{(1+x)}\text{S}$ (or $\text{FeS}_{(1-x)}$) where $x=0.057$ to 0.064 and has a tetragonal crystalline structure⁽²¹⁰⁾ and is black in colour⁽²¹¹⁾. It is known to be the initial product in the bacterial reduction of sulphate in the presence of ferrous ions and the initial product of the reaction between ferrous (iron II) sulphate and sodium sulphide⁽²¹⁰⁾.

Pyrrhotite

The chemical formula for pyrrhotite is $\text{Fe}_{(1-x)}\text{S}$ where $x=0.14$ to 0 . This is an iron-deficient iron sulphide with a structure ranging from Fe_7S_8 to stoichiometric troilite (FeS). The crystal structure is that of nickel arsenide and it is a p-type

semiconductor⁽²⁰⁹⁾. It has been found in old batch cultures of SRB and is presumed to be formed by the long aging of mackinawite, greigite and smythite⁽²¹⁰⁾.

Greigite

The chemical formula for greigite is Fe_3S_4 , it has a cubic structure. It is the product of the sulphidation of mackinawite⁽²¹⁰⁾. It is black in colour⁽²¹¹⁾.

Smythite

The chemical formula is $\text{Fe}_{(3+x)}\text{S}_4$ where $x=0$ to 0.25 and has a rhombohedral structure. Smythite results from the sulphidation of siderite (FeCO_3)⁽²¹⁰⁾.

Marcasite

The chemical formula for marcasite is FeS_2 and its structure is orthorhombic. This ferrous polysulphide is formed from mackinawite and elemental sulphur⁽²¹⁰⁾.

Cubic FeS

This does not occur naturally⁽²⁰⁹⁾.

Pyrite

The chemical formula for pyrite is FeS_2 . This is the cubic dimorph of marcasite. It is the product of the reaction between either a ferrous salt or mackinawite and a polysulphide solution⁽²¹⁰⁾. It is a semiconductor and is yellow in colour⁽²¹¹⁾.

Mara and Williams⁽²¹⁰⁾ demonstrated that all the naturally occurring iron sulphides except smythite (which was not tested) caused both anodic and cathodic depolarisation of iron electrodes. It was found that chemically prepared samples gave greater depolarisation than biogenically produced sulphides.

Mara and Williams⁽¹³⁸⁾ suggested a cathodic depolarisation mechanism for corrosion by iron sulphides, in which hydrogen evolved at cathodic sites on the steel surface is absorbed by the iron sulphide in proportion to its cationic defects. King⁽¹³⁵⁾ carried out weight-loss experiments which contradicted this theory. It was suggested that iron sulphide was the cathode in a galvanic cell with iron as the anode. The hydrogen evolution reaction would then occur on the sulphides. The corrosion rate would decrease in relation to the rate of hydrogen build-up in the iron sulphide.

The corrosiveness of dissolved sulphides has been shown to be closely related to both sulphide concentration and pH⁽²⁰⁹⁾. At sulphide concentrations above 515ppm in the oil/brine/H₂S system a hard adherent iron sulphide scale was observed to form on the steel surface which gave a fair degree of protection. Lower sulphide concentrations resulted in a film that was non-adherent, gelatinous and gave little or no protection.

In the H₂S/CO₂/H₂O/Fe system, protective scales were formed which were mainly composed of pyrrhotite and pyrite at low sulphide ion concentrations (15 to 1700ppm). At higher concentrations (1700 to 66000ppm) a non-protective mackinawite scale was formed.

The composition and protectiveness of iron sulphide scales is affected by the initial solution pH. The least protective, mackinawite, formed preferentially when the initial pH was 6.5 to 8.8, a more protective pyrrhotite/pyrite forming outside this pH range.

The primary film created by SRB corrosion appears to be mackinawite and siderite (FeCO_3). Only the latter is protective, but both are transformed by sulphidation under anaerobic conditions to greigite and smythite, with eventual transformation to pyrrhotite which is non-protective⁽²¹²⁾. These processes are shown schematically in figure 17.

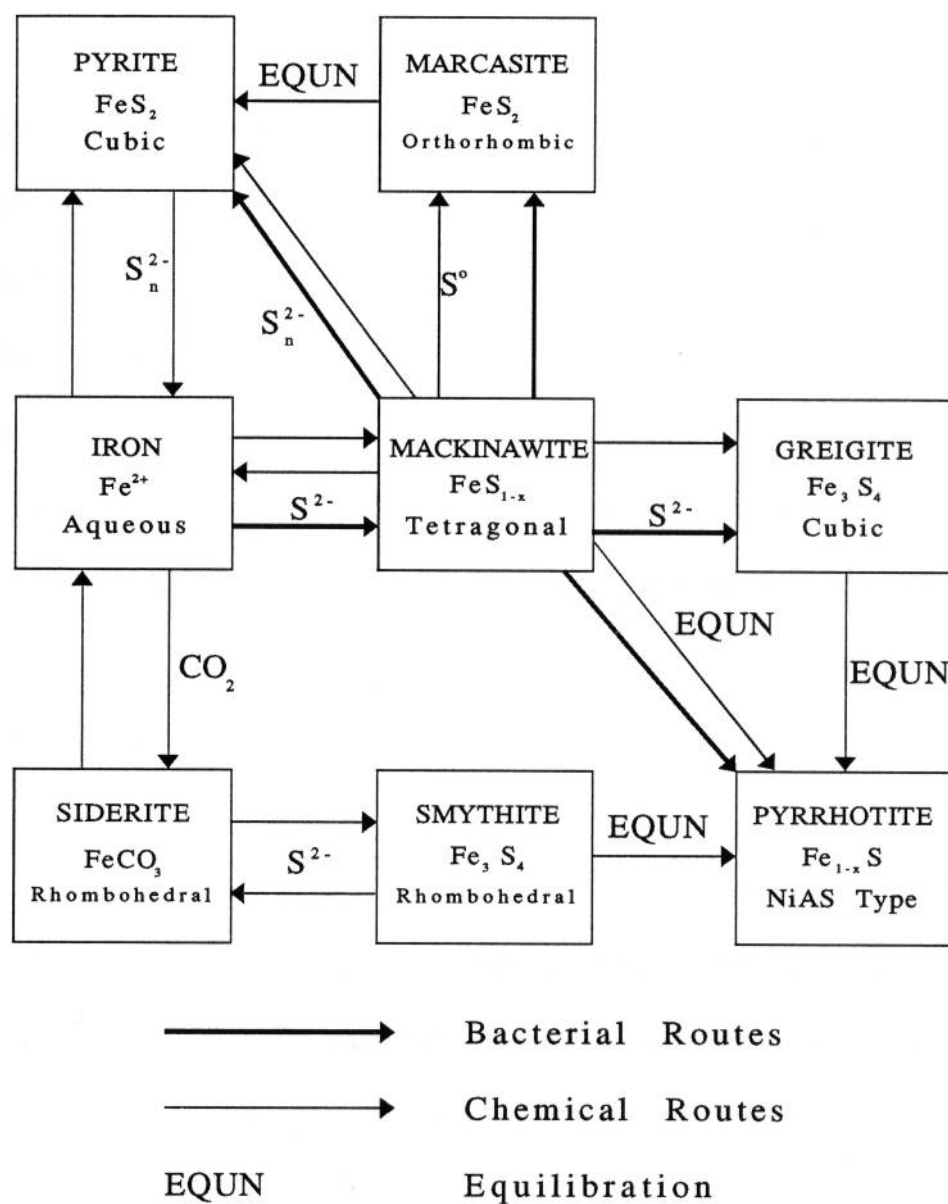


Figure 17. Interrelationships Between the Sulphides of Iron
(After Tiller)

2.6 CORROSION FATIGUE OF OFFSHORE STRUCTURAL STEEL

2.6.1 INTRODUCTION

Corrosion fatigue can be defined as the result of the combined effects of a corrosive environment and applied cyclic stress to produce failure of a metal by the development and growth of cracks. It has been found that no metal is immune from some reduction of its resistance to cyclic stresses due to corrosion fatigue⁽²¹³⁾. Of the failures that occur in engineering components, 90% can be attributed to fatigue⁽²¹⁴⁾. Corrosion resistant metals are protected against continuous damage by the formation of primary films (usually oxides). Cyclic stresses continually disrupt the protective films causing fresh surfaces to be exposed to the corrosive environment, so creating weakening fissures and cracks to be increasingly formed.

The effect of seawater waves on static metal structures such as offshore oil production platforms provides a combination of a corrosive environment with cyclic stresses. These stresses on offshore structures are mostly produced by the hydrodynamic loading of the structure due to wave action ($\sim 10^8$ wave cycles of stress in 20 years), in addition, there are relatively high frequency vibrations due to machinery and low-frequency transient stresses produced by wind and cargo movements. Sea waves have an average frequency of 0.167Hz ($\sim$ one wave every six seconds), with the wave action having most effect on the parts of the structure between and just below the tide marks. In open seawater the corrosion is greatest around the tidal area, due to the very high oxygen availability.

It is well established that compared to fatigue in air or vacuum, a saline or seawater environment lowers the fatigue strength of steels. The presence of pollutants like oil, urea and ammonia in seawater do not seem to affect the corrosion fatigue behaviour of steel⁽²¹³⁾. Generally, higher acidity is known to decrease corrosion fatigue strength of steels, while highly caustic solutions are known to improve corrosion fatigue performance⁽²¹³⁾. Testing of the same steel in saltwater solutions with different pH values indicated that variations over a broad range of pH (4-10) showed little influence on fatigue resistance⁽²¹⁵⁾. Only values of pH below 4 decrease fatigue resistance, while at pH values above 12 fatigue strength is not affected. These pH values however, are for bulk aqueous solutions and may be different to those existing at the mouth of any pits formed during corrosion fatigue testing⁽²¹⁶⁾.

Until recently, the fatigue testing of steels intended for offshore use had been carried out with unrepresentative conditions, such as high frequency cyclic loading. Once it was realised that more realistic environmental conditions were required, tests began to be carried out in seawater at frequencies closer to those of sea waves. Unfortunately problems arose with the use of natural seawaters due to the non-reproducibility of results. The use of seawater of varying origin and thus composition (inorganic and organic) was the cause, so artificial seawater (no organics) became the standard test environment. The effects of sulphide on stress corrosion cracking (SCC) and HE have been studied for some time, but use of H₂S containing environments for corrosion fatigue testing is a recent development. Some early work on corrosion fatigue in aqueous H₂S environments was carried out to investigate crack growth mechanisms, but

the possibility of bacterially generated H_2S being important in the corrosion fatigue of offshore steels was overlooked or dismissed. However, the safety problems of biologically produced H_2S in enclosed areas such as the interiors of jacket legs and oil storage tanks led to a realisation that H_2S can reach significant levels in seawater in and around offshore structures. This, coupled with the problems associated with the transport of 'sour' oil and gas, created a demand for corrosion testing in H_2S environments.

2.6.2 SEAWATER AND SALINE SOLUTIONS

If a steel does not exhibit SCC in seawater, but displays 'true' corrosion fatigue, there are two possible mechanisms of crack growth, anodic slip (stress assisted) dissolution and/or hydrogen embrittlement⁽²¹⁷⁾. Dissolution occurs during corrosion by the anodic reaction;



Assuming a bare surface exists at the crack tip, the maximum possible crack velocity, V , due to dissolution⁽²¹⁸⁾ is given by:

$$V = (M_A i_a) / (n \rho F) \quad (58)$$

where M_A is atomic weight, $n=2$, ρ is the metals density, F is the Faraday constant and i_a is the current density of the bare surface. In aqueous environments, the cathodic reaction at the crack tip involving hydrogen evolution is:



As shown in section 2.4.1, reaction (32) occurs in two stages, making it possible for hydrogen to enter the metal. Changes to the chemical environment of the solution may promote or inhibit these reactions. Consequently it is possible to utilize solution additions to determine whether hydrogen entry is the relevant crack growth mechanism for the overall environmental conditions of temperature, potential, solution composition and loading conditions of R ratio and frequency, such solution additions have been used in several studies^(219,220). Concern has been expressed⁽²¹⁸⁾ that the passivation rate may also be altered by these solution additions. However, it was suggested⁽²¹⁸⁾ that this was only of concern for SCC tests, as a bare surface can be continuously maintained during

the opening part of a fatigue cycle. Therefore, the use of solution additives is a useful diagnostic method, especially for corrosion fatigue crack growth mechanisms.

Although some success has been achieved in producing quantitative models of environmental crack growth based on the dissolution model^(218,221), the dissolution mechanism has been challenged on the grounds that an impossible high current density is required to produce the observed cracking rates, and that as ΔK increased the necessary current density would also increase⁽²²²⁾. The successful prediction of environmental crack growth rates^(218,221) refutes this claim and the maximum possible environmental enhancement of crack growth rates due to dissolution mechanism is considerable for mild steel^(223,224). The maximum enhancement is larger than those observed by Vosikovsky⁽²²⁵⁾ for X65 pipeline steel in 3.5% NaCl solution. Nevertheless, there remains many environments (dry H_2 , sour oils) and situations (high strength steels in seawater) where a dissolution mechanism is not responsible for the environmental enhancement of crack growth rates, which are then due to the operation of a hydrogen embrittlement mechanism.

Cowling⁽²¹⁷⁾ concluded that at the free corrosion potential the mechanism of fatigue crack growth for BS4360:50D in 3% NaCl or seawater appeared to be anodic dissolution. Altering the environmental conditions to promote hydrogen entry into the steel causes the mechanism to change to that of hydrogen embrittlement. Increased hydrogen absorption can occur due to CP, and it is not clear whether the anodic dissolution mechanism would be relevant to corrosion fatigue crack growth of correctly protected

steel.

It is well known that the application of CP to steel in seawater and saline solutions can improve the corrosion fatigue resistance, sometimes giving crack growth rates similar to that found in air tests^(175,226-229). In some cases it has been reported that the improvement gives performance better than that found in air^(172,230). Cowling⁽²¹⁷⁾ found that crack growth rates increased as the CP potential went more negative than -800mV(SCE) and more positive than -700mV(SCE), in other words, a minimum in the enhancement of crack growth was seen. It was concluded that the former effect was due to increased formation of hydrogen at the crack tip and the latter was due to an alternative mechanism operating (anodic dissolution). Another suggested reason for the minimum in the enhancement is that the polarisation effects the hydrogen embrittlement mechanism⁽²³¹⁾. Cowling⁽²¹⁷⁾ argues against this, stating that the pH for maximum hydrogen embrittlement in his material would be 5.4, and that the pH of seawater is ~8 rising to at least 11 in the crack when protected at -1000mV(SCE).

Other work⁽¹⁷⁵⁾ has shown that -800mV(SCE) gives crack growth rates similar to air, but increased protection (-1000 and -1100mV(SCE)) was clearly harmful to the crack growth. Similar results have been found by other workers⁽²³²⁾, and has often been explained by the increased hydrogen being produced within the crack as the potential becomes more negative.

The enhanced corrosion fatigue crack growth rates observed in cathodically protected

low alloy steels in saline environments are a result of absorbed hydrogen atoms⁽²³²⁾. The magnitude of the crack advance occurring during a fatigue cycle will depend generally on the hydrogen atom concentration which accumulates local to the crack tip (region of triaxial stress) and also on the response of the steel to this hydrogen content under the local stress/strain conditions. The concentration of atomic hydrogen which accumulates is dependent on mass transport (by diffusion and dislocation transport), the nature and density of trapping sites and the actual concentration of atomic hydrogen in the steel⁽²³³⁾. The main source of hydrogen atoms in cathodically protected structural steel is from reduction of water (equation 32). That portion of hydrogen which does not recombine to form H_2 enters the metal lattice, diffuses within the crack tip region, segregates at microstructural trap sites and enhances fatigue damage as well as crack growth rates⁽²³⁴⁾. The kinetics of this process will vary between the crack tip, crack walls and external specimen surfaces (bulk charging) because of both localized crack tip straining and the differences in environmental conditions between the crack and bulk environment⁽²³³⁾.

Turnbull⁽²³³⁾ has developed a model to predict the generation rate of atomic hydrogen at the tips of fatigue cracks for cathodically protected steels in marine environments. The model predicted that external specimen surface can become the dominant atomic hydrogen source at potentials greater than -900mV(SCE) (cyclic frequency of 0.1Hz and R of 0.5). This prediction was not dependent on the specific cracking mechanism. The model also predicted that the tendency for bulk charging would become dominant with decreasing frequency. Also, increasing the stress level through increasing R or ΔK will

increase the state of charging of the steel local to the tip if crack tip charging is dominating, and this effect can be explained on the basis of the increased area of active surface at the tip. Therefore, the relative importance of bulk charging depends on the specific test conditions and is influenced by the potential, bulk chemistry, cyclic frequency, specimen thickness, temperature and use of coatings⁽²³⁶⁾. Laboratory test times are usually short in relation to the time required for hydrogen transport. Thus measured crack growth rates may be lower than those occurring in practice, where there is sufficient time for full hydrogen charging^(233,237). In order to obtain reliable crack growth measurements of value to long life endurance predictions, test times in the laboratory should be at the very least be long enough to ensure that steady state conditions of hydrogen charging are obtained. Ideally, a time dependent solution involving the contribution from the crack tip, crack walls, and notch would provide the most definitive information, but no solution of the relevant transport equations exist at present. Nevertheless, a reasonable approximation of the time to achieve steady state charging can be derived by considering only bulk charging and ignoring the presence of the crack. If tests are insufficiently long, bulk charging would be expected to have an influence on the shape of the crack front as the crack grows with the growth rate near the surface, where hydrogen supply is easier, being greater than at the midpoint of the specimen. This would cause the slightly concave crack front common in testing of fracture mechanics specimens to become straight or convex.

For a uniformly charged plate specimen the concentration at the mid thickness tends asymptotically to a steady state. An arbitrary time has been adopted, which is the time

to achieve a concentration of 50% of the steady state value at mid thickness. The quantitative expression for this time constant ($t_{0.5}$) is :

$$t_{0.5} = 0.38 L^2 / D_{\text{eff}} \quad (59)$$

where L is the half thickness of the specimen and D_{eff} is the effective diffusion coefficient. Whether this adequately approximates the time to steady state depends on the sensitivity of crack growth to hydrogen content. Nevertheless, it allows an assessment of the effects of thickness and diffusion coefficient. The diffusion coefficient for hydrogen atoms is particularly variable in steels. For BS4360 50D steel, permeation measurements suggest an effective diffusion coefficient of $4.0 \pm 2.0 \times 10^{-7} \text{ cm}^2\text{s}^{-1}$. The time constant would be 17 days for a 25mm compact tension specimen and test times should be well in excess of this value. Diffusion coefficients lower than this have been measured on quenched and tempered steels, for example $2.0 \times 10^{-8} \text{ cm}^2\text{s}^{-1}$. In this case the test period would be about one year. Griffiths⁽²³⁷⁾ found that the effect of bulk charging was greater than predicted. It was suggested that the Turnbull model⁽²³³⁾ may be non-conservative and even longer term testing may be necessary.

Dvoracek⁽²²⁶⁾ tested cathodically protected carbon steel specimens which had been butt welded. The author states that the hardest part of the weld ($23R_c / 254\text{VPN}$) was hard enough to be affected by hydrogen embrittlement, and so when the specimen did not fail after 10^7 cycles, it was concluded that overprotection ($-1200\text{mV}(\text{SCE})$) does not promote hydrogen embrittlement or the embrittlement does not promote corrosion fatigue. It could be argued that the maximum weld hardness is on the borderline of susceptibility, so the lack of obvious hydrogen embrittlement could be expected.

The main difference between NaCl solutions and seawater is the presence of carbonate and bicarbonate buffer in seawater. Application of CP to a metal in seawater causes a calcareous deposit to be deposited onto the metal surface and within cracks. Calcareous deposits deposited into the crack play an important role in the reduction of crack growth rates in seawater⁽¹⁷⁵⁾. Hartt⁽¹⁷²⁾ has emphasized that the formation of calcareous deposits plays an important role in decreasing fatigue crack growth under CP in synthetic seawater. Okada⁽²³⁸⁾ did not find any calcareous deposits within the crack so concluded that the pumping action associated with the open-close behaviour of the crack squeezed the calcareous products out of the crack. This effect has been observed by other researchers^(162,239), and offers an explanation why crack growth rates in seawater have been found to be lower than those in 3% NaCl solution⁽¹⁷⁵⁾.

Many workers^(225,175,240) have obtained corrosion fatigue results for which there is a part of the da/dN versus ΔK curve where the crack growth rate is constant over a range of values of ΔK , ie there is a region where the crack growth where da/dN does not depend on ΔK . These regions have been called 'plateaus' and for mild steels in seawater or 3% NaCl solution their cause is attributed to hydrogen embrittlement occurring at the crack tip. It is probable that the plateau represents a rate limiting step operating in the sequence of events that leads up to the actual embrittlement of the metal by hydrogen. This rate limiting step could be the transport of hydrogen through the metal from the surface to the actual site of embrittlement, the formation of H_{abs} on the metal surface or its entry into the metal, or even the transport of fresh solution down the crack. The last possibility is supported by the work of Vosikovsky⁽²⁴¹⁾ on X65 pipeline steel in crude oil

containing H_2S . In corrosion fatigue, the oscillating load contributes to the exposure of fresh metal surface by resharpening of the crack and breaking surface films. In addition, it promotes the transport to the crack tip region of fresh solution and the removal of corrosion products.

For BS4360:50D steel in 3.5% NaCl solution, Cowling⁽²¹⁷⁾ found no effect of R ratio over the range $0.1 < R < 0.7$ at the free corrosion potential. Fatigue crack growth rates in a C-Mn steel have been shown⁽²⁴²⁾ to be insensitive to the R ratio for a lakewater environment. These results are not consistent with other work⁽²¹⁷⁾, Murakami⁽¹⁷⁵⁾ found that the crack growth rate in their steel increased with increasing R ratio at -800mV(SCE) in seawater. Scott⁽²⁸²⁾ showed that positive stress ratios significantly accelerate the crack growth rates and that the effect saturates between $R = 0.5$ and 0.7 . In air, the stress ratio effect has been explained⁽¹⁷⁵⁾ by using the effective stress intensity which takes into account crack closure. This effect in seawater becomes complicated because of calcareous deposits precipitated within the crack planes^(217,175).

Hamono⁽²⁴³⁾ found that corrosion products were produced within the fatigue crack of a steel specimen in 3.5% NaCl protected at -1100mV(Ag/AgCl), and concluded that the corrosion products had caused a crack closure effect. It was argued that the reaction in cracks is regarded a function of the local electrode potential and solution composition which is different to that of the bulk solution, so dissolution may occur at a crack tip during effective CP of the outer surface. Other work⁽²⁴⁴⁾ has displayed corrosion product wedging of fatigue cracks in steel, and even crack arrest due to the build up of corrosion

products has been reported⁽²⁴⁴⁾.

2.6.3 EFFECTS OF HYDROGEN SULPHIDE AND FOULING

There are four ways in which marine fouling may affect offshore structures⁽²⁴⁶⁾:

1. Obscuring the substratum.
2. Enhancing corrosion.
3. Increasing hydrodynamic loading.
4. Enhancing corrosion fatigue.

Corrosion of metals below marine fouling can be enhanced as follows⁽²⁴⁶⁾:

1. By its physical presence creating macro/microscopic concentration cells.
2. By producing corrosion promoting metabolites (H_2S).
3. Stimulation of the cathodic or anodic reaction.

The most important fouling community metabolite connected with corrosion fatigue enhancement is H_2S , it is particularly aggressive, as sulphide ions both stimulate anodic dissolution and poison the hydrogen recombination reaction thus making more hydrogen available for embrittlement⁽²⁴⁶⁾. Dramatic increases in crack growth rates have been demonstrated in H_2S saturated environments^(241,247,248). Indeed, the effect of H_2S on corrosion fatigue crack growth in seawater is usually assessed by tests conducted in seawater saturated with H_2S (~3150ppm)⁽²⁴⁰⁾. This very severe test represents a condition extremely unlikely to exist in natural environments^(240,86), typical values of H_2S produced by SRB are given in section 2.2.1.

Recent studies^(162,86) have used more realistic concentrations of H_2S . Edyvean⁽⁸⁶⁾ carried out corrosion fatigue tests on steel in both H_2S saturated seawater and seawater containing various levels of H_2S produced by the bacterial decomposition of algal material. Crack growth rates

were found to be very similar between the two conditions when the biological sulphide was at a concentration of 600ppm. It was suggested that there may be a threshold concentration of H_2S above which no further effect on corrosion fatigue crack growth rates are seen. This suggestion was supported by work carried out by Assefpour-Dezfuly⁽²⁴⁰⁾.

Assefpour-Dezfuly⁽²⁴⁰⁾ carried out similar work on steel and steel weldments but used a seawater solution with H_2S (abiological source) concentrations in the range 10-150ppm. In seawater the application of a cathodic potential of -1V(SCE) caused the crack growth rate to double (in the intermediate ΔK region where plateau behaviour is observed) compared to freely corroding steel in seawater. Similar trends were observed for weldments, although higher crack growth rates were observed compared to the base plate because of differences in microstructure and the presence of residual stresses. The addition of 2 to 10ppm of H_2S to the seawater caused crack growth rates in the protected specimen (-1V(SCE)) to increase by 2.5 times in the plateau region. Increasing the H_2S concentration to 30 to 50ppm gave no significant change in crack rates but increasing the concentration to 100 to 150ppm caused a significant increase.

It was concluded that because the crack growth rates obtained were similar to those obtained using a biological source of H_2S that the use of abiological H_2S adequately simulated the environment created by SRB. The enhancement of crack growth rate with CP and increasing H_2S concentration is the result of HE or HAC. The plateau behaviour during stage II growth was thought to result from the rate limiting diffusion of hydrogen atoms to the position of maximum triaxial stress ahead of the crack tip. The effect of H_2S in enhancing the hydrogen assisted fatigue crack growth is by increasing the available H^+ concentration in solution and

hence increasing the surface hydrogen fugacity and by acting as a poison for the hydrogen recombination reaction and thereby catalyzing the hydrogen entry reaction into the metal lattice.

Any basic understanding of the effects of SRB on cracking are hindered by several factors⁽²³⁴⁾. Fatigue tests are generally carried out with the aim of obtaining steady state cracking kinetics. The chemistry of the bacterial environment generally changes with time as the bacterial population progresses through different growth stages^(78,91). The chemical composition of the solutions is complex, both biologically and electrochemically. SRB may populate test chamber surfaces, boldly exposed specimen surfaces and within the occluded crack. The relative importance of SRB at each location has not been defined. Finally the mechanical mechanisms for environment enhanced fatigue cracking are unclear, even for steels in sterile NaCl solution. SRB may affect both atomic hydrogen production and hydrogen uptake through the action of their metabolism⁽²⁴⁹⁻²⁵¹⁾. The cathodic depolarisation theory of SRB influenced corrosion is based on the idea that bacterial utilisation of hydrogen removes the product of the cathodic reaction in the corrosion reaction couple, thus leading to an increase in the open circuit corrosion rate of steel⁽¹¹⁸⁾. Gangloff⁽²³⁴⁾ has suggested that the removal of atomic hydrogen has the effect of reducing the amount of atomic hydrogen available to enter the metal.

The production of sulphide or other metabolite may increase the uptake efficiency of the hydrogen produced on the occluded crack tip or boldly exposed metal surface by the corrosion processes. Walch^(249,250) has shown that hydrogen uptake into palladium and steel is enhanced in near neutral solutions containing SRB.

Gangloff⁽²³⁴⁾ observed a transgranular crack morphology for fatigue of HY130 steel in moist air and sterile 3%NaCl solution with cathodic polarisation, which is typical of fatigue in sterile NaCl solutions. In a SRB containing environment the fatigue crack morphology was intergranular with respect to the prior austenite grain boundaries, although initial cracking was a mixture of intergranular and transgranular. It was suggested that in sterile chloride solutions the morphology correlated to transgranular interface separation and crystallographic cleavage. Gao⁽²³⁵⁾ proposed that intergranular cracking indicates that SRB enhanced hydrogen production on metal surfaces results in increased hydrogen partitioning to trap sites at prior austenite grain boundaries within the fracture process zone. Gangloff⁽²³⁴⁾ suggested that the fracture strength of the austenite grain boundaries must more strongly depend on local hydrogen concentration, compared to the behaviour of the more coherent lath interfaces, in order to rationalize the observed crack path transition. Okada⁽²³⁸⁾ found that in laboratory air, a transgranular surface is evident. In synthetic seawater, the surface consists of both transgranular and intergranular fractures with or without CP.

3.0 EXPERIMENTAL

3.1 MATERIALS

3.1.1 STEEL SELECTION

The two steels selected were Creusot SE500 (35mm plate) and Dillenger DSE690 (50mm plate). The first is a typical quenched and tempered offshore steel with a yield strength of 500MPa and hardness of 225VPN (range 213-233VPN). The second is a higher strength quenched and tempered steel with a yield stress of 690MPa and hardness of 257VPN (range 240-270VPN)⁽²⁵²⁾. Composition of the steels is given in Table 4.

Table 4 Steel Composition (Wt%)

ELEMENT	DSE690	SE500
C	0.15	0.09
Mn	0.9	1.13
Si	0.33	0.31
S	0.001	0.0005
P	0.009	0.008
Ni	1.28	0.48
Cr	0.49	0.18
V	< 0.03	0.05
Al	-	0.02
Nb	-	< 0.01
Mo	0.45	0.24
Ti	< 0.01	0.005
Cu	0.20	0.30

3.1.2 WELDING PARAMETERS

The double cantilever beam (DCB) specimens were designed to allow testing of hydrogen embrittlement of the HAZ of welds in the steels. Due to the length of the DCB specimens (300mm), the testing of welded plate was considered impractical. A real weld would produce the desired hard microstructure, but it would occur as a narrow band down the specimen with no guarantee that it would be straight and lie centrally. Using such a welded specimen would risk that deviations of the crack tip from this hard region would result in it seeing a softer microstructure and ultimately cause the crack to stop prematurely. For this reason, instead of welding, heat treatments of the steels to simulate the HAZ microstructure throughout the specimen were carried out, as described in section 3.3.3.

The first step was to determine what microstructure was required to be produced by the heat treatments. Bead on plate (BOP) tests were conducted on each steel with the weld bead deposited onto a 32mm plate section (machined from the centre of the original plate) in a single pass using submerged arc welding. A low heat input of 1.5kJmm^{-1} was used for this and all other welding, as previous work⁽²⁵³⁾ had found this to give a harder HAZ in SE500 and other steels, compared to higher heat input welds. After welding, sections from the BOP tests were polished (down to $1\mu\text{m}$) and etched (2% nital) to allow measurements of prior austenite grain size and microhardness to be taken across each weld.

There was no problem in using welded material for the fatigue tests. Fatigue cracks will continue propagating and should remain in the region of the hardest microstructure. Thus the corrosion fatigue specimens were machined from 30mm plate sections which were welded as follows. Half K preparations were machined on the steel plates and welded using submerged arc welding as before except for it being multi-pass. The use of a half K preparation means that after welding one side of the weld has a straight HAZ. The welding parameters for the corrosion fatigue specimens and the BOP tests are shown in Table 5.

Table 5 Welding Parameters

Submerged Arc
Oerlikon Wire (SD3Mo 4mm Diameter)
Oerlikon Flux (OP121TT)
Single Pass (BOP) / Multi-Pass (Fatigue)
1.5kJ/mm heat input
30V, 585A
Speed 700mm/min
No preheat
Interpass Temperature 100°C (Fatigue)

3.2 TEST ENVIRONMENTS

3.2.1 STERILE ARTIFICIAL SEAWATER

An artificial seawater solution was made up from a pre-prepared salt mixture for use in the sterile seawater tests. As it is totally free from organic material it can be assumed to be sterile. Once made up the seawater had an initial pH of 8.2. The concentrations of the major components of the artificial seawater are given in Table 6.

Table 6 The Major Constituents of Seawater⁽²⁵⁴⁾

ANIONS	CONC ($\mu\text{g l}^{-1}$)	CATIONS	CONC ($\mu\text{g l}^{-1}$)
Chloride	18980	Sodium	10561
Sulphate	2649	Potassium	380
Bicarbonate	142	Magnesium	1272
Bromide	65	Calcium	400
Fluoride	1.4	Strontium	13
Borate	24.9		

3.2.2 BIOLOGICALLY ACTIVE SEAWATER

Biologically active seawater solution was taken from two anaerobic fermenters. Fermenter 1 was established using a sample of coastal sediment from the south coast of England which contained a mixed population of marine micro-organisms^(255,256). This first fermenter was used to create a second fermenter (number 2), which was maintained initially as a back-up for the first. The fermenters consisted of 5 litre plastic containers sealed with an air lock on the top and a tap at the base. To increase the surface area available to the sessile bacteria the fermenters were half filled with perlite. Every three to four days, 500ml of the solution was drained from each fermenter and the fermenter topped up with 500ml of freshly prepared nutrient solution⁽²⁵⁶⁾ which had been allowed to reach the fume cupboard air temperature. The fermenters were kept in a fume cupboard at room temperature, with all operations being carried out in the fume cupboard. The nutrient solution is based on Postgate's B solution⁽⁷⁸⁾, its composition is described in Table 7.

Table 7 Fermenter Nutrient Solution

<i>Ascorbic Acid</i>	<i>0.1g</i>
<i>Thioglycollic Acid</i>	<i>0.1g</i>
<i>Sodium Lactate</i>	<i>6.0g</i>
<i>Glucose</i>	<i>3.0g</i>
<i>Yeast Extract</i>	<i>2.g</i>

The solution was made up to a litre with artificial seawater at a concentration of 3.5%. Using 0.2M NaOH solution the pH of the nutrient solution was adjusted to 7.5 before being autoclaved for 20 minutes. Once it had cooled the solution was ready for

immediate use or for storage for short periods in a refrigerator.

Later in the work the second fermenter was given a nutrient solution made up as described above except for the omission of the thioglycollic acid. Addition of this acid is to poise the redox potential of the solution to a value between 0 to -100mV. This addition is recommended at the start of a culture due to the strict redox potential requirements of the SRB for growth. Once a culture is flourishing the hydrogen sulphide produced by the SRB should create reducing conditions such that additions of thioglycollic acid are unnecessary. In addition, it is known that thioglycollate is inhibitory to the growth of some SRB and becomes slightly toxic towards some anaerobes during storage⁽²⁵⁷⁾. Evidence of enhanced metabolism was seen in fermenter 2, and is discussed in more detail in later sections.

Disposal of the waste biogenic solution from the fermenters and the test cells was carried out with extreme caution. In the fume cupboard, the waste solution had sodium hydroxide pellets added to give a very alkaline solution in which hydrogen sulphide could only exist at negligible concentrations. It was assumed that such harsh conditions would kill the SRB and any other bacteria present, but a disinfectant (Gerard ASAB biocide, 1% vv) was added as an extra precaution. The solution was then considered safe for disposal.

3.2.3 PREPARED SULPHIDE SOLUTION

The prepared sulphide solution was used to provide a solution which contained sulphides in similar concentrations to the biogenic solution obtained from the fermenters, but was free from SRB and organic material. It was made by deaerating artificial seawater by gently bubbling oxygen free nitrogen through it for two hours. Immediately before addition of the solution to the test cell, the required amount of crystalline sodium sulphide was dissolved into the seawater. A sample of the solution was taken during its addition to the test cell so the initial total sulphide (TS) concentration could be measured.

The solution had to be prepared fresh as it readily decomposed to give hydrogen sulphide, which apart from giving problems in maintaining a constant concentration, created a handling and storage problem due to the extreme toxicity of hydrogen sulphide, which is discussed further below.

It is recommended that hydrogen sulphide concentrations exceeding 20ppm are not encountered during an 8 hour working day. This value is much higher than the level detectable by smell, this level, the threshold concentration of H_2S , is between 0.025 and 0.25ppm in clean water. However, the olfactory nerves can become deadened to the odour after exposure of 2 to 15 minutes, depending on the concentration. Exposure to concentrations in the range of 150 to 200ppm for prolonged periods may cause edema of the lungs. Other symptoms of poisoning in this range include nausea, stomach distress, belching, coughing, headache, dizziness and blistering. Pulmonary complications, such as pneumonia, are strong possibilities from such subacute exposure. At 500ppm, unconsciousness usually

occurs within 30 minutes and results in acute toxic reactions. In the 700 to 1000ppm range, unconsciousness may occur in less than 15 minutes and death within 30 minutes. At concentrations above 1000ppm, a single lungful may result in instantaneous unconsciousness, with death following due to respiratory failure and cardiac arrest.

3.2.4 SEDIMENT

The sediment was collected from the tidal estuary on the south bank of the River Mersey (Figure 18) and was used principally to test the design of the cell prior to using it with marine sediments. Although the sample was collected from the river estuary, it was subject to tidal movements producing saline conditions. The pollutants present in this water were thought to promote the growth of SRB making this sediment worthy of study.

Sampling was carried out using the PVC cell shown in Figure 19. The cell tube was pressed into the sediment and a complete core was taken to limit contact with the air. The base of the cell was immediately plugged and a thin layer of estuary water was poured into the top to avoid the sediment drying out. The sample was returned to the laboratory and a hydrogen permeation cell was attached to the side (see section 3.5), with the steel membrane initially at a potential of -850mV(SCE). No nutrients were added to the cell and with the exception of replenishing the water the sediment was maintained in the as-collected condition. Transfer of the sediment to the laboratory is not thought to have had a serious effect on the micro-organisms present.

North Sea sediment samples were supplied by Amoco and were collected by a diver in about 160m of water from the base of platforms in the North West Hutton field. Samples were taken at or near the surface of the seabed and contained oil (reported 10 to 20%) from drilling cuttings around the platforms. Oil is known to be a suitable

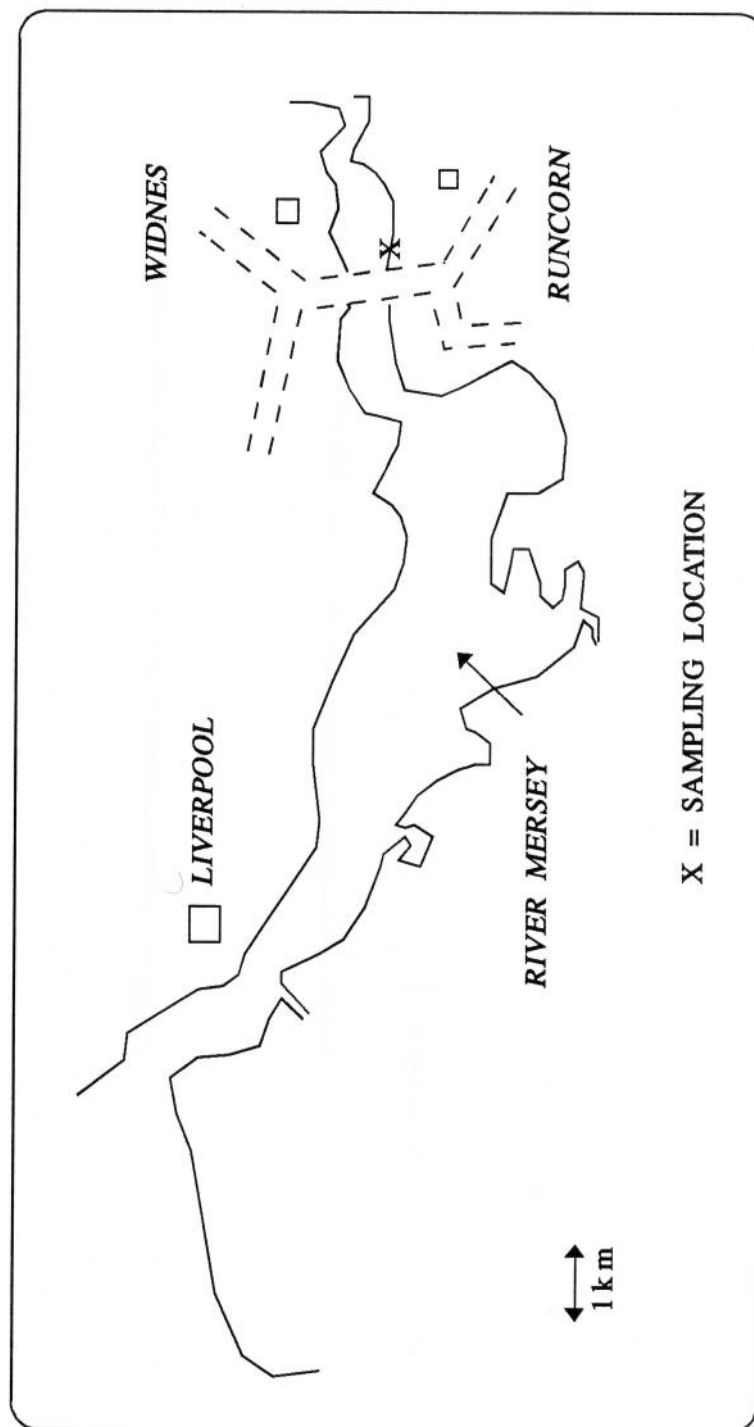


Figure 18. Location of Sediment Sampling on the River Mersey

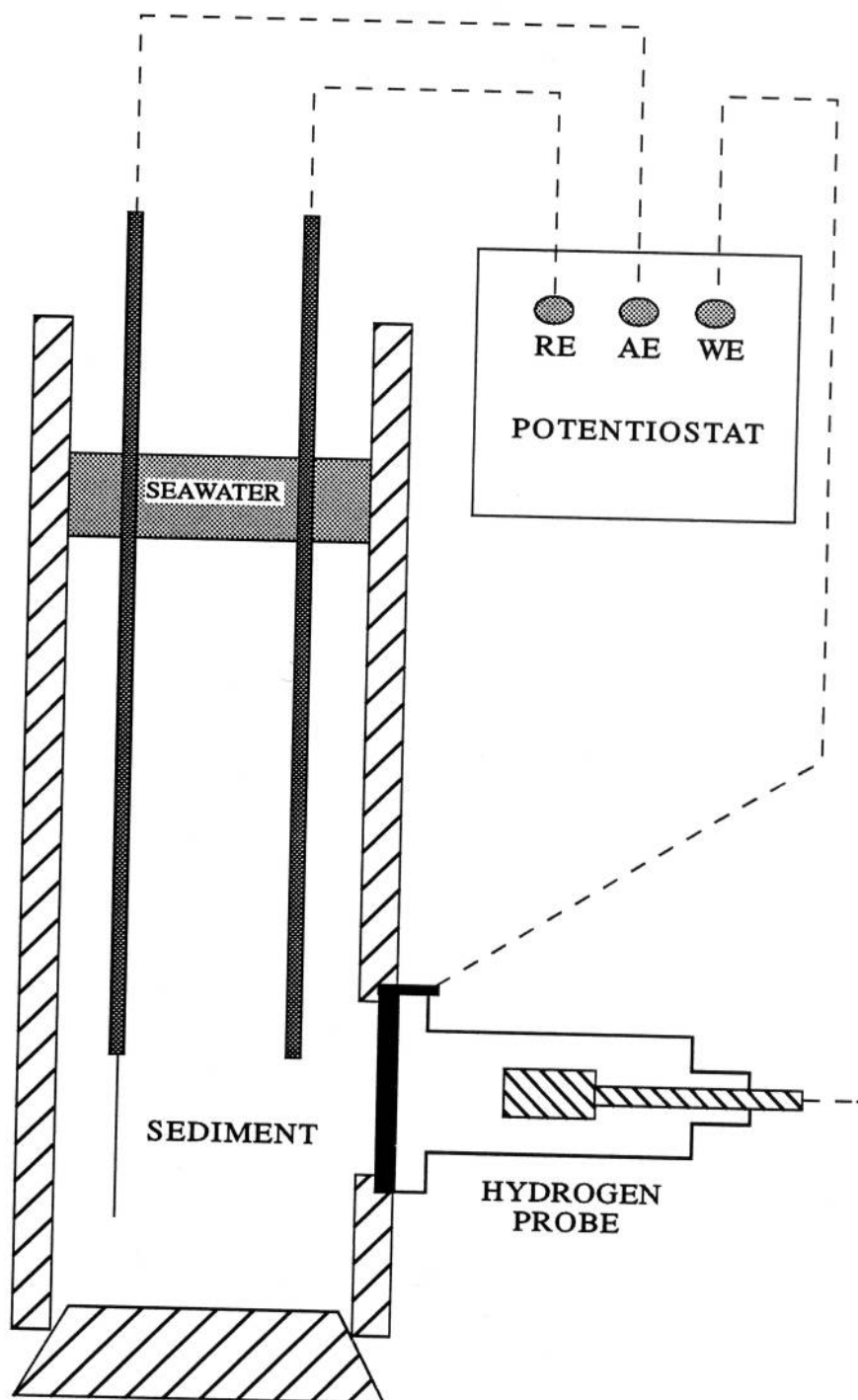


Figure 19. Sediment Cell

carbon source for the growth of SRB and it was thought that as a result the microbial numbers and activities would be high in these samples. The sediment was transported in sealed containers but the possible effects of temperature fluctuations prior to arrival at the laboratory are unknown.

3.3 AC POTENTIAL DROP METHOD

3.3.1 BACKGROUND

Since the early 1960's, the standard electrical potential method of crack measurement has employed DC, even though the method can also use AC⁽²⁵⁸⁻²⁶⁰⁾. The reason for the previous preference for DC over AC was mainly due to the advanced electronics required in using AC. The advantages and disadvantages of the two techniques are compared in Table 8.

Table 8 Comparison of the Advantages and Disadvantage of the AC and DC Potential Drop Methods^(258,260).

	ADVANTAGE	DISADVANTAGE
DC	1. Simple technique does not rely on advanced electronics	1. Well established technique between PD and cracklength
	2. Well established for set specimen sizes and geometries	2. Technique sensitive to specimen size and geometry
		3. Thermal emf effects
AC	1. Ease of calibration for differing specimen geometries	1. Reliance on advanced electronics
	2. Inherently linear response	2. Lead interactions
	3. Lack of size dependence of method	3. Requirement for high stability in electronics
	4. Ease of amplification of input signal	
	5. Multiple PD probe systems can be used	

The DC potential drop method entails passing a constant current through a cracked

testpiece and measuring the potential difference across the crack. When the crack extends, the uncracked cross-sectional area of the testpiece decreases, its electrical resistance increases, and hence the potential difference between the two points either side of the crack rises (Figure 20). By monitoring this potential difference and comparing it to a reference voltage measured from a region not affected by the crack growth, it is possible to compute the length of the crack.

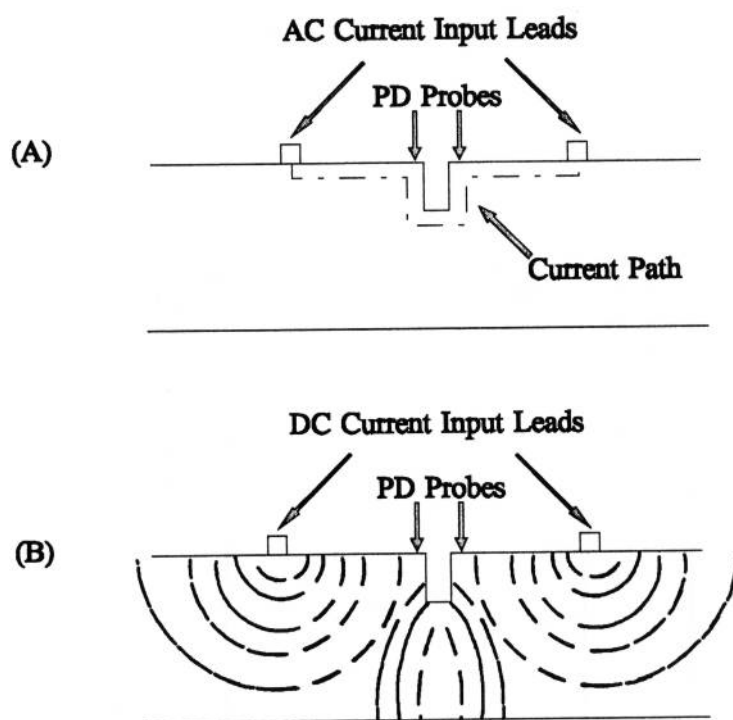


Figure 20. Comparison of AC (A) and DC (B) Potential Drop Methods Illustrating the Skin Effect in the ACPD Method.

The AC potential drop (ACPD) method is essentially the same as DC except for one major difference. With high frequency AC, the current is contained in a thin layer at

the metal surface. This phenomenon is called the skin effect (Figure 20). Thus the current required to produce a given field strength at the surface is much less in the case of AC. The depth of the AC carrying layer is determined by the frequency, higher frequencies give better sensitivity but increase lead interaction problems⁽²⁵⁸⁾.

The ACPD technique has another advantage over the DC methods due to the skin effect in that the current, because it is contained in a thin layer, follows the surface of the crack. In the case of DC, the current is much more widely spread (Figure 21) so the method detects only the cross-sectional area of the specimen, and therefore the AC method is more sensitive.

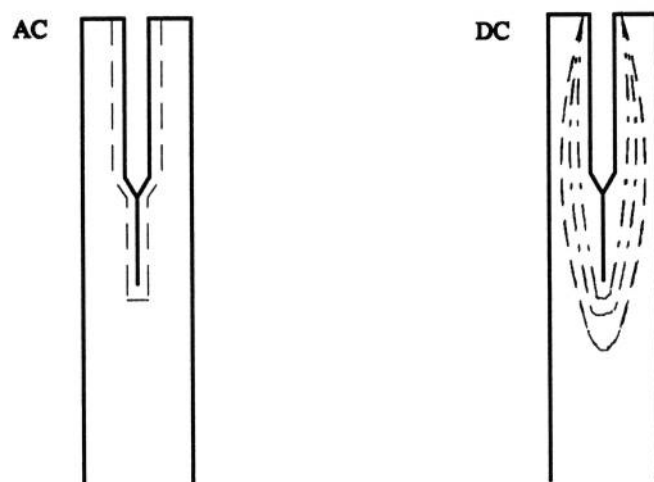


Figure 21. Distribution of Current in DCB Specimens

An ACPD instrument is in basic terms a current source coupled with an extremely sensitive voltmeter. In normal usage four contacts are required for operation, two to

apply the current and the other two to measure surface voltage. The voltage probes are usually of the form of two fixed contacts with known separation, which can be placed onto the metal surface where required.

ACPD can be used on any metal body to detect or size surface breaking cracks. No special surface preparation is required for the contacts except that good electrical contact is made. The AC method has been used successfully in fatigue work^(258,259,262) and also for hydrogen embrittlement tests using DCB specimens^(65,262).

3.3.2 PRACTICAL

Before attachment of the microgauge leads to the specimen suitable points of attachment had to be created. These points had to be rigid, of low electrical resistance and protected from the corrosive environments they would come into contact with during testing. The first stage of making the attachment points was to spark machine three holes into the specimens. The locations of the holes is indicated in Figure 22. For the DCB specimen the holes were positioned on the inside face of the beams at the top of the specimen, and for the fatigue specimen they were positioned on the face with the notch running across it. The holes were spark machined with 1mm diameter copper wire to give a hole of just over 1mm diameter and depth of 1.5 to 2 mm. For both specimens the distance between the points d_{COM} and d_{REF} was made to be 10mm and is referred to as the reference distance. The other hole was positioned as shown in Figure 22, the distance between d_{COM} and d_{CRACK} is referred to as the crack distance.

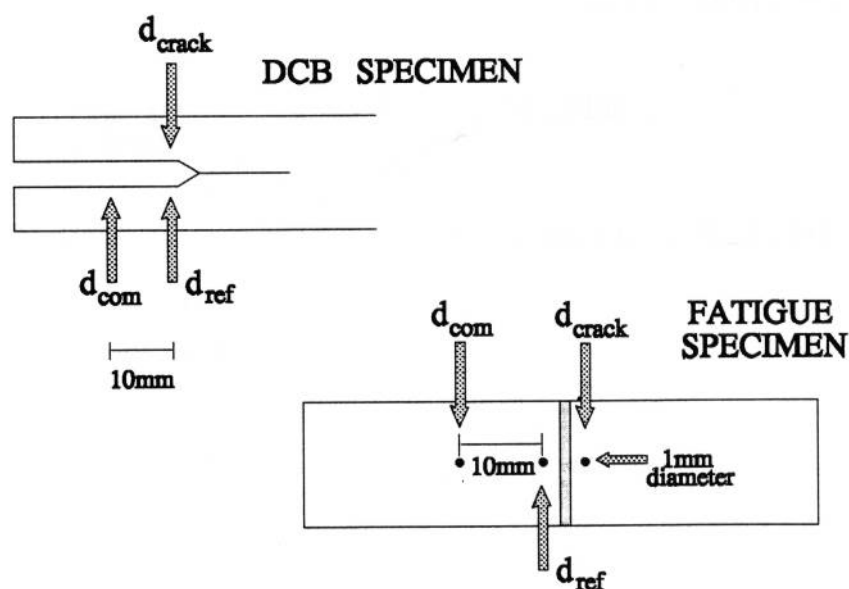


Figure 22. Location of Connections to Microgauge and Testpieces

Once the holes had been spark machined, pieces of 1mm diameter copper wire were resistance welded into each hole to leave approximately 3mm of the wire visible. The resistance of each wire was then measured to make sure a sound contact had been made, if a significant resistance was found then the wire was rewelded. The wires were then fixed in place further, by placing a small bead of epoxy resin (Araldite Rapid) around the base of each. Once the resin was set, the wires intended for connection to the microgauge were soldered onto the required copper contact. These wires were twisted around each other to avoid the effects of electric fields. The soldered connections were then covered with more epoxy resin and when this had set the whole area was covered in silicone sealant. The arrangement is shown schematically for the fatigue specimen in Figure 23. The same arrangement was used for the DCB specimens.

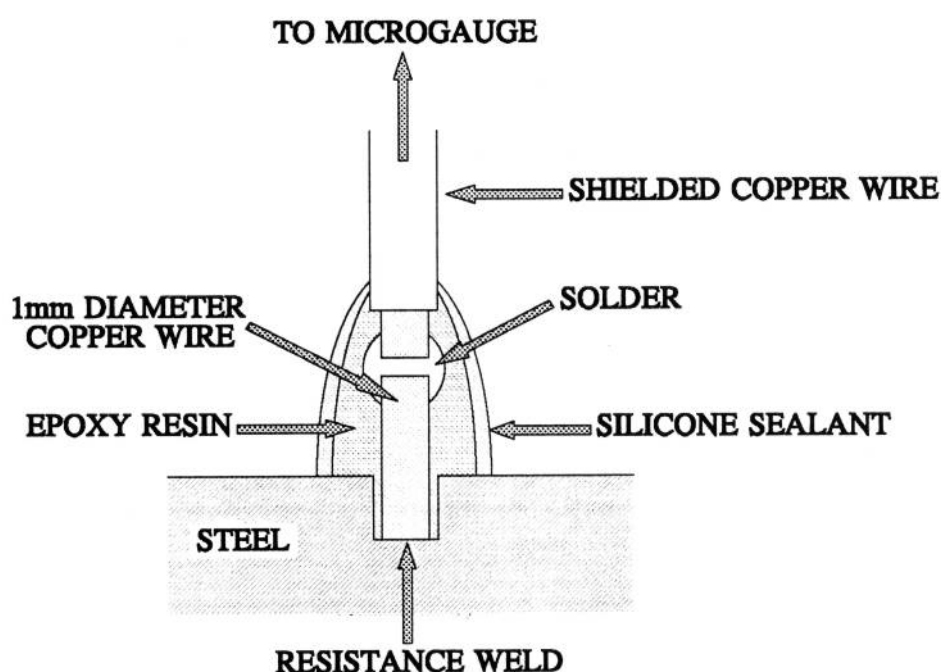


Figure 23. Schematic of Electrical Connection to Fatigue Specimen

Once the connections had been made the microgauge could be connected to the specimen as shown in the schematic wiring diagram, Figure 24. The leads producing the field were attached to the fatigue specimen by use of magnetic connections. This was possible because the ends of the fatigue specimens were outside the test cell and so avoided contact with the corrosive environments. One of these connectors was used as the working electrode connection to the potentiostat for the application of CP where required.

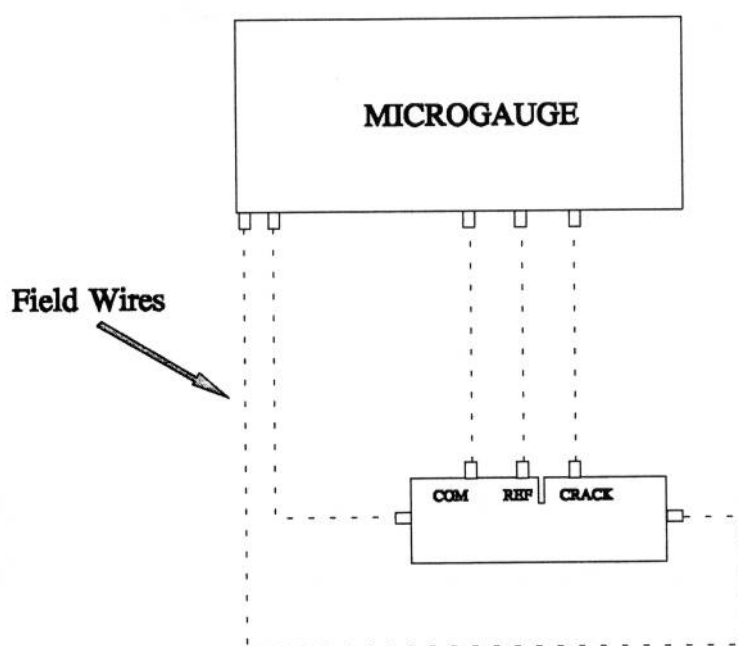


Figure 24. Schematic Diagram for Connection to Microgauge

For the DCB specimens the field connections and the working electrode connection were made by attaching wires to bolts which were screwed into the top holes used previously in the connection of the dial test indicator (DTI) (see sections 3.4.2 and 3.4.4) to the specimen as shown in Figure 25. These connections were not submerged into the bulk solution but

were close enough to the solution to be affected and therefore needed some corrosion protection. The method employed was similar to that used above in that the connection was covered in epoxy resin and that in turn covered in silicone sealant.

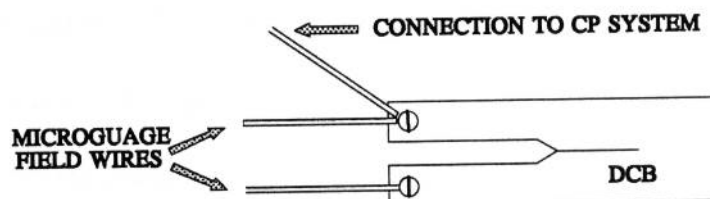


Figure 25. Schematic of Field Wire and CP Connections to DCB

It was found that during the DCB tests that all connections degraded over a period of time and had to be repaired. For the tests in seawater repairs were required approximately every 2-3 months, with this time being reduced to 3-6 weeks for the test in biogenic solutions.

3.4 DOUBLE CANTILEVER BEAM TESTING

3.4.1 CRACK GROWTH RATE TESTING

Sustained load fracture is the general term given to time-dependent crack growth under loading which is often well below that required to cause failure in a tensile test.

Examples of sustained load fracture are as follows;

1. Creep and creep crack growth.
2. Stress corrosion cracking.
3. Cracking due to embrittlement by internal or external hydrogen.
4. Liquid metal embrittlement.

The stress intensity factor, K , is used to describe sustained load fracture and is based mainly on procedures similar to those employed in fracture toughness testing. This includes the use of mostly standard specimens, fatigue precracked and tested under plane strain conditions. Full plane strain is not always strictly necessary if the test specimen has a thickness which is representative of the section thickness of the component in service.

There are two categories of experimental methods for fracture mechanics evaluation of sustained load fracture. 1. Time-to-failure (TTF) tests on precracked specimens and 2. Crack growth rate testing. In TTF testing, precracked specimens are configured such that a constant load causes an increase in K corresponding to an increase in crack length. Specimens are therefore loaded to the required initial stress intensity level and

the TTF recorded.

Of the many specimen types that have been proposed for sustained load crack growth studies most are either increasing K (constant load) or decreasing K (constant displacement). Advantages of the decreasing K specimens are as follows:

1. Fatigue precracking from a sharp notch is not always required as initial mechanical ('pop-in') crack growth is stable and usually has no influence on subsequent fracture.
2. Nearly all of the crack growth curve is obtainable from one specimen.
3. Steady state conditions for crack growth and arrest at K_{th} are more readily achieved.

Two types of decreasing K specimens are commonly used, the modified crack line wedge-loaded and the DCB specimen, both require the elastic compliance to be calculated before the K values can be worked out.

Possible experimental problems that can occur during sustained load fracture testing are listed below;

Incubation Time

Incubation times before the onset of cracking depend on the specimens initial K and previous loading history. This loading history will arise from the fatigue precracking process (if used) and can include effects of plastic deformation. Exposure to an aggressive environment before loading and subsequent testing can affect the incubation time. Incubation times or the apparent incubation times are dependent on the sensitivity of the method of crack growth detection being employed.

Non-Steady State Crack Growth

High initial K values applied to a decreasing K specimen can lead to crack growth rates which are initially lower than those expected from the da/dt versus K_I diagram. This non-steady state crack growth is caused by changes in the electrochemical reactions at the crack tip.

Effect of Precrack Morphology

Stress corrosion tests on aluminium alloys using DCB specimens have demonstrated that mechanical pop-in precracks can result in displacement of the crack growth curve (particularly region I, figure 5, section 2.1.3) to higher K values as compared to fatigue precracks⁽²⁶³⁾. The explanation given suggested that fatigue precracks result in relatively planar stress corrosion cracks with uniform crack fronts, but pop-in cracks, being more irregular, lead to similarly irregular stress corrosion cracks requiring a greater driving force.

Influence of Sustained Load Crack Morphology

Crack front morphology is particularly important for tests designed to measure K_{th} values. In decreasing K tests crack tip blunting and/or microbranching lead to apparent K_{th} values higher than those obtained from increasing K tests, where crack initiation occurs from a sharp and unbranched fatigue precrack.

Curved Crack Fronts

Curvature of the crack front often occur during sustained load fracture testing. The curvature becomes more pronounced as the specimen thickness is decreased. Generally the curvature is caused by the change in stress state from plane strain in the interior of the specimen to plane stress at the surface. Side grooves are helpful in reducing curvature. Curvature is undesirable as it causes errors in using the surface crack length

in the calculation of the crack growth rates and K_I values.

Corrosion Product Wedging

One disadvantage of using decreasing K specimens is corrosion product wedging, which occurs for some material-environment combinations. Decreasing K specimens have their initial displacement fixed, so the crack tip tends to narrow during propagation. Corrosion products can form a wedge between the crack surfaces and result in a higher crack growth rate for a given K and lower K_{th} values. To determine whether corrosion product wedging has influenced crack growth, specimens can be unloaded after testing and the deflection at the load line can be measured and compared to that at the beginning of the test. If the two deflections are almost the same, then no substantial amount of corrosion products could have accumulated in the crack, thus wedging has not occurred.

3.4.2 DCB DESIGN

DCB specimen design was based on DCB specimens used in similar work at Cranfield^(63,262). The specimen were machined from plate in the SL orientation (Figure 26) to the dimensions given in Figure 27. Each side of the specimen had 2mm (16% beam width) side grooves to maintain the crack in the centre of the specimen. The main design criterion was the thickness (B) of the DCB, which in effect was keeping B as small as possible, whilst making sure the results were obtained under plane strain conditions.

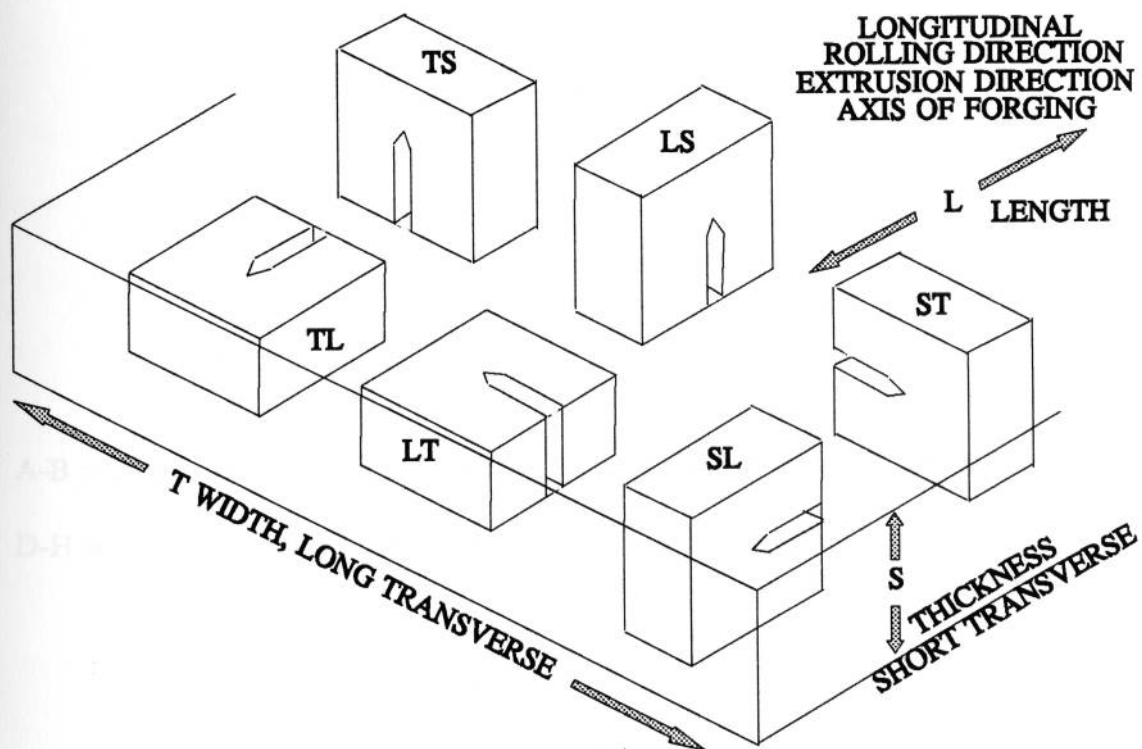
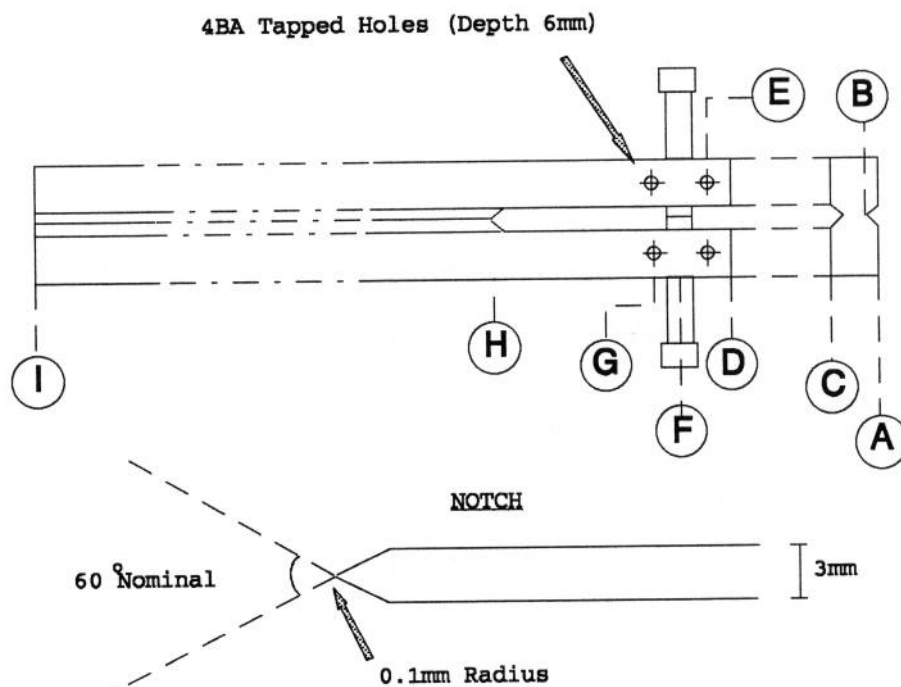


Figure 26. Specimen Orientation



A-B = 2mm A-C = 12.5mm D-E = 12.5mm D-F = 20mm D-G = 27.5mm

D-H = 70mm D-I = 320mm H-I = 250mm Width = 30mm

Figure 27. Dimensions of DCB Specimen

A thin specimen was desirable for this work as it would firstly, increase the chances of obtaining a uniform microstructure when heat treating the specimen (section 3.3.3).

Secondly, the time taken for a constant hydrogen concentration throughout the specimen to be achieved during hydrogen charging is reduced as B decreases⁽²⁶⁴⁾.

The plane strain criterion⁽²⁶⁵⁾ is as follows,

$$B \geq 2.5 (K_I / \sigma_{ys})^2 \quad (60)$$

where K_I is the crack tip stress intensity and σ_{ys} is the yield stress of the material. After heat treatment of the DCB specimen its σ_{ys} would have changed so the new value had to be calculated. An estimate of σ_{ys} was obtained by comparing the expected DCB hardness (319 and 425VPN for SE500 and DSE690 respectively) to tabulated σ_{UTS} v VPN values⁽²⁵⁴⁾ (see appendix B) and putting the σ_{UTS} value into equation 61.

$$\sigma_{ys} \approx 0.741 \sigma_{UTS} \quad (61)$$

The initial high values of K_I did not have to meet the plane strain criterion as the important values were the lower ones obtained close to K_{th} . A value of 12.5mm was decided upon for B, which meant that the plane strain criteria would be met at a K_I value of $53\text{MNm}^{-3/2}$ or below for the SE500 DCB, and a value of $73\text{MNm}^{-3/2}$ or below for the DSE690 DCB (assuming σ_{ys} values of 746 and 1032MNm^{-2} for SE500 and DSE690 respectively).

The crack tip stress intensity, K_I , was calculated from the following relationship⁽²⁶⁶⁾ which includes a factor determined by Heady⁽⁶⁸⁾

$$K_I = \frac{8EH[3h(a+0.6h)^2+h^3]^{1/2}}{4[(a+0.6h)^3+h^2a]} \left[\frac{B}{B_n} \right]^{1/\sqrt{3}} \quad (62)$$

where δ is the displacement at the load line, E is Young's Modulus, a is the crack length measured from the load line, h is the specimen half height and B and B_n are the width of the grooved and ungrooved specimen respectively.

3.4.3 HEAT TREATMENT

As stated earlier (section 3.1.2), the length of the DCB specimens (300mm) meant that testing of welded plate was impractical due to non-uniformity in the weld. Instead, the specimens were heat treated to give a microstructure similar to that found in the HAZ.

First, bead on plate (BOP) tests (welding parameters given in section 3.1.2) were carried out to identify the prior austenite grain size of the region of maximum hardness within the HAZ. After welding, the plates were sectioned across the weld and the surface polished down to 1 μ m. The polished surfaces were then etched to allow microhardness measurements to be made across various parts of the weld HAZ. In addition, grain size measurements were made using the methods described below.

$$(1) \quad S_v = 2N_L \quad (63)$$

where S_v is the grain boundary area per unit volume and N_L is the mean number of intercepts of random test lines with grain boundaries per unit length of test line. If D is the mean grain diameter;

$$2S_v = [4\pi (D/2)^2] / [(4\pi/3) (D/2)^3] \quad (64)$$

$$D = 3/S_v = 3/2N_L \quad (65)$$

$$(2) \quad A = (2\pi/3) (D/2)^2 = \pi D^2/6 \quad (66)$$

$$D = \sqrt{6/\pi N_A} \quad (67)$$

where N_A is the number of grains per unit area and A is the mean area on a plane of

polish passing through spheres of constant size.

(3) Mean intercept length of random test lines. Divide total length by the number of grains traversed.

Next, heat treatments were carried out on both steels using samples with similar dimensions to the DCB specimens except the height was 50mm (compared to 300mm in the DCBs). Various heat treatments were tried in an attempt to match the microstructure of the heat treated samples to the BOP tests. The heat treatments are listed in the results section. The optimum heat treatment was found to be oil quenching from 1100°C after a 5 minute soak for the DSE690 and ten minutes for the SE500. When heat treating the DCB specimens they were quenched into the oil in the orientation shown in Figure 28. The reason for this was to reduce the amount of deformation to the DCB during quenching.

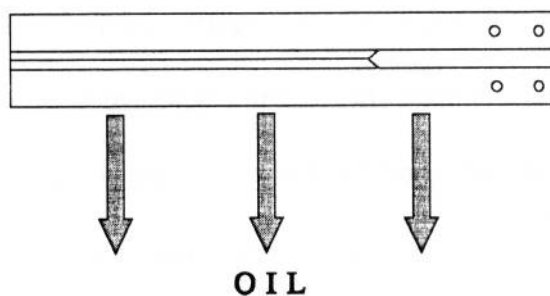


Figure 28. Schematic of DCB Orientation During Quenching

3.4.4 SPECIMEN PREPARATION

After heat treatment the DCB specimens required the black scale formed during the process to be cleaned off, so the specimens were polished, down to 1200 grit paper. Next the three holes for the microgauge connections were spark machined into each specimen as described in section 3.3.2. In addition, a chevron was spark machined at the top of the notch to act as a stress raiser upon loading.

The specimens were then ready to be loaded across the beams by use of two bolts, whose ends had been ground flat. Between the two bolts an insulating block was placed to prevent a short circuit path for the microgauge. The insulating block was formed from two 10 x 10 x 1mm square pieces of high strength steel either side of a layer of paper which was sandwiched between layers of epoxy resin (Araldite).

Loading of the DCB specimen was effected by the tightening of the bolts to cause a predetermined displacement of the DCB's arms. This displacement was measured using a DTI fixed across the arms in line with the load line. The displacement to give the desired initial stress intensity was calculated using equation 62 from section 3.4.2., the values used are given in Table 9;

$$K_I = \frac{\delta E h [3h(a + 0.6h)^2 + h^3]^{1/2}}{4[(a + 0.6h)^3 + h^2 a]} \left[\frac{B}{B_n} \right]^{\frac{1}{\sqrt{3}}} \quad (62)$$

Table 9 Values for DCB Specimens

PARAMETER	SE500	DSE690
Modulus (E), GPa	207	207
Half height (h), m	0.01500	0.01500
Crack length (a), m	0.05065 (Sterile) 0.05054 (Active)	0.05005 (Sterile) 0.04981 (Active)
Width (B) (Ungrooved), m	0.01250	0.01250
Width (B) _n (Grooved), m	0.00850	0.00850
Hardness (VPN)	319	425
[UTS]*, MPa	1007	1393
[Yield Strength]*, MPa	746	1032
Displacement (δ), m	0.0028 (Sterile) 0.0013 (Active)	0.0025 (Sterile) 0.0010 (Active)
Initial K_I , $\text{MNm}^{-3/2}$	125 (Sterile) 60 (Active)	113 (Sterile) 46 (Active)

*Values are estimated using measured hardness.

A DSE690 DCB specimen intended for tests in biologically active seawater was loaded to $113\text{MNm}^{-3/2}$. After a short time protected at a CP potential of -850mV(SCE) the specimen failed across the arms at the top of the specimen. It should be noted that the values for initial K_I are above those for plane strain criteria so that the values are only meaningful when they are below or equal to $53\text{MNm}^{-3/2}$ for the SE500 and $73\text{MNm}^{-3/2}$ for the DSE690.

3.4.5 DOUBLE CANTILEVER BEAM TESTING

Initial procedures prior to testing in both solutions (sterile and biologically active seawater) were identical and as follows;

1. Hydrogen permeation cell set up and depletion started (section 3.5.1). This was only carried out at the very beginning of the tests.
2. Heat treatment to simulate HAZ (section 3.4.3)
3. Cleaning (section 3.4.4)
4. Spark machining holes and chevron (section 3.3.2 & 3.4.4)
5. Attachment of microgauge wires around crack (section 3.3.2)
6. Loading the DCB via the bolts (section 3.4.4)
7. Attachment of microgauge field wires and CP connection (section 3.3.2)
8. Lacomit coating the top region of the DCB (area which was not submerged in the solution).

Sterile Seawater

Sterile seawater tests were performed in an open top polythene tank with a capacity of 25 litres (Figure 29a). Attached to one side of the tank was an electrochemical cell which allowed hydrogen permeation determinations to be made. The operation of this hydrogen permeation cell is discussed in detail in the next section. DCB specimens (one of each steel) were suspended in the tank, which was then filled with artificial seawater until it covered the chevrons but not the microgauge wires. The level of the seawater was marked on the side of the tank. The leads were connected to the microgauge and

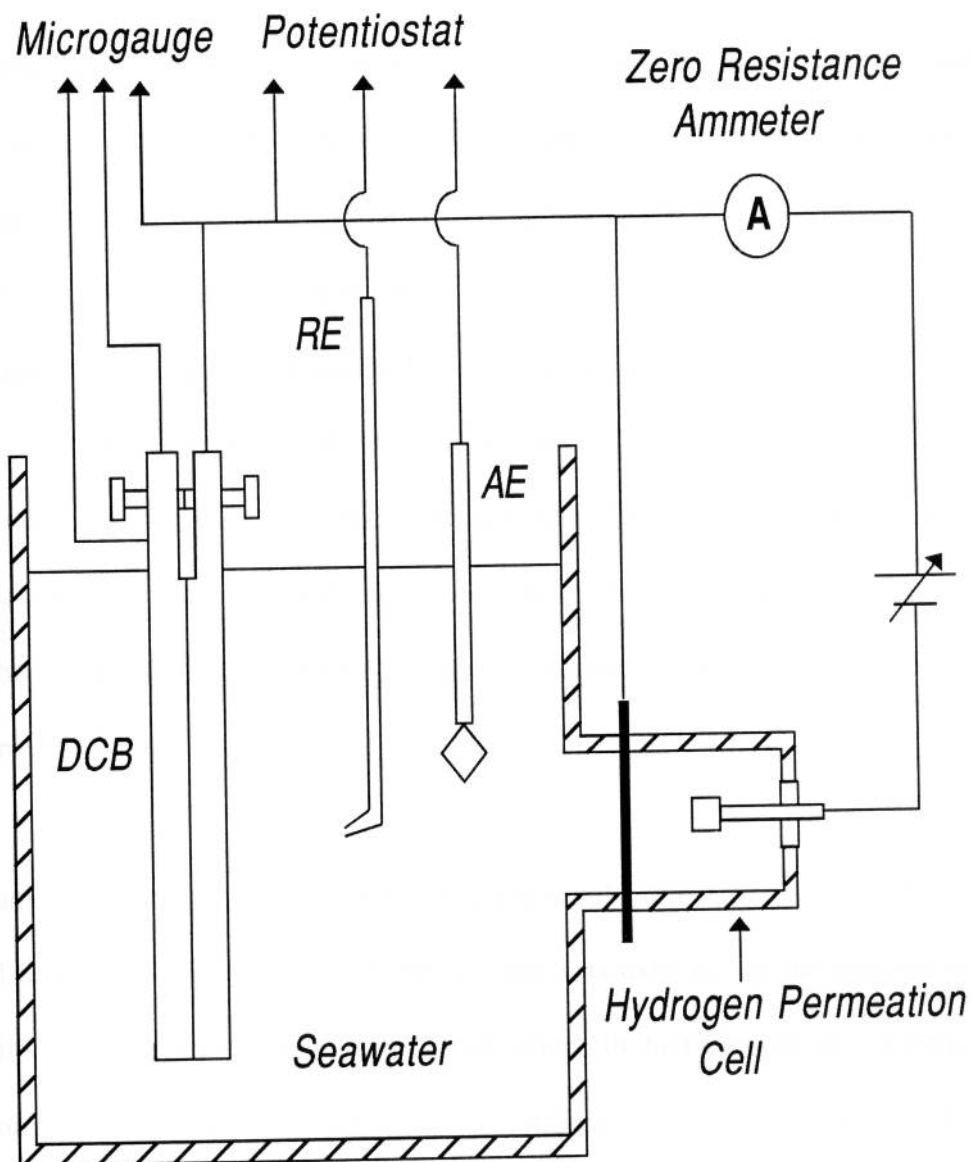


Figure 29a. Schematic of Seawater Tank

potentiostat and the CP set initially to -850mV(SCE) .

Cracklengths in the specimens were monitored alternately using the U8 microgauge. Occasionally the DCBs were removed from the tank to allow optical cracklength measurements to be made with a travelling microscope. DCBs were washed with distilled water and then iso propanol alcohol (propan-1-ol) and allowed to air dry. The notch region at the top of the specimens was cleaned of calcareous deposits using 1200 grit paper. Cracklengths (a) measured were plotted against time (t) from which the crack velocity (v) could be calculated (slope of the line). When v dropped to 10^{-10} ms^{-1} the crack was assumed to have stopped propagating. The applied cathodic potential was then decreased to -950mV(SCE) and further crack growth monitored as before. Each time the crack was deemed to have stopped the potential was decreased by 100mV until -1250mV(SCE) was reached.

The tank was open to the air, so evaporation would affect the seawater level over a period of time. To counter this distilled water was used to top the tank up each day. In addition, to maintain constant ion concentrations in the tank seawater, 10 litres of the solution was removed and freshly prepared artificial seawater added every 14 days.

At the lower levels of CP (-850 to -1050mV(SCE)), the amounts of chlorine produced at the platinum anode were not significant. As the levels of CP were increased the amount of chlorine produced also increased. For the last two tests (-1150 & -1250mV(SCE)) the anode was removed from the bulk seawater and placed inside a

glass container as shown schematically in Figure 29b. The anode still had an ionic path to the bulk solution, but produced chlorine was contained away from the bulk seawater. This chlorine was removed from the anode cell by vigorously bubbling air through the contained seawater.

Active Seawater

Two glass cells were constructed to allow testing of DCB specimens in anaerobic seawater containing the mixed populations of marine micro-organisms. Due to the requirement of SRB for totally anaerobic conditions, the cells were completely enclosed to exclude air (Figure 30). Hydrogen detectors, similar to those used in the above seawater tests were attached to the side of the cells to record the hydrogen concentrations. The platinum anodes had to be placed outside of the bulk solution as they produced oxygen and chlorine. The anodes were kept in separate glass containers which were in ionic contact with the bulk solution. The seawater in the anode cells had oxygen free nitrogen bubbling through them to remove the produced gases.

The DCBs (one of each steel) were placed into the glass cells and the attached wires fed through a lid entry point. The lids were fitted in place and clamped. The reference electrode luggin probe (with electrode fitted) and the two glass tubes were put in place and sealed. Using the two glass tubes oxygen free nitrogen was passed through the cell for twenty minutes. Solution was removed from a fermenter and added to the cell using one of the glass tubes. When the cell was three quarters full the luggin probe was filled by drawing solution up with a pipette filler. The cell was then filled so the DCBs

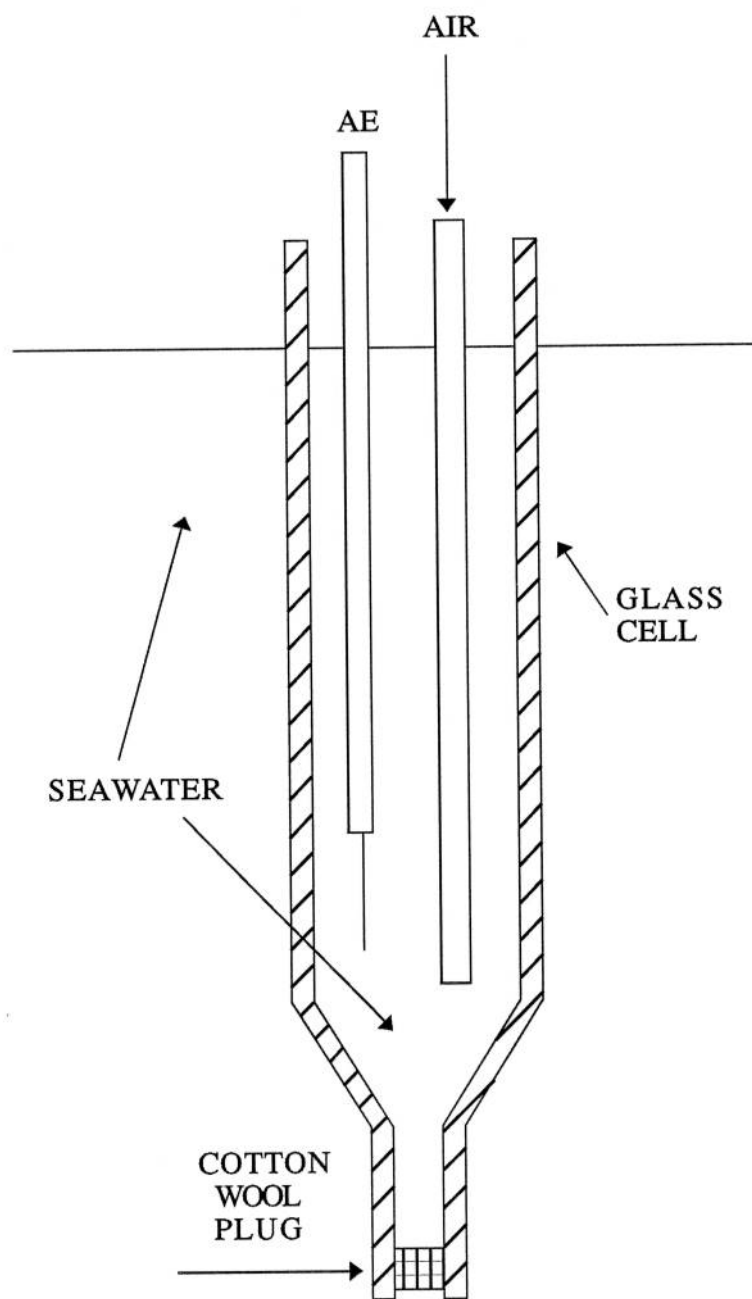


Figure 29b. Seperate Anode Cell

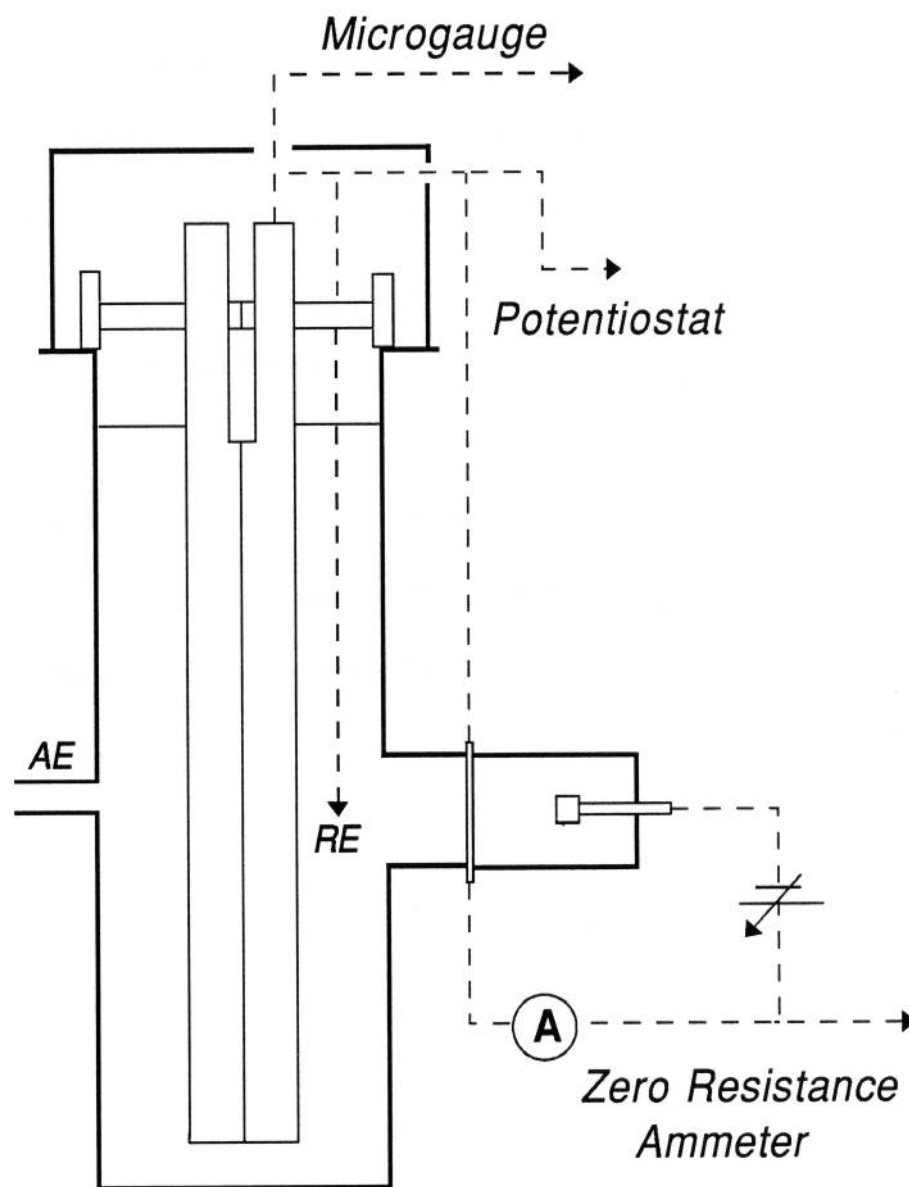


Figure 30. Schematic of Anaerobic Cell

chevrons were immersed but not the wires. The anode cell was filled with deaerated seawater and oxygen free nitrogen bubbled through it. The anode cell was positioned so that the solution levels were identical. The CP system was set to -850mV(SCE) and cracklength measurements were made with the microgauge. Optical measurements were made as before and involved the same cleaning procedure. Each time the DCBs were removed, the cell solution was changed. When the crack velocity reached 10^{-10} ms^{-1} the next potential of -950mV(SCE) was applied. As before the process was repeated in steps of 100mV until -1250mV(SCE).

During the initial test at -850mV the total sulphide concentration and bacterial numbers were monitored in the cells and also in the fermenters. The results (section 4.4.2) indicated the optimum time to replenish the solution in the cell to maintain a fairly constant level of sulphide.

3.5 HYDROGEN PERMEATION MEASUREMENTS

3.5.1 BACKGROUND

Electrochemical hydrogen permeation measurements using a double cell arrangement were developed by Devanathan and Stachurski⁽²⁶⁷⁾. They studied the instantaneous rate of permeation of electrolytic hydrogen through palladium membranes. Measurements are made by creating a concentration gradient across a thin metal membrane. Hydrogen atoms generated on the charging side of the membrane by cathodic polarisation can diffuse into the metal (Figure 31). At the entry surface the absorbed hydrogen concentration is termed as C_0 . On the exit surface of the membrane emerging hydrogen atoms are oxidised to give an effective hydrogen concentration, C_L , of zero. The hydrogen oxidation reaction produces a current (μA) which is a measure of the hydrogen permeation rate.

The breakthrough time, t_b , for hydrogen to diffuse through a membrane of thickness L and be detected is given by;

$$t_b = L^2 / 15.3D \quad (68)$$

measurement of t_b allows the apparent diffusion coefficient, D , to be determined.

A typical transient curve for the hydrogen permeation current during constant hydrogen absorption is shown in Figure 32. Initially, there is a delay as the first hydrogen atoms diffuse through the membrane to the exit surface. The current then steadily increases until a plateau is reached, the value of this equilibrium position, J_∞ , allows the surface

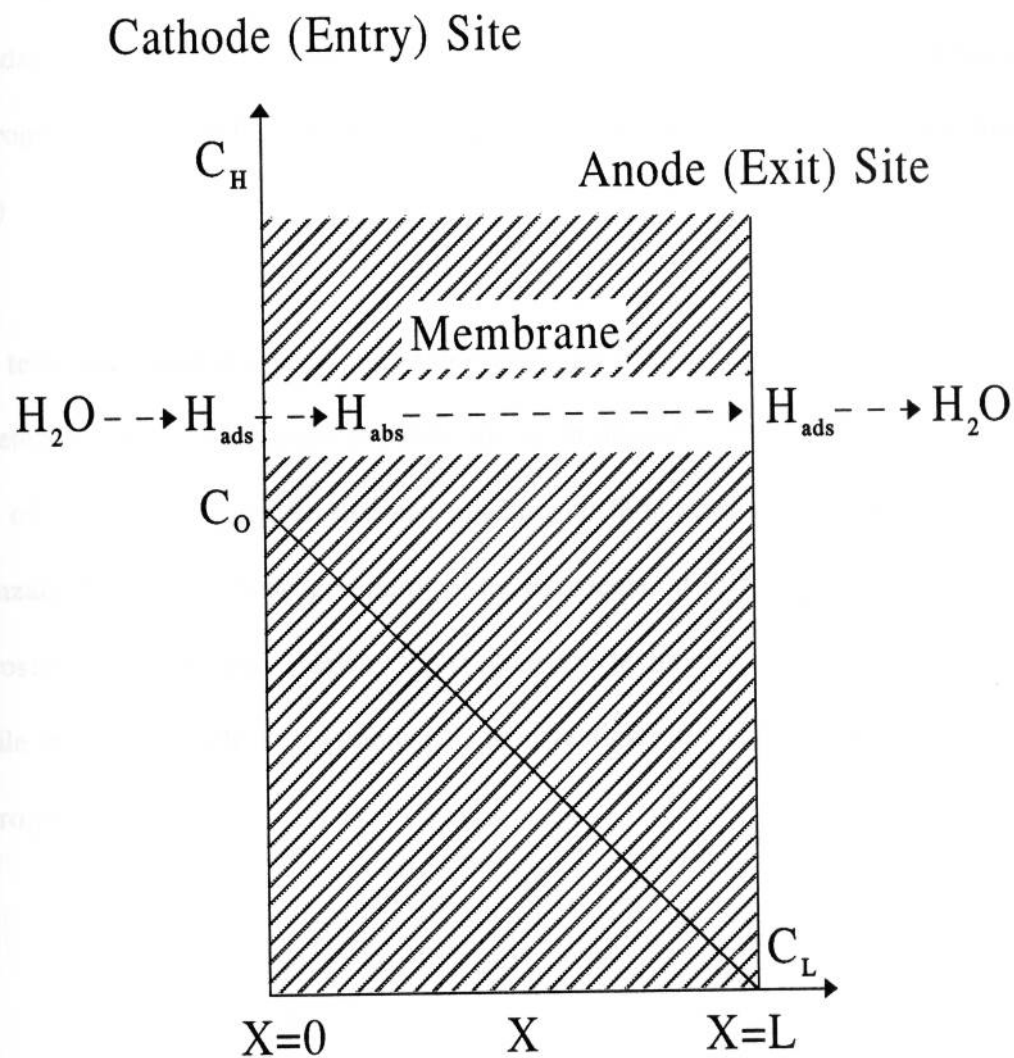


Figure 31. Steady State Permeation of Electrolytic Hydrogen Through a Thin Metal Membrane of Thickness L .

hydrogen concentration to be calculated (equation 69).

$$J_{\infty} = (C_0 F D) / L \quad (69)$$

where J_{∞} is the steady state permeation rate (μAcm^{-2}), C_0 has units $10^{-6} \text{ gH/cm}^3\text{Fe}$, F is Faraday's constant ($96500 \text{ coulombs mol}^{-1}$), D is the apparent diffusion coefficient for hydrogen in shim steel (measured to be $2 \times 10^{-8} \text{ cm}^2\text{s}^{-1}$) and L is the membrane thickness (cm)

The technique has been used very extensively for hydrogen permeation measurements to determine D and C_0 values in steels and other alloys^(70,73,74,195). Lucas^(63,262) used it as part of a study of hydrogen assisted cracking in 50D steel. Using similar apparatus, Hamzah⁽²⁶⁸⁾ obtained hydrogen permeation transients, at different CP levels in various corrosive environments. Newby⁽²⁶⁹⁾ applied the technique to biologically active and sterile solutions, with and without CP, to investigate the effect of marine fouling on hydrogen absorption.

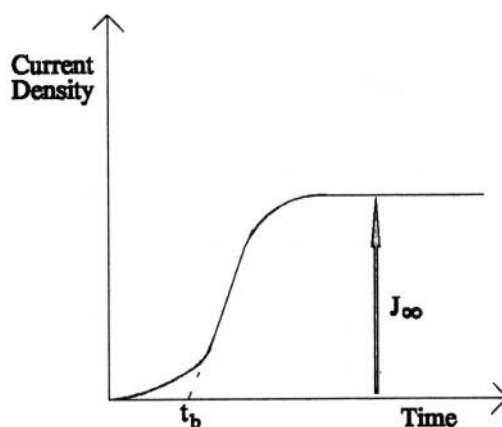


Figure 32. Typical Transient Curve For Hydrogen Absorption During Constant Charging

3.5.2 HYDROGEN PERMEATION MEASUREMENTS

The experimental arrangement consisted of two cells separated by a thin steel membrane (Figure 33). The hydrogen charging (cathodic) side was a cell containing the charging environment, which was normally the test container. This cell contained a SCE (RE) and a platinum anode (AE) connected to a potentiostat which was connected to the membrane (WE). This arrangement allowed the membrane to be cathodically protected. For tests with SRB the anode had to be placed external to the cell as the anodic reactions produce oxygen and chlorine.

Throughout the work the cell on the hydrogen exit (anodic) side of the membrane remained virtually the same. The cell had a nominal diameter of 3.5cm and was of length 10cm, and was able to hold approximately 120ml of solution. This cell contained 0.2N sodium hydroxide solution and normally a Ni/NiO cathode although a platinum electrode was used when using a potentiostat. The Ni/NiO electrode was produced by anodising nickel plate in 10% sulphuric acid at a current density of 15mAcm^{-2} for 30 minutes.

The steel membranes were cut from a sheet of 57 μm thick shim steel (0.04C %Wt., 0.24Mn, <0.01Cr, 0.02Ni, 0.04Cu). Before use they were polished with 1200 grit paper and degreased in an ultrasonic bath. The two halves of the permeation cell were held together using four to five bulldog clips, with the steel membrane sandwiched in between. To ensure good seals between the cells and the membrane, PTFE washers coated in silicone grease were used. The cathode was placed into the cell and the cell filled with 0.2N sodium hydroxide solution. Residual hydrogen was depleted from the membrane by using a power supply to hold it at

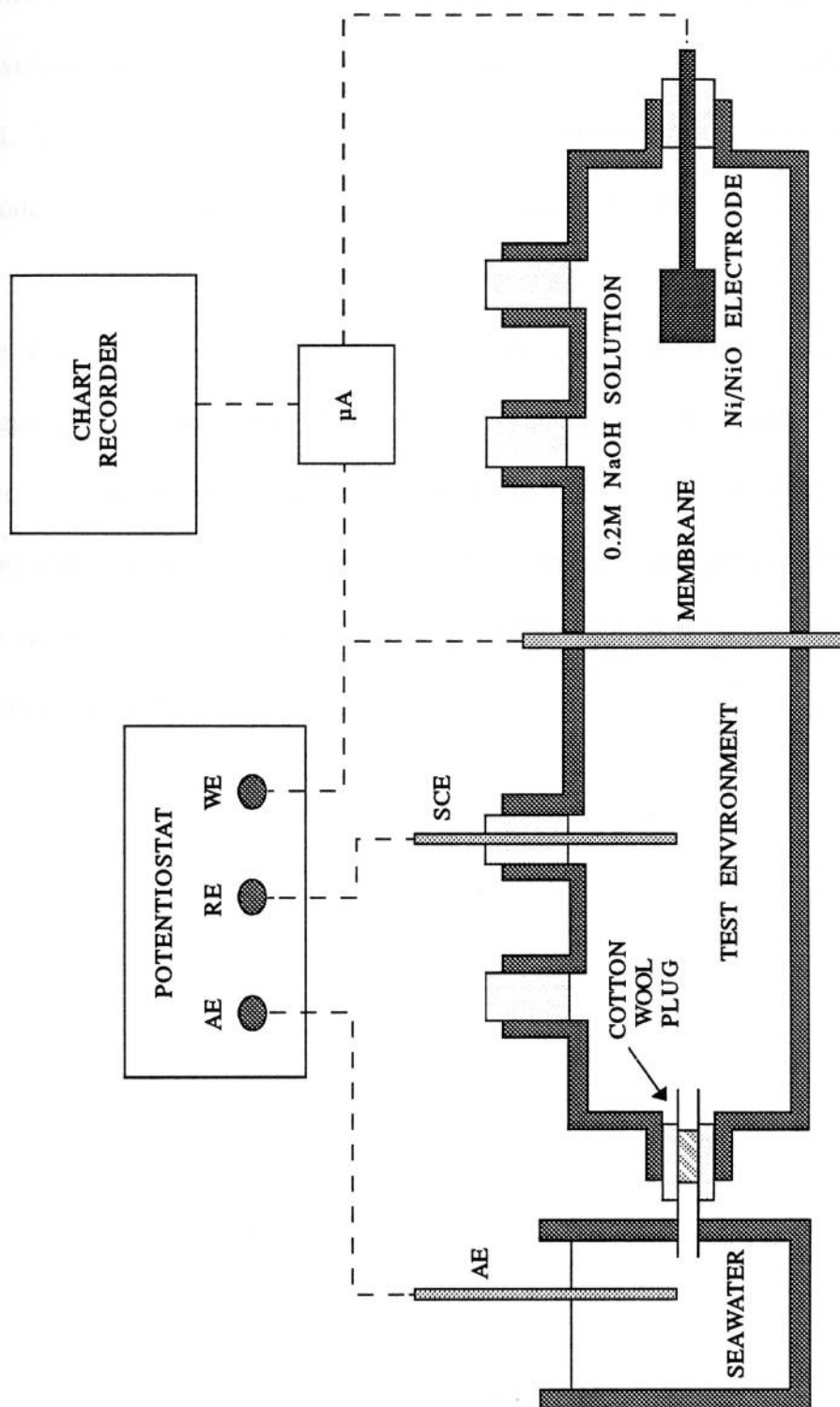


Figure 33. Double Hydrogen Permeation Cell

+150mV (-96mV(SCE) with respect to the Ni/NiO electrode (Ni/NiO electrode $\approx$ 0mV(NHE)). A zero resistance ammeter was used to monitor the resulting current. Depletion was considered satisfactory when a small background current of $0.015\mu\text{Acm}^{-2}$ or less was achieved. In some cases the power supply was substituted for a potentiostat, and therefore the cathode was a platinum electrode and a SCE had to be used.

Once the membrane had been depleted the charging cell (sediment cell (Figure 19), seawater tank (Figure 29a), anaerobic cell (Figure 30) or another glass cell (Figure 33)) was filled with sediment, seawater, biologically active seawater or sodium sulphide solution. The CP was turned on and set to the required potential. The current resulting on the anodic side of the cell was monitored and used to calculate the surface hydrogen concentrations as described previously in section 3.5.1.

3.6 FATIGUE TESTING

3.6.1 SPECIMEN DESIGN AND PREPARATION

Tests were made on single edge notch specimens suitable for tension/tension loading under three point bending. Specimen design was based on BS 5762⁽²⁷⁰⁾. Their dimensions were width (W) 24mm, thickness (B_F) 18mm and length 110.4mm with a 8 x 1.5mm notch as shown in Figure 34.

Fatigue specimens were machined, in the TL orientation, from the centre of the welded plate without the notch. Both sides of the sample were polished (down to 1 μ m) and etched (2% Nital) to indicate the HAZ position. Microhardness measurements were made across the HAZ on both sides of the specimen to identify the band of maximum hardness. Notches were machined so the notch root pointed down the band of maximum hardness.

The specimens then had holes sparked machined for the microgauge wires, which were attached as described in section 3.3.2. Specimens were prefatigued at 16Hz using a reducing load method. Values given in Table 10 were used to give a 3mm precrack.

Table 10 Prefatigue Values

CRACKLENGTH (mm)	MAX. LOAD	MIN. LOAD
8 to 9	10	1
9 to 9.5	9	0.9
9.5 to 10	7	0.7
10 to 11	6	0.6

Specimens were then put into a seawater tank and cathodically protected at the test potential for two weeks. In previous work, the aim of the two week soak at the CP test potential was to give a uniform hydrogen concentration throughout the specimen. Calculations have shown that two weeks was insufficient to give a uniform concentration (see discussion). As the time required for this uniform concentration to be achieved is impractical, the two week soak was adopted so results could be compared to those achieved in earlier test programmes. After the soak period specimens were then ready for testing.

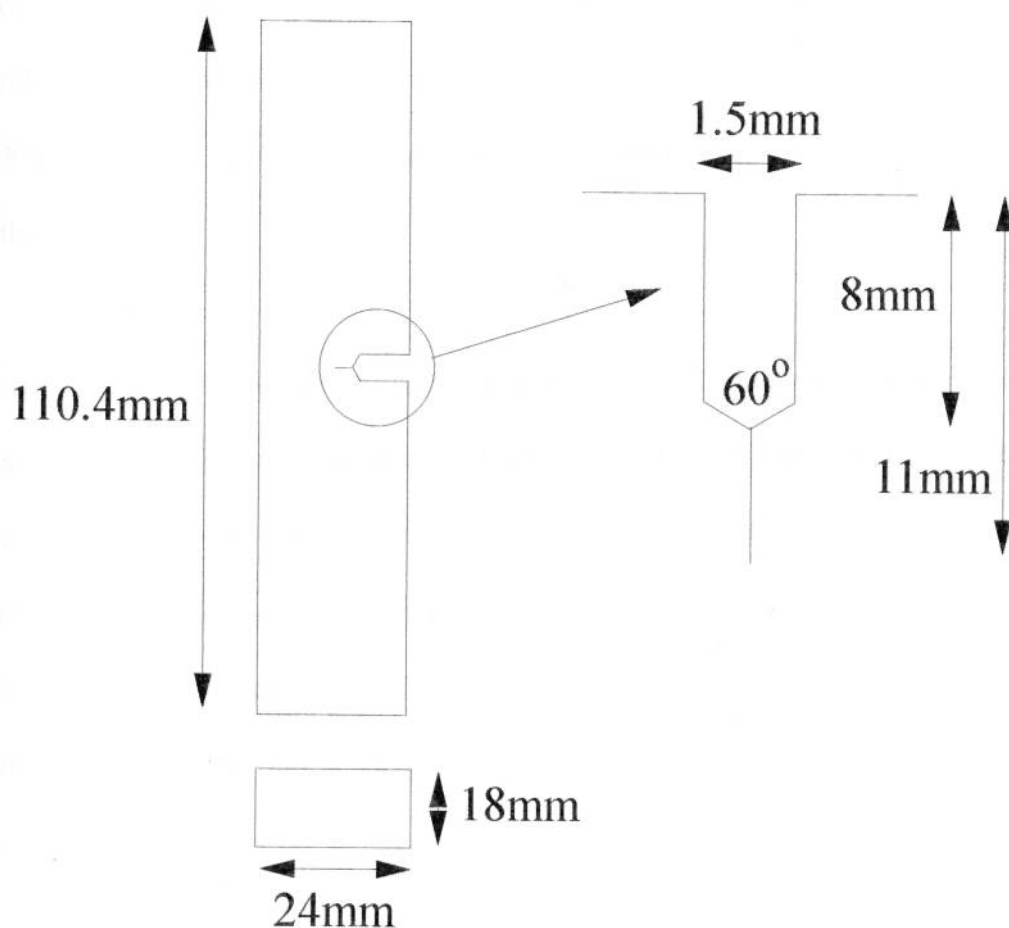


Figure 34. Fatigue Specimen Design

3.6.2 TEST CELL

The requirement for anaerobic testing meant that the fatigue specimens had to be totally enclosed by the test cell. Such a cell had to be flexible and also allow one roller to be in contact with the centre of the fatigue specimen and the other two to be in contact with the end regions. In addition, the cell had to allow CP to be applied to the specimen when required. The cell that was designed and used is shown in Figure 35.

It comprised of two circular (50mm diameter x 10mm) PTFE end pieces which clamped around the fatigue specimen which were separated by a perspex sheet which located the central roller. The flexible shell (70mm length) of the cell was tubular and formed from silicon rubber which was moulded using a RTV silicon rubber (Silastic E RTV Silicone Rubber Kit). The two PTFE end pieces had entry and exit holes for solution to be pumped around the test cell.

CP was applied by putting a SCE in the entry flowline with the platinum electrode connected to the exit flow line. For reasons discussed previously the platinum electrode could not be connected directly into the flow of test solution. Instead a beaker was attached to the exit flow line via a glass tube with a cotton wool plug inserted. The cell was used for the sterile seawater tests as well as the biologically active solutions. Hydrogen permeation measurements were made during fatigue testing by placing a hydrogen detector cell in the entry flow line.

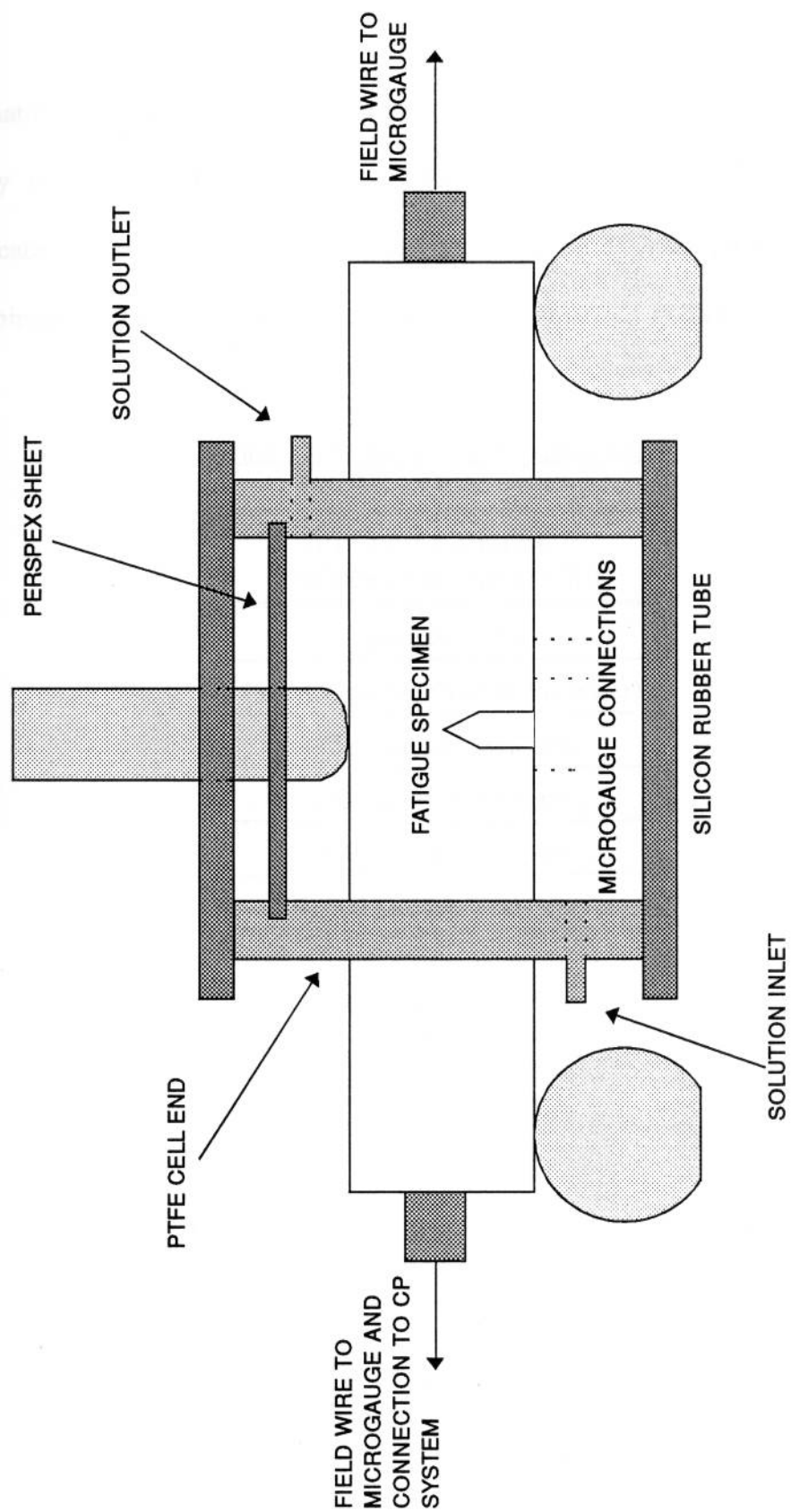


Figure 35. Corrosion Fatigue Cell

3.6.3 TEST APPARATUS

A schematic of the test apparatus is shown in Figure 36. Testing was carried out at a frequency of 0.5Hz and with $R=0.6$. The microgauge readings of cracklength were automatically taken every 12 seconds and recorded on a chart recorder (speed set at 0.5mm/minute). The various tests carried out are summarised in Table 11.

Table 11. Summary of Fatigue Tests

APPLIED CATHODIC POTENTIAL [mV(SCE)]
Laboratory Air
Free Corrosion (Sterile Seawater)
-950 (Sterile Seawater)
-1100 (Sterile Seawater)
-950 (Active Seawater)
-1100 (Active Seawater)

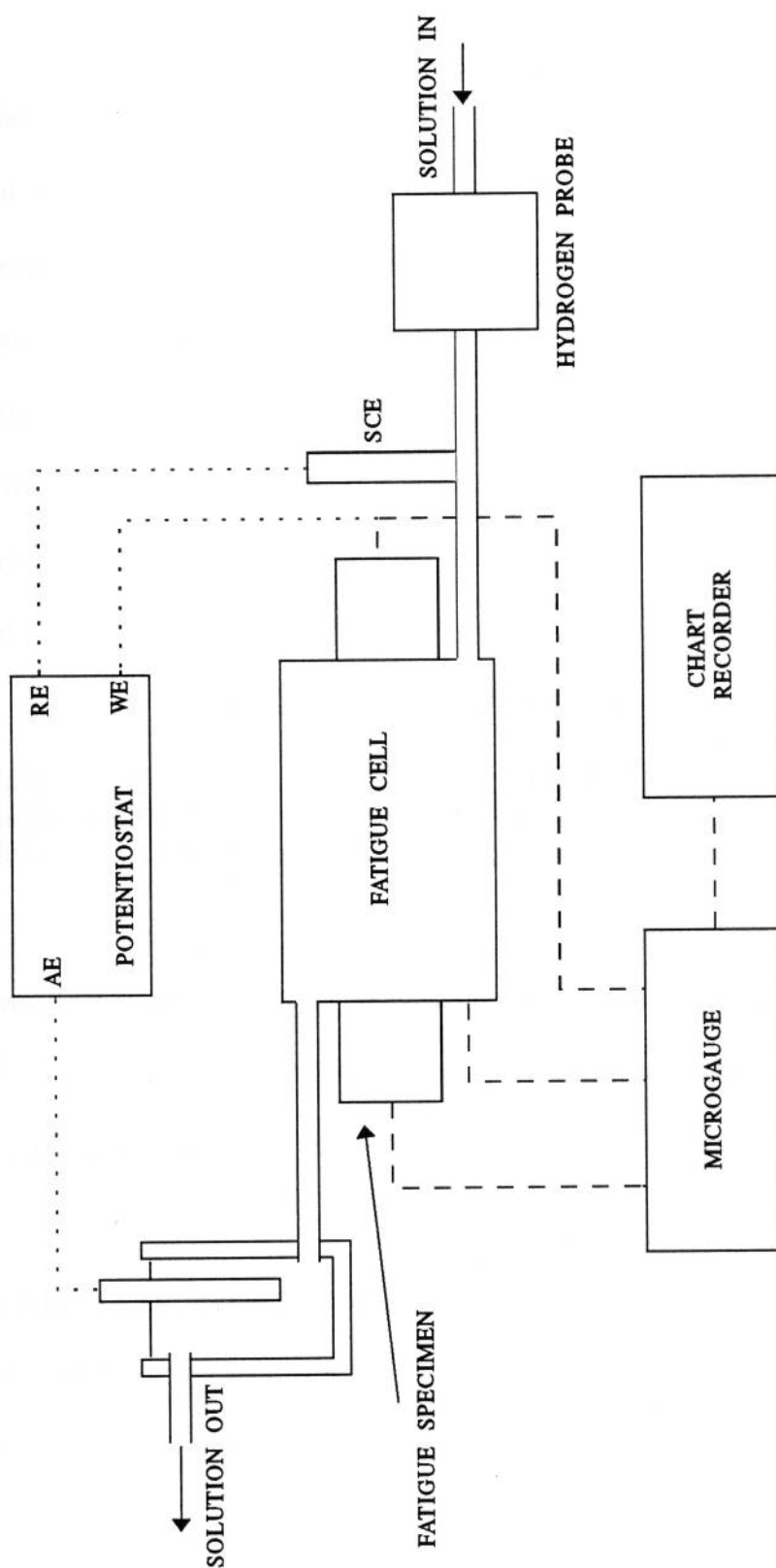


Figure 36. Schematic of Fatigue Test Experimental Arrangement

3.7 TOTAL SULPHIDE MEASUREMENTS

Measurements of total acid soluble sulphide (TS) concentrations were employed to give not only TS but also to provide an indirect assessment of SRB activity in the test environment. Hydrogen sulphide generated by SRB can exist in several forms. It may be present either in the gas phase or dissolved in the bulk liquid. In the latter case, dissociation results in the formation of HS^- ions and, at high pH, S^{2-} ions (Figure 16). In addition, the sulphide may combine with ions in solution to form iron sulphides which cause the characteristic blackening of the solution. For this reason it is preferable to determine the total sulphide concentration present and not just H_2S .

Table 12 Solubilities of Sulphides

Soluble in water	Na_2S K_2S $(\text{NH}_4)_2\text{S}$ BaS
Soluble in 0.3M H^+	ZnS FeS MnS CoS
Soluble in aqua regia	HgS

These measurements have been carried out using two methods, firstly a standard iodimetric titration⁽²⁷¹⁾ and secondly a VACUette test kit (CHEMetrics). The principles, method and reason for use for both tests is given below.

Iodimetric Titration for Determination of Total Sulphide⁽²⁷¹⁾

This is an inexpensive and simple method to perform and requires only standard laboratory equipment, but gives very accurate and precise results. This method utilises the reversible reaction;



For reasonably satisfactory results, the sulphide solution must be dilute ($\leq 0.02\text{N}$), more

concentrated solutions risk the precipitated sulphur enclosing some iodine and thus giving an incorrect result. The sulphide solution should be added to the acidified iodine solution and not conversely else produced hydrogen sulphide will be lost.

The titration was carried out as follows. 10ml of 0.1N iodine solution was pipetted into a flask and 15ml of 1.5N HCl added using a small measuring cylinder. 25ml of the sulphide solution was slowly pipetted into the acidified iodine solution. The excess iodine solution was then titrated against 0.1N sodium thiosulphate solution (equation 71). When the colour of the iodine had become faint, starch was added as an indicator. The purple coloration produced fades as thiosulphate is added and the end point is indicated by the solution becoming clear. The volume (ml) of thiosulphate used (titre) is recorded and used to calculate the TS concentration (equation 72). Three replicate titrations were carried out for each measurement if sufficient test solution was available.



$$C_s = [20C_i - (C_T \times \text{Titre})] / 50 \quad (72)$$

where C_s is the total sulphide concentration (M), C_i is the iodine solution concentration (M), and C_T is the thiosulphate solution concentration (M). The molar concentration of sulphide can be converted to $\mu\text{g/l}$ (ppm) by multiplying by 3.4076×10^4 .

VACUette Test Kit

The test employs the highly sensitive and specific methylene blue colorimetric test method. In an acidic solution, sulphide reacts with N,N-dimethyl-p-phenylenediamine and ferric chloride to produce methylene blue. The test measures hydrogen sulphide and total acid soluble sulphides. The blue colour formed is directly proportional to the sulphide

concentration in the sample. By following the instructions provided with the test kit, the test solution TS concentration is determined by comparison of the depth of colour to standards. The great advantage of this test is that it only requires 10 μ l of test solution.

3.8 ENUMERATION OF VIABLE SRB

Standard methods for bacterial counts become complicated when applied to SRB due to the requirement of storage of the media under oxygen free conditions. Methods such as plate spreading would not only be very time consuming, but if used routinely, would require a vast number of anoxic containers. For these reasons, it was decided to use the most popular method to date for SRB counts, which employs universal bottles in a most probable number (MPN) test. In addition, another MPN test using sloppy agar in deep test tubes was employed as a comparison for the first method. This time consuming test required anaerobic jars, so was carried out less frequently.

MPN tests are based on successive dilutions of the original test solution giving positive results indicating the presence of bacteria, until they reach a point where there are no bacteria in a dilution, and therefore, give a negative result. The previous dilution to this negative is assumed to have contained between 1 and 9 bacteria, thus allowing calculation of the original bacterial numbers as demonstrated in Table 13. Details of both MPN test methods are given below.

Table 13 Enumeration of viable SRB

10^{-1} only	1-9
10^{-1} to 10^{-2}	10-99
10^{-2} to 10^{-3}	100-999
10^{-3} to 10^{-4}	1000-9999 etc.

Both tests required three sets of serial dilutions from 10^{-1} to 10^{-9} to be made. Thirty universal

bottles were autoclaved and allowed to cool to room temperature. Using three of the universal bottles, three samples were taken from the test solution. From the first of these bottles, 100µl of solution was removed using a micropipette and added to a sterile universal bottle. To this 900µl of freshly prepared and deaerated Postgate B solution⁽⁷⁸⁾ (Table 14) was added and the solutions mixed to produce the 10^{-1} dilution. 100µl of this solution was removed and placed into another bottle and again 900µl of Postgate's B was added to make the 10^{-2} dilution. This process was repeated up to the 10^{-9} dilution to make the first set of serial dilutions. The whole process was repeated twice more using the remaining two samples to give three sets of dilutions. The universal bottles were filled to the very top with more Postgate B solution ensuring sure no air bubbles were trapped within. Initially, one extra set of dilutions were made in which the initial test solution was substituted for Postgate B solution. This dilution set was used as a blank to assess contamination during the procedure. After no contamination was found in the first eight sets of blanks their production was limited to every third enumeration.

The filled bottles were incubated at 30 to 35°C for a period of 21 days. A black discolouration of the solution due to the formation of iron sulphide was a positive test indicating the presence of SRB by their metabolism. Any bottles which had a pink discolouration due to oxygen were ignored (see notes after Table 14).

Sediment samples were taken using along glass tube containing a closely fitting PTFE rod. This arrangement acted as a syringe allowing core samples to be taken from any location in the sediment. The cores were then ejected into universal bottles for weighing and testing. Solutions could be sampled for bacterial enumeration directly but sediments needed a

pretreatment before a MPN test. Sediment samples were placed into a pre-weighed sterile universal bottles and reweighed to give the wet weight of the sediment (between 3 to 6g). 10ml of deaerated half strength Ringers solution which contained 0.01mg/l of the surfactant cetyl trimethylammonium bromide (CTAB) was added and the top of the bottle loosely sealed with aluminium foil. A glass tube was pushed through the foil to allow oxygen free nitrogen to be passed into the headspace above the solution for ten minutes. Another layer of foil was added as the glass tube was removed from the bottle and the screw cap fitted. The bottles were shaken for 20 minutes. Sampling of the solution was then carried out and the above procedure used for the enumeration.

The second method relied on serial dilutions being made as described above. The dilutions were transferred to sterile deep glass test tubes and filled with deaerated sloppy agar (Postgate's B, 0.05-0.1% marine agar and resazurin). The tubes were transferred to an anaerobic jar (BBL GasPak System) which was sealed after the oxygen removal reaction was initiated (appendix C). The sloppy agar includes reducing agents in its formulation, so oxygen contamination is minimised during the filling of the tubes. The procedure was carried out under aerobic conditions so the top 1cm of the sloppy agar became contaminated with oxygen (as indicated by the resazurin), but as convection currents are much reduced over aqueous solutions, the lower portion remains anaerobic. Once placed into the anaerobic jar the top layer is rapidly deaerated and in this respect anaerobic conditions are guaranteed in this lower portion during the whole procedure.

Table 14 Postgate's B Solution

<i>KH₂PO₄</i>	0.5g
<i>NH₄Cl</i>	1g
<i>CaSO₄</i>	1g
<i>MgSO₄.7H₂O</i>	2g
<i>Sodium Lactate</i>	3.5g
<i>Yeast Extract</i>	1g
<i>Ascorbic Acid</i>	0.1g
<i>Thioglycollic Acid</i>	0.1g
<i>FeSO₄.7H₂O</i>	0.5g

Made up to one litre with 3.5% NaCl solution and pH adjusted to between 7 and 7.5 with 0.2M NaOH solution. This solution always contains a precipitate. Resazurin (0.0001% weight per volume) was added to the media as a redox indicator. When reduced it is colourless but develops a pink coloration on exposure to oxygen, thus giving a visual indication of aerobiosis.

Table 15 Ringers Solution

<i>Sodium Chloride</i>	2.15g
<i>Potassium Chloride</i>	0.075g
<i>Calcium Chloride, anhydrous</i>	0.12g
<i>Sodium Thiosulphate Pentahydrate</i>	0.5g

This is a physiological saline which has the same osmotic pressure as microorganisms. It is a 0.85% solution of NaCl which is ironically balanced so that the toxic effects of the metallic ions neutralize one another. The pH should be 6.6.

4.0 RESULTS

4.1 Bead on Plate Results

Microhardness measurements made across the HAZ of each steels BOP test are given in Figures 37 to 42. Maximum hardness values found in the HAZ together with their corresponding grain sizes gave the target values for the heat treatment. Figures 37 to 39 are for SE500 and show maximum HAZ hardness values of 362, 361 and 370VPN occurring respectively at 16, 9 and 6% of the total HAZ distance from the fusion line. Figures 40 to 42 are for DSE690 and show maximum values of 452, 466 and 473VPN occurring respectively at 45, 50 and 55% of the total HAZ distance from the fusion line. Once the hardest region in each weld had been identified, hardness measurements were taken in this region and are summarised in Table 16.

Table 16 Summary of Maximum Hardness Measurements (VPN)

SE500	370	374	355	356	362	365	362	361
DSE690	473	466	452	456	456	448		

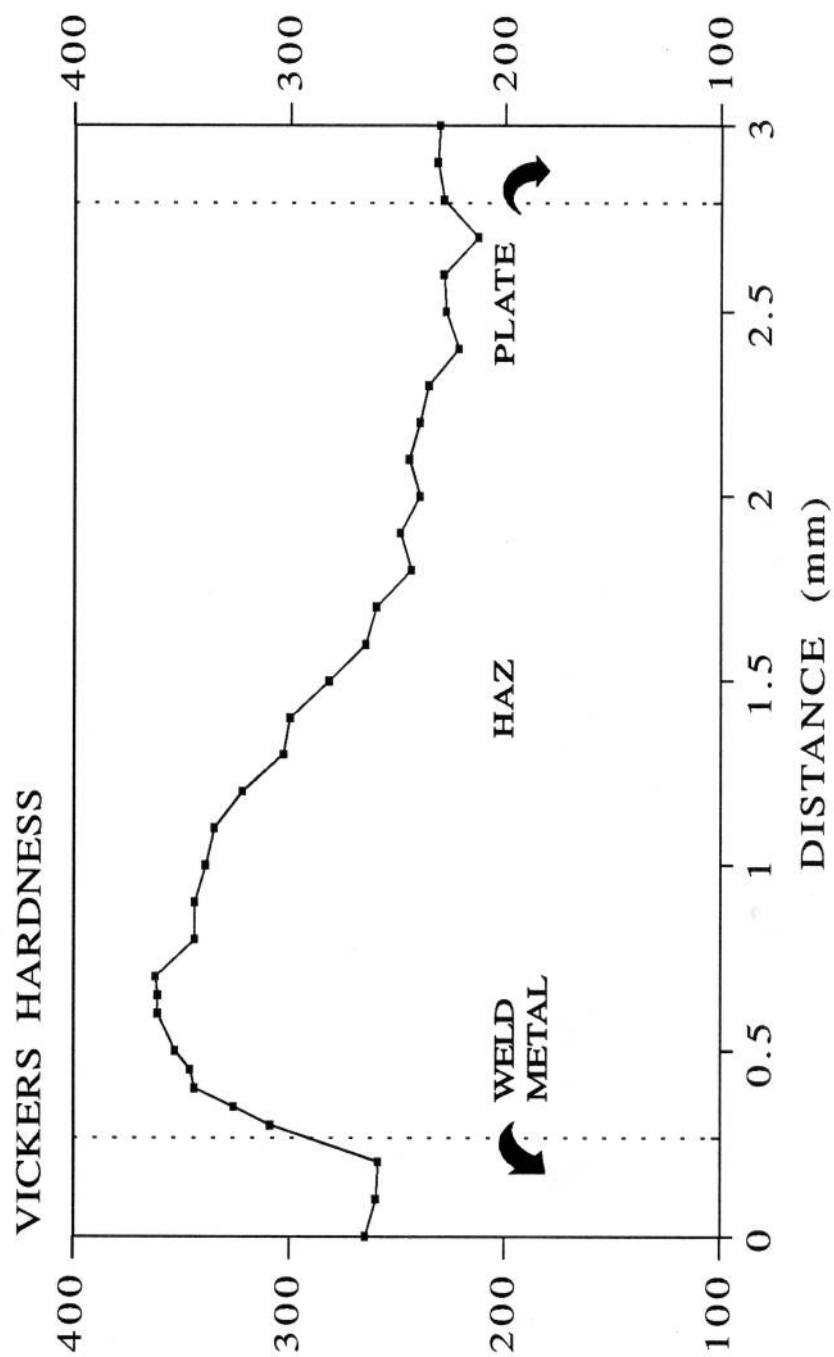


Figure 37. Microhardness Measurements Across SE500 HAZ

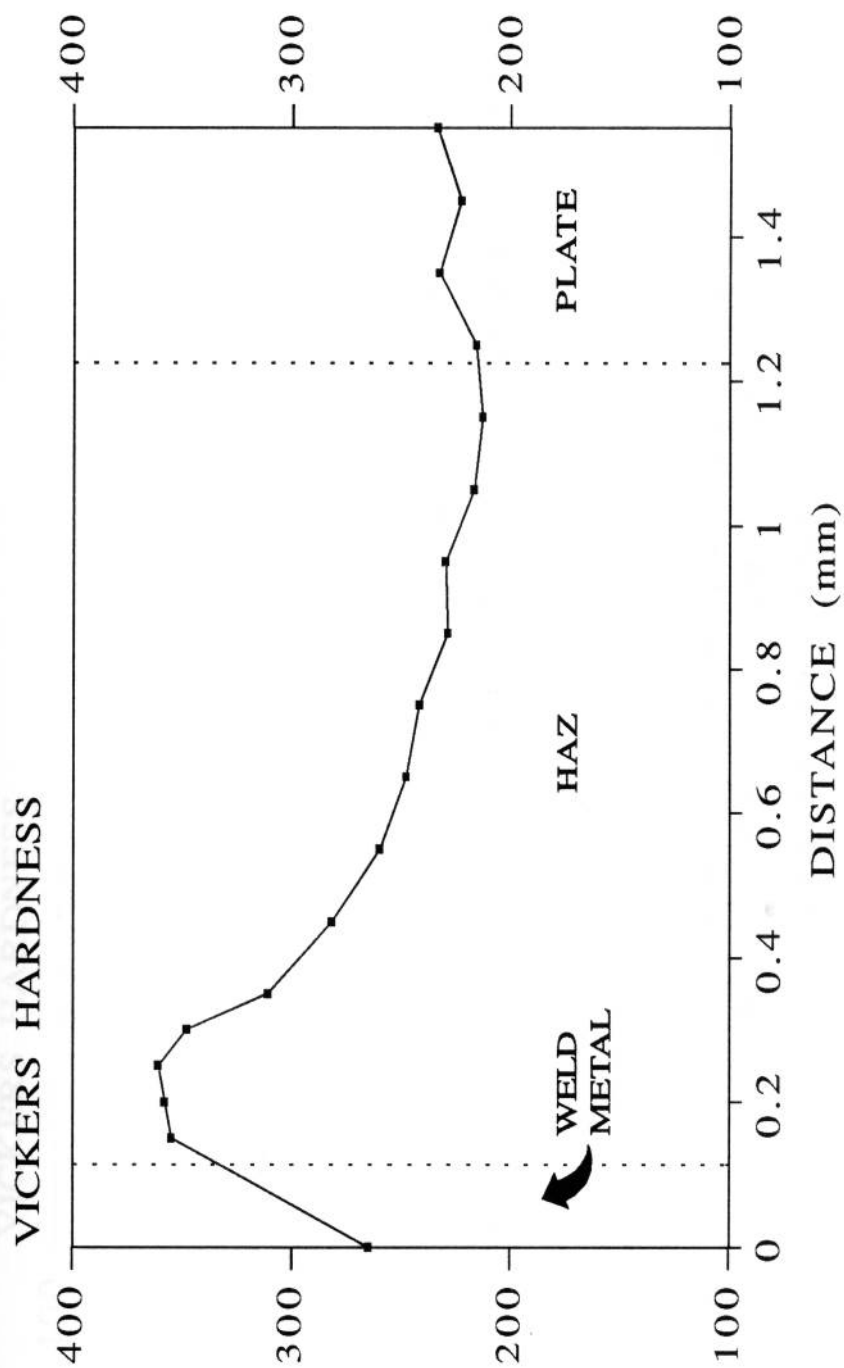


Figure 38. Microhardness Measurements Across SE500 HAZ

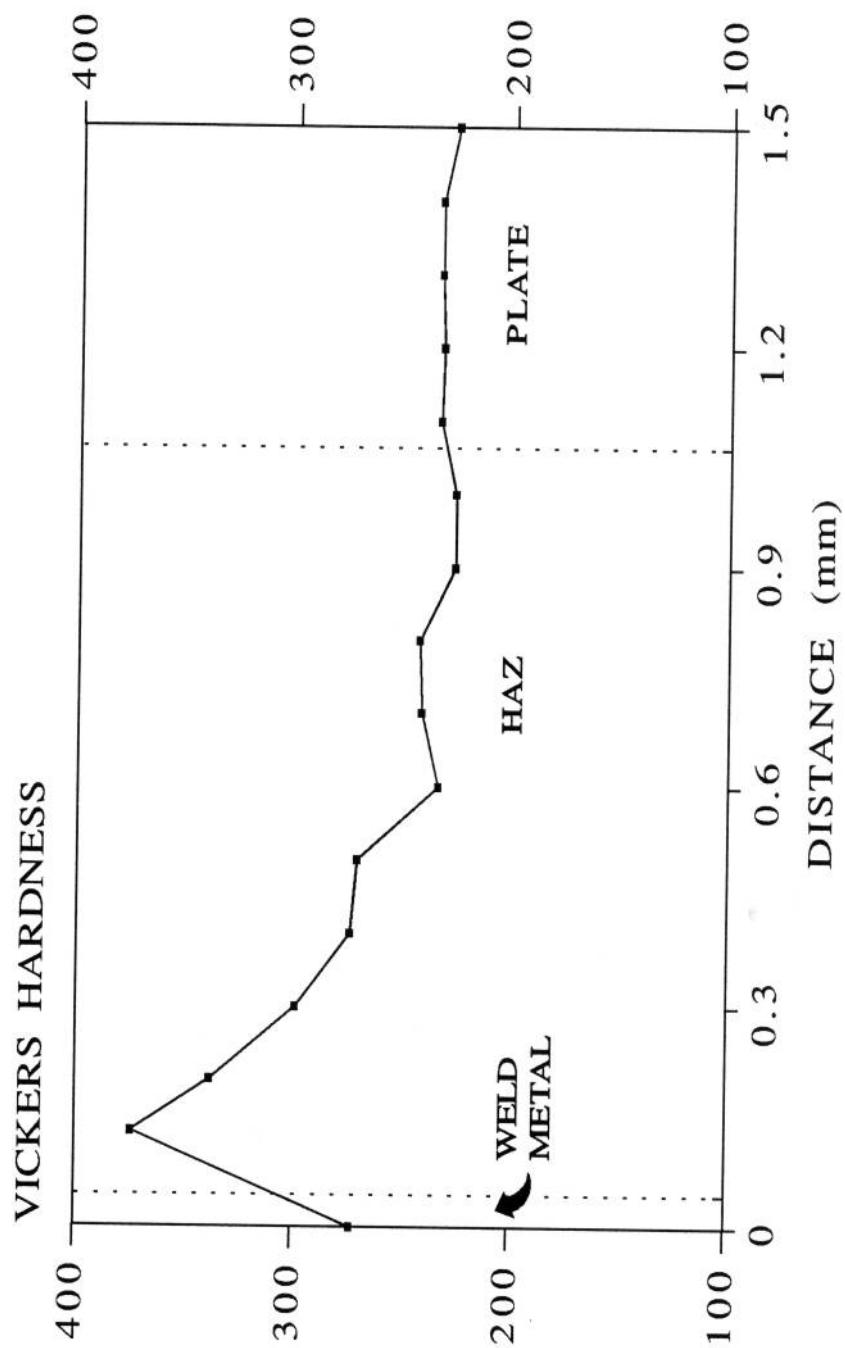


Figure 39. Microhardness Measurements Across SE500 HAZ

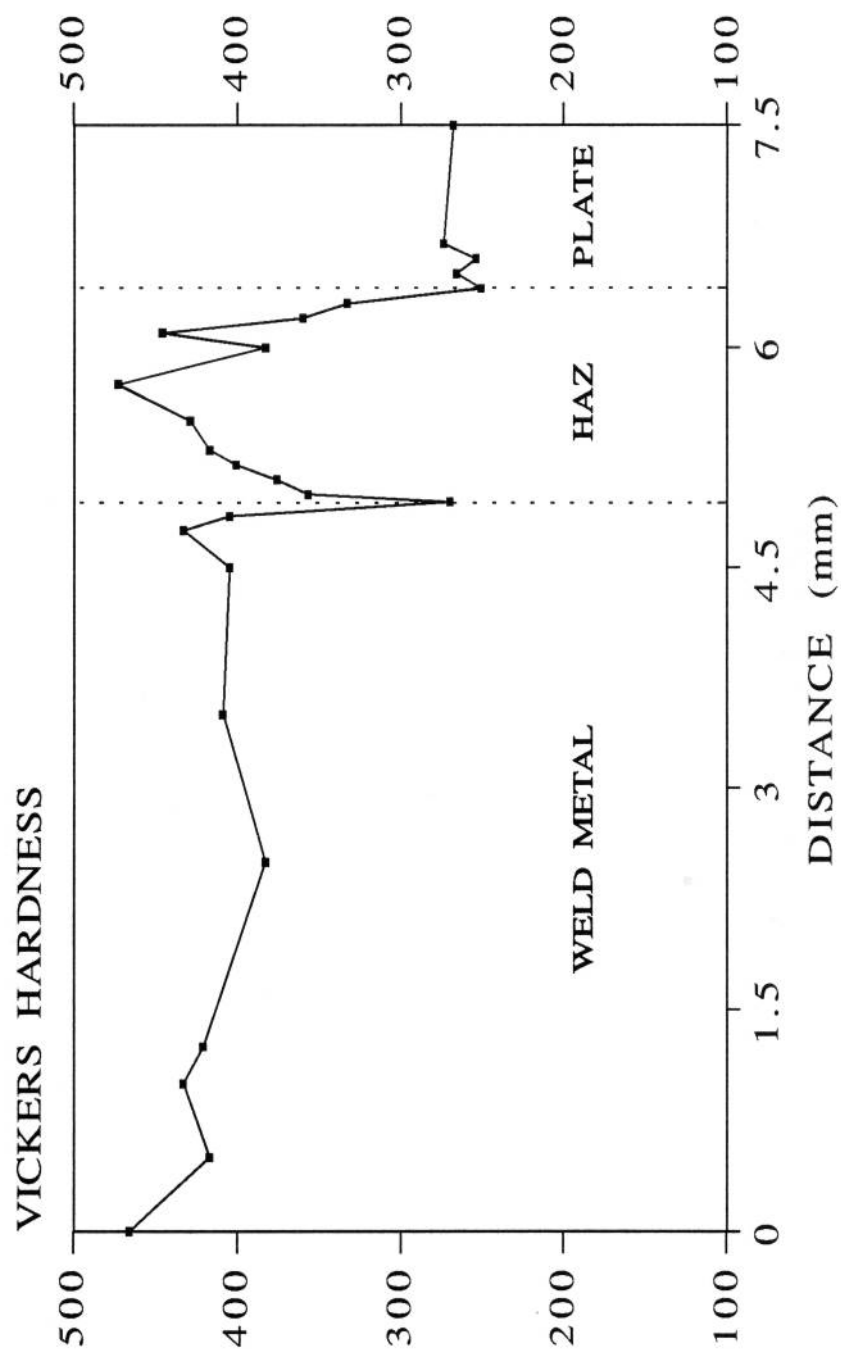


Figure 40. Microhardness Measurements Across DSE690 HAZ

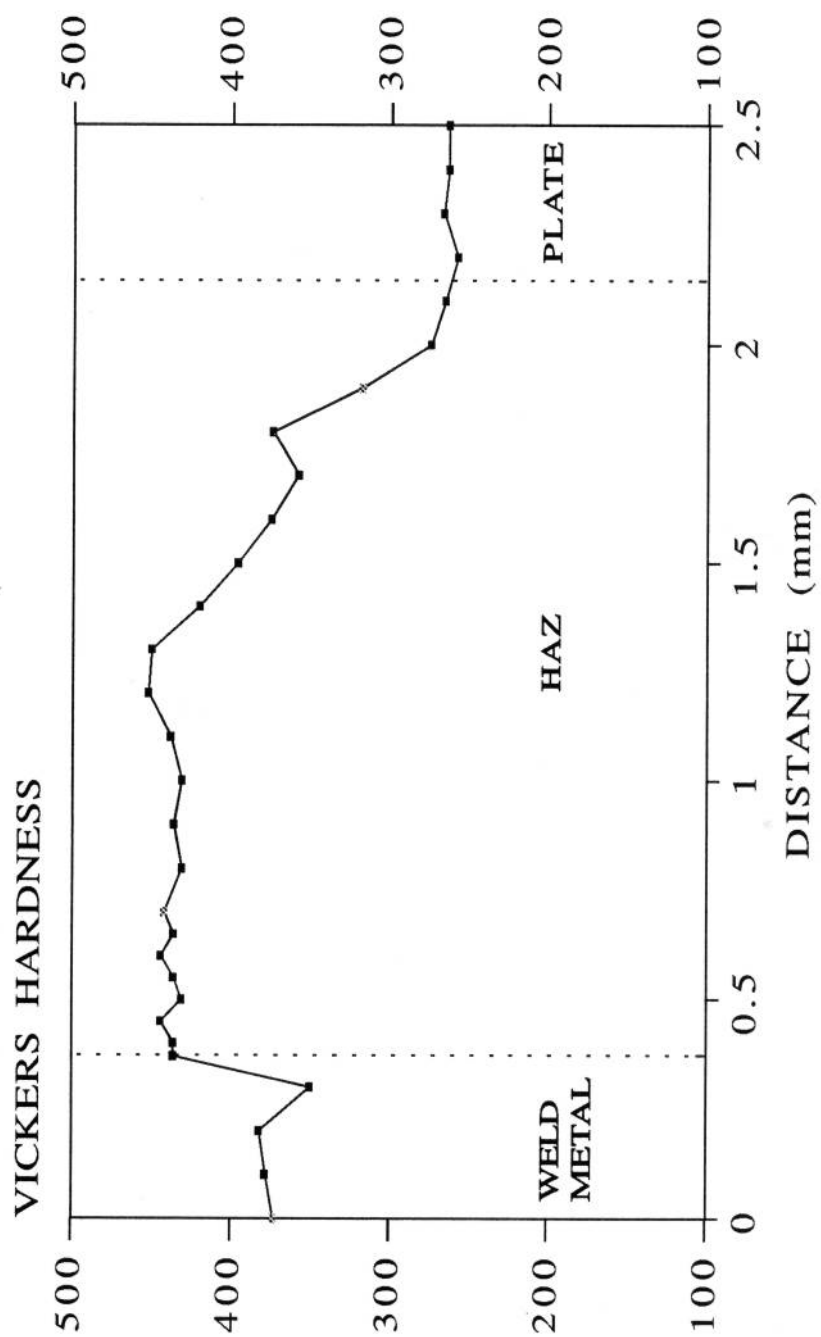


Figure 41. Microhardness Measurements Across DSE690 HAZ

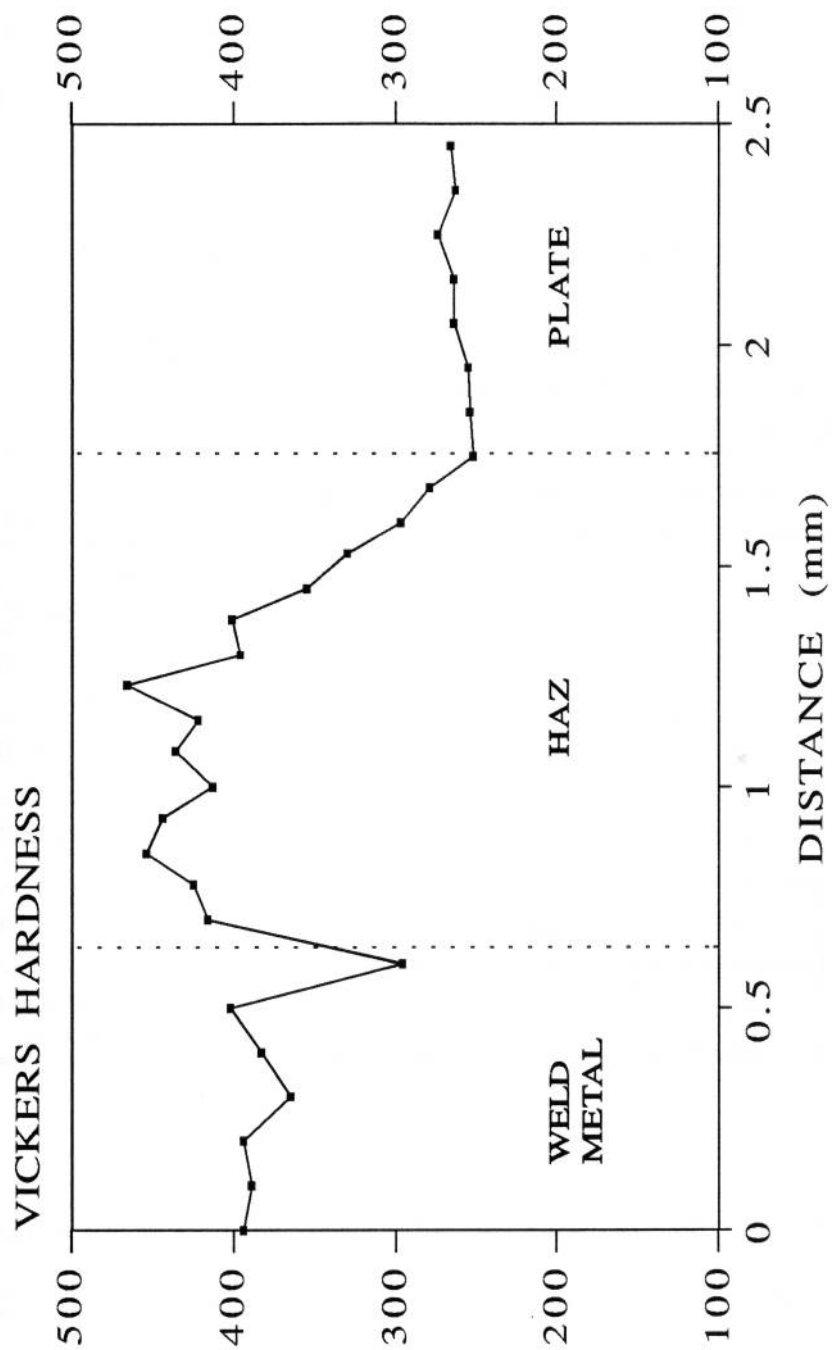


Figure 42. Microhardness Measurements Across DSE690 HAZ

4.2 Heat Treatment

The BOP tests indicated a mean hardness and grain size of 363 VPN and 30 μ m for the SE500 and 459 VPN and <5 μ m for the DSE690. The corresponding values obtained from different heat treatments are given in Table 17.

**Table 17 Hardness & Grain Size Measurements For
Heat Treated Steels**

HEAT TREATMENT	HARDNESS (VPN)		GRAIN SIZE (μ m)	
	DSE690	SE500	DSE690	SE500
60 mins at 900°C Water Quench	430	390	-	-
40 mins at 1100°C Oil Quench	418	317	-	-
20 mins at 1100°C Oil Quench	-	341	-	49
15 mins at 1100°C Oil Quench	426	320	39	53
10 mins at 1100°C Oil Quench	428	323	-	33
5 mins at 1100°C Oil Quench	429	-	< 5	-

The heat treatment decided upon for the two steels was oil quenching after soaking at 1100°C for 10 minutes for the SE500 and 5 minutes for the DSE690.

4.3 TEMPERATURE DEPENDENCE OF C_o

It has been observed in other work^(159,272) that C_o values measured using electrochemical techniques are temperature dependent. Increases in temperature during hydrogen permeation measurements are reflected by increases in the value of J_{∞} recorded and thus the C_o values calculated. The measured current increase is therefore interpreted as an increase in C_o . In reality, the increase in J_{∞} is caused by variation of the diffusion coefficient (D) and the kinetics of the hydrogen evolution and absorption reactions. The diffusion coefficient for steel is known to be very temperature dependent and is related to temperature (T) as shown in equation 73.

$$D = A \exp (-Q / R_U T) \quad (73)$$

where A and Q are constants, R_U is the Universal Gas Constant and T is measured in Kelvin. If it is assumed that the effect of temperature on the kinetics is small and that D is constant then C_o would be expected to depend on temperature in the following way.

$$\ln C_o = G/T + C \quad (74)$$

where G and C are constants. The value of C is dependent on the chemical nature of the environment and the applied cathodic potential. This expression can be used to construct calibration plots for C_o values obtained over a range of laboratory temperatures.

In the experimental work, measurements of surface hydrogen concentration were carried out at laboratory temperatures in the range 16 to 25°C. Clearly, it is important to know the effect of these temperature differences on the measured hydrogen concentrations.

Experimental values of $\ln C_o$ from tests in different environments and at different CP potentials have been plotted against $-1/T$ in Figure 43. The gradients of the lines obtained are summarized in Table 18. The results allowed the permeation measurements made over a range of temperatures to be corrected to a temperature of 21°C (293K). The choice of this figure was made as it is central in the temperature range and was the most common temperature recorded.

Table 18 Summary of Gradients From Figure 43

Potential (mV)	Sterile Seawater	Active Seawater	Sediment
-850	6203	6121 & 6282	6234 & 4480
-950	5415	5952 & 4669	-
-1050	-	-	-
-1150	5316	-	-
-1250	4828	-	-

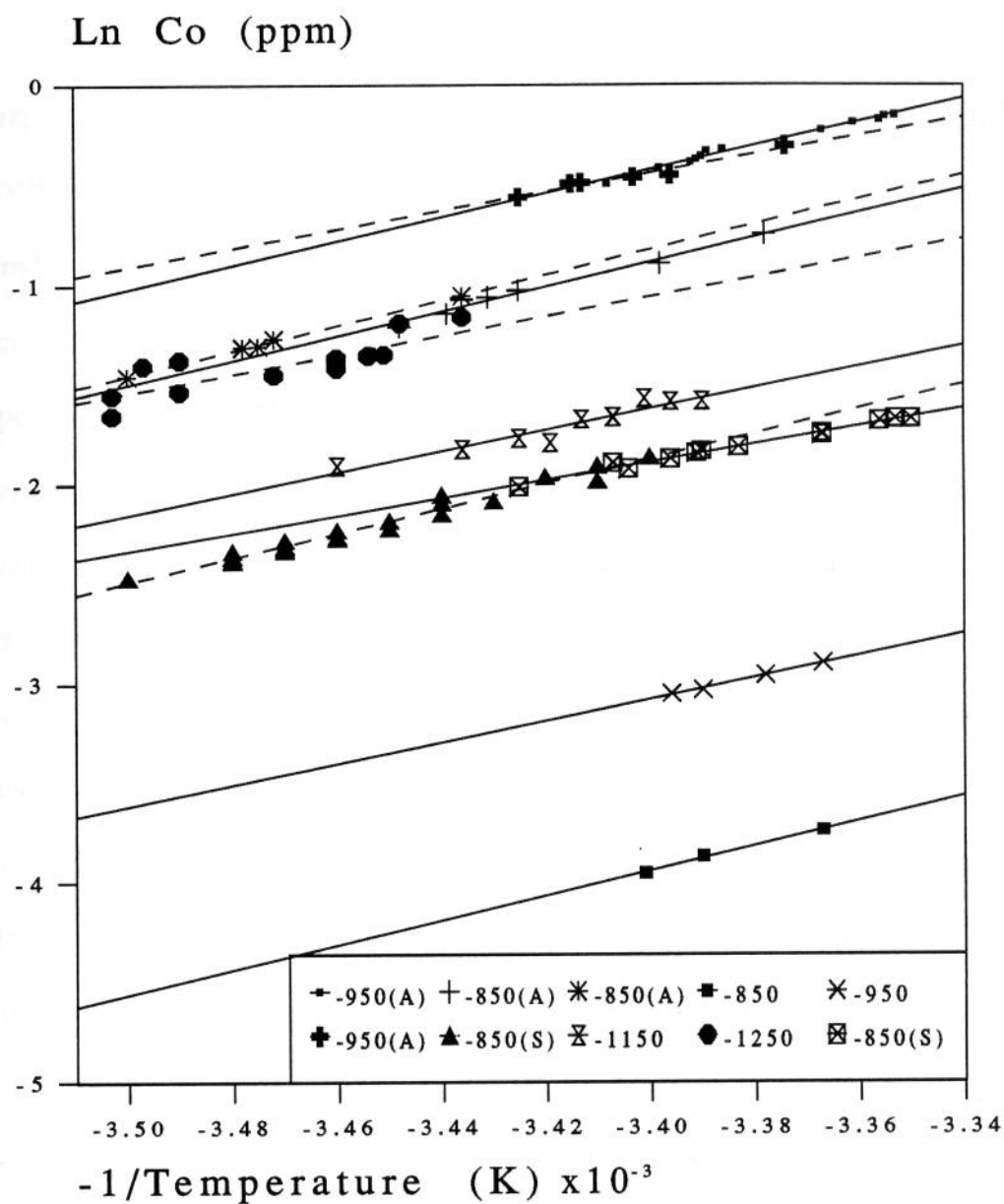


Figure 43. Temperature Dependence of Co Measured in Sterile Seawater, Biologically Active (A) Seawater & Sediment (S)

4.4 DOUBLE CANTILEVER BEAMS

4.4.1 STERILE SEAWATER

The graph of cracklength (a) against time (t) for DSE690 at an applied potential of -850mV(SCE) in sterile seawater is shown in Figure 44. The gradient of the line, measured using the tangent method, at given cracklengths gave the crack velocity (v) at each cracklength. The cracklengths were then used in equation 62 to give the corresponding K values. This allowed the v : K plot to be drawn as shown in Figure 45. The same process was carried out to produce v : K diagrams for the other applied potentials. An idealised v : K diagram is shown in Figure 5. The line consists of three distinct regions which are marked as I, II and III. Region III occurs at high K and v values, and in decreasing K tests, this region is often not seen. Stage II crackgrowth is a plateau region where v is independent of K . Region I occurs at lower K and v values and the slope is normally so steep that it is taken as a measure of the threshold stress intensity, K_{th} (shown as K_{ISCC} in Figure 5). In this work, when v became 10^{-10} ms^{-1} the crack was assumed to have stopped propagating and the K value was taken as K_{th} .

At a potential of -850mV(SCE) the crack in DSE690 grew to a length of 30mm and was considered to have stopped after approximately 1200 hours of testing (Figure 44). Lowering the applied potential to -950mV(SCE) resulted in renewed crack growth (6mm) after a further 1200 hours of testing. Altering the potential to -1050mV(SCE) caused the crack to propagate 21mm in 1000 hours. Application of a more negative potential (-1150mV(SCE)) did not cause any further crack growth but at -1250mV(SCE)

the crack grew a further 5.5mm in 1200 hours of testing.

The lower strength steel, SE500, did not crack in sterile seawater at any of the test potentials. The threshold values obtained for DSE690 and the corresponding Figure numbers for each test are summarised in Table 19. The v:K plots obtained for all the tests in sterile seawater are compared in the discussion section

Table 19 Summary of Threshold Values in Sterile Seawater

	SE500	DSE690	
mV(SCE)	RESULT	K_{th} (MNm ^{-3/2})	FIGURE NO.
-850	NO CRACK	51	45
-950	NO CRACK	45	46
-1050	NO CRACK	30	47
-1150	NO CRACK	NO FURTHER CRACKGROWTH	-
-1250	NO CRACK	27	48

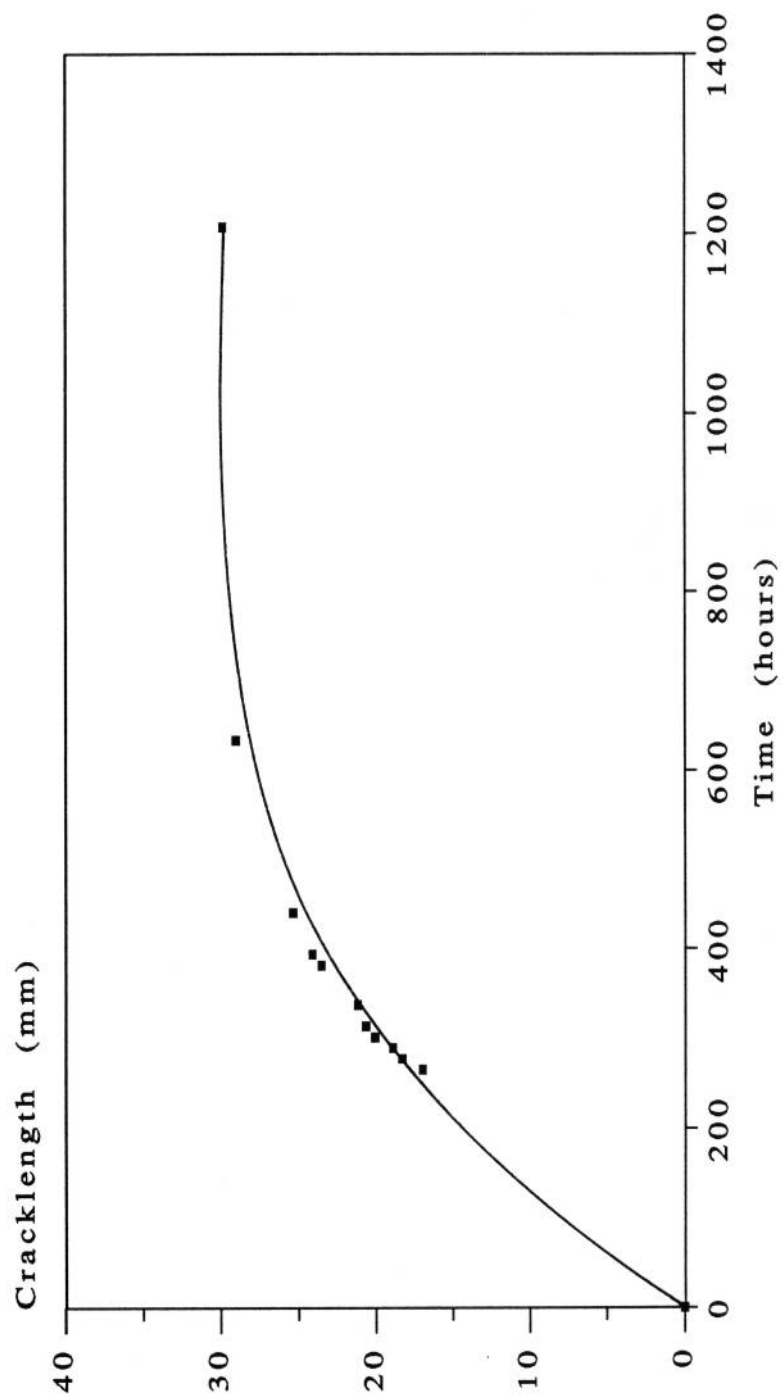
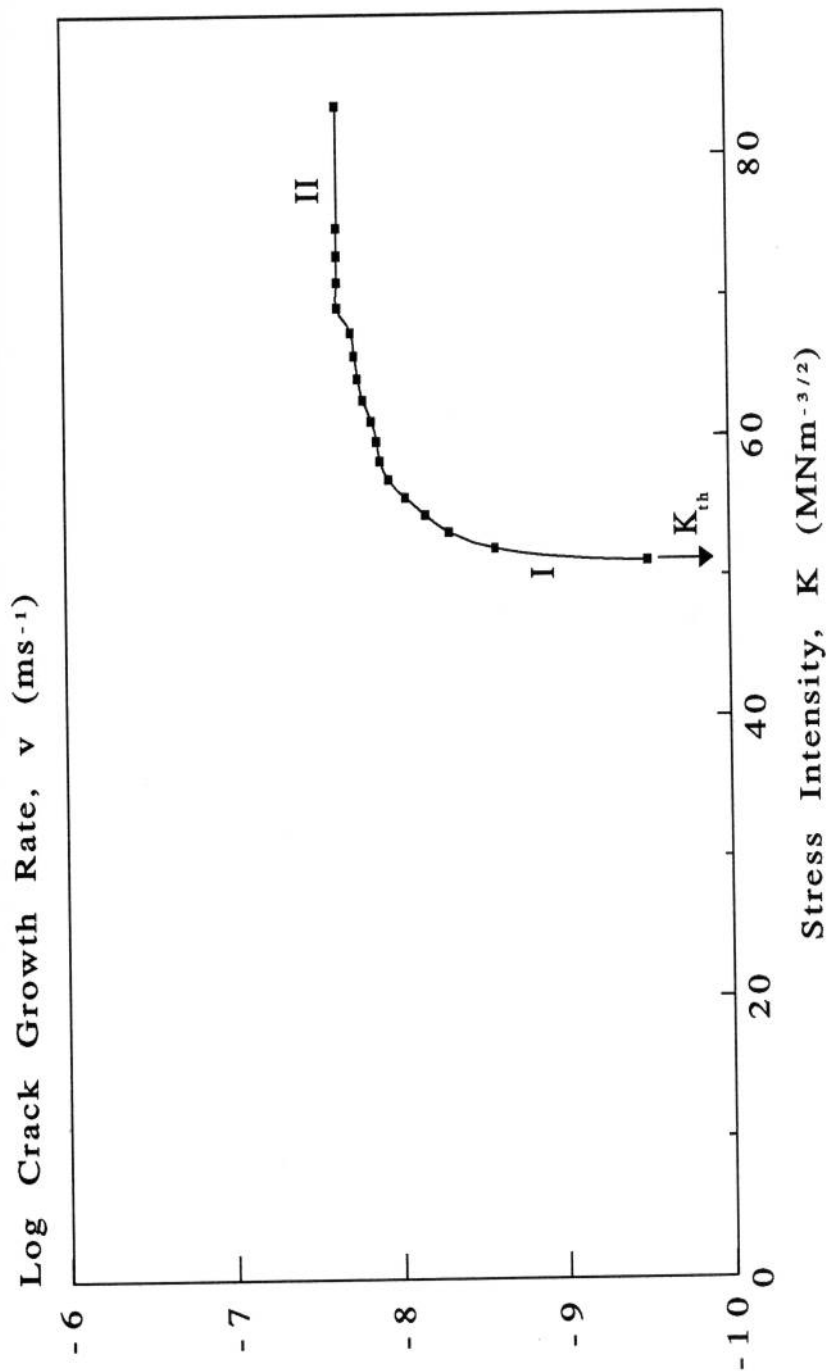


Figure 44. Cracklength (a) Against Time (t) For DSE690 DCB at Potential of -850mV(SCE)



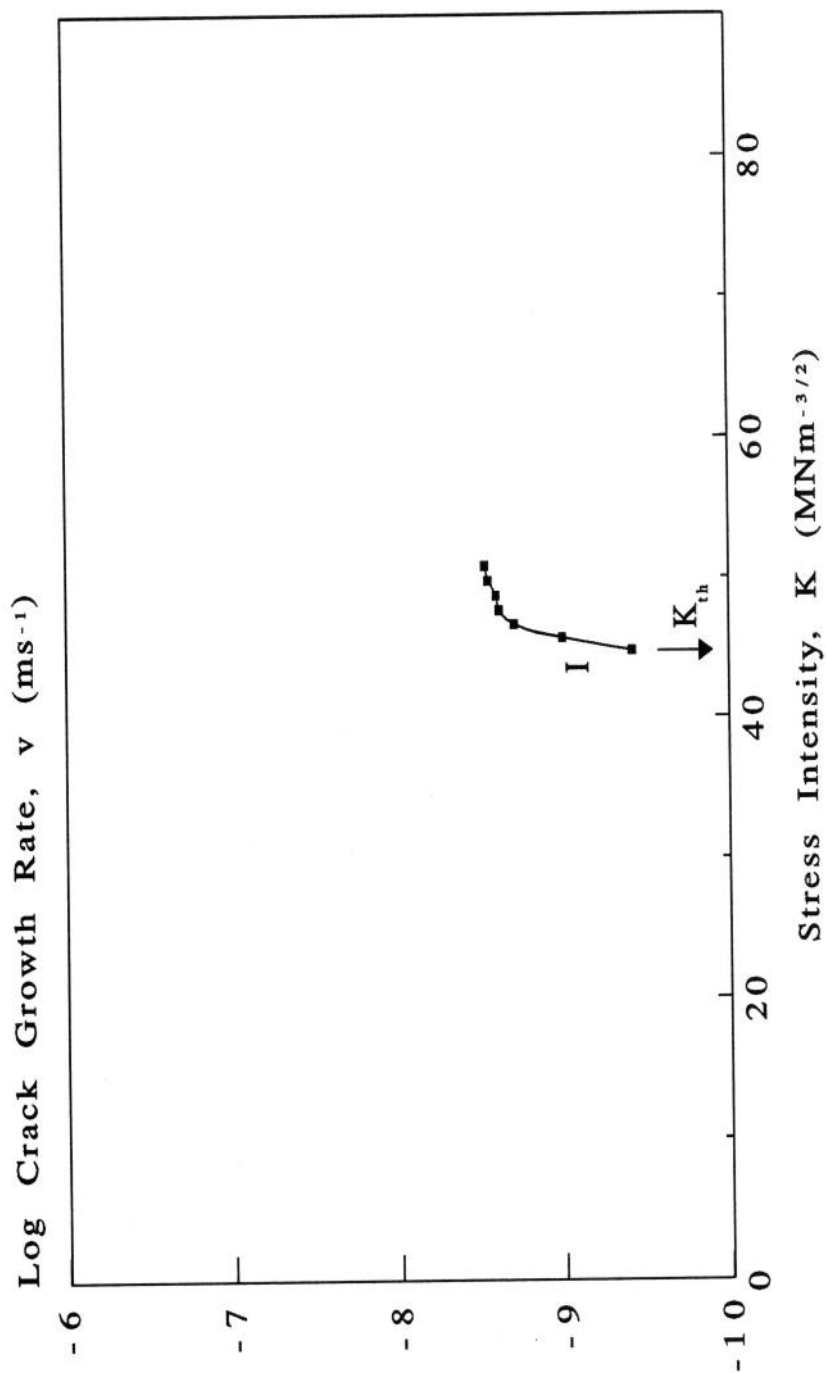


Figure 46. v : K Diagram For DSE690 DCB at Cathodic Potential of -950mV(SCE) in Sterile Seawater

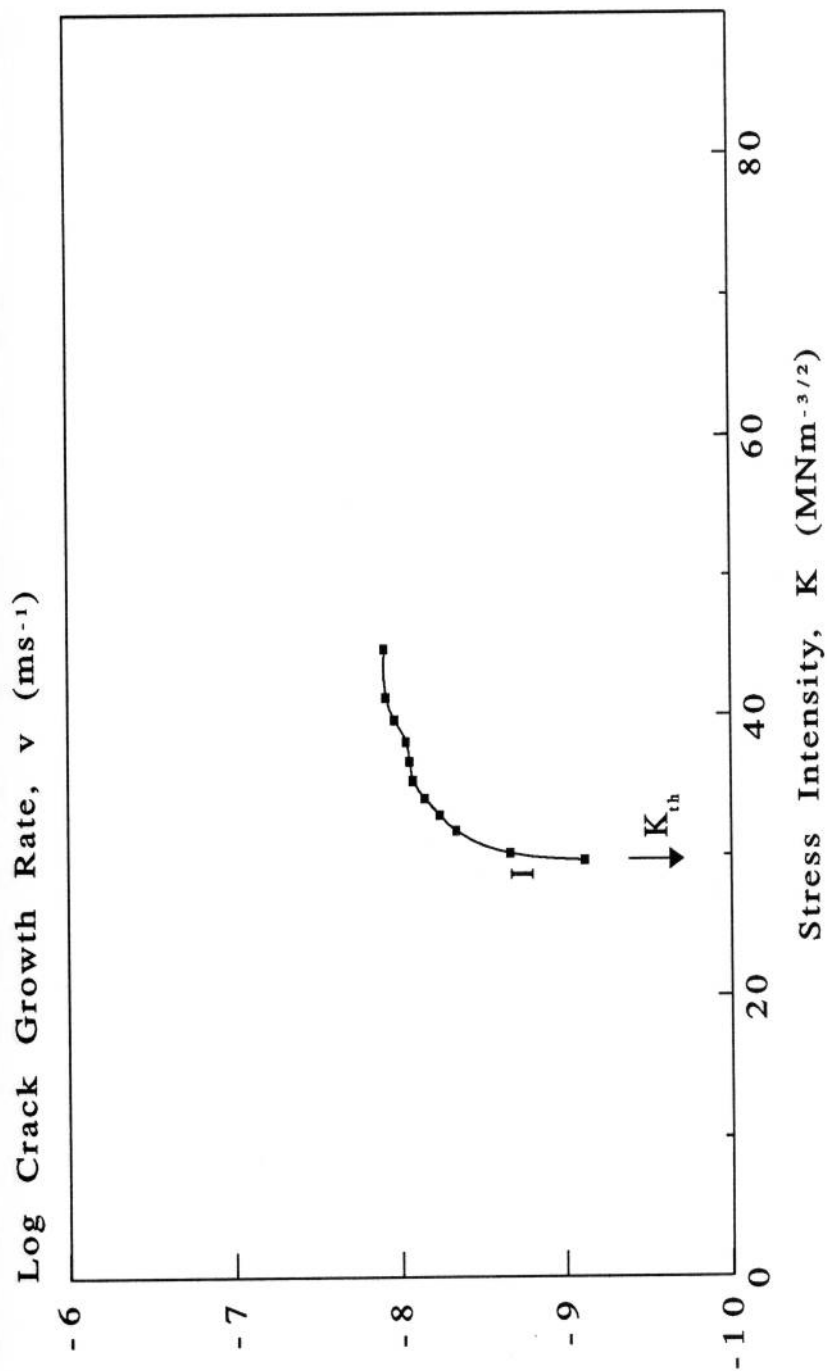


Figure 47. v:K Diagram For DSE690 DCB at Cathodic Potential of -1050mV(SCE) in Sterile Seawater

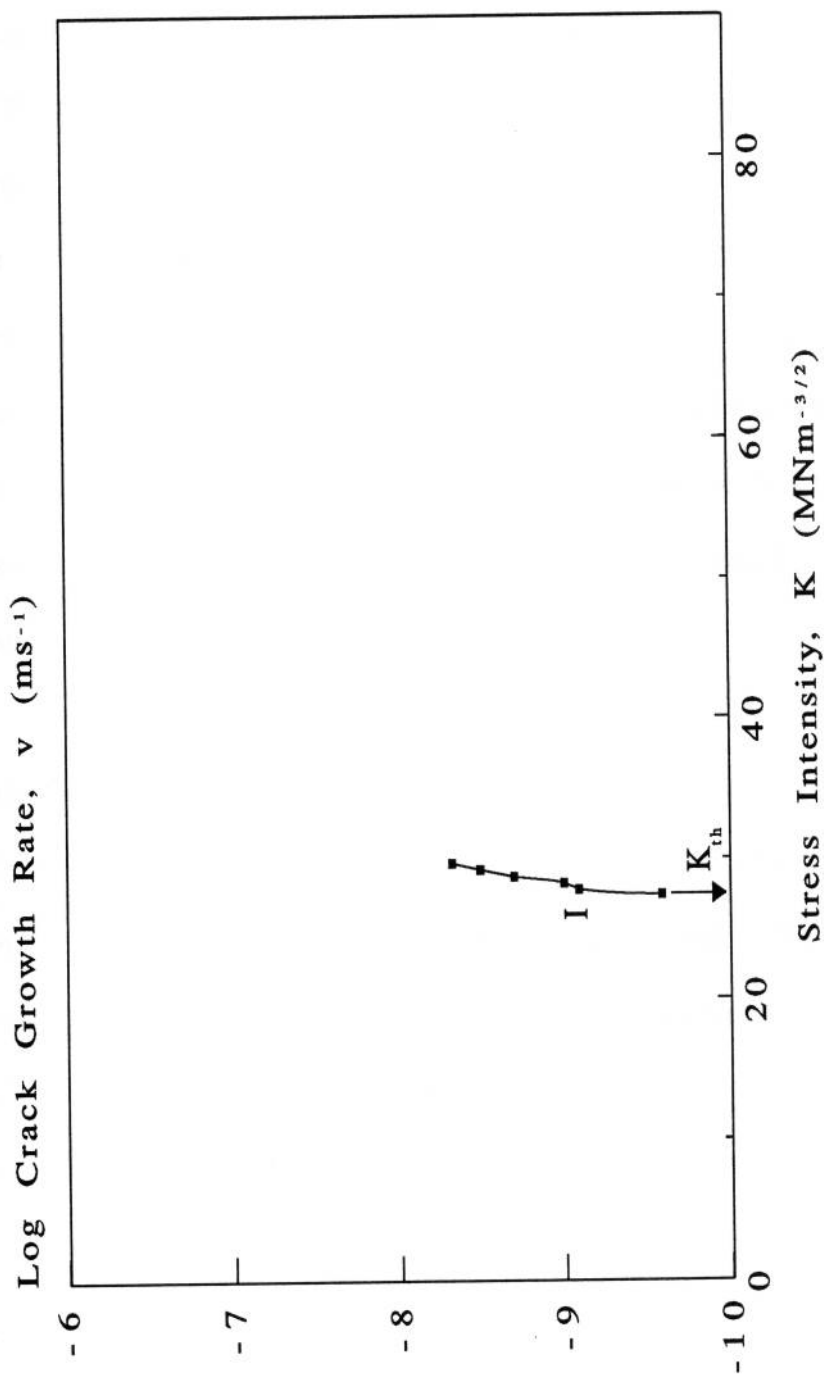


Figure 48. v:K Diagram For DSE690 DCB at Cathodic Potential of -1250mV(SCE) in Sterile Seawater

4.4.2 BACTERIAL NUMBERS AND TOTAL SULPHIDE

The bulk solution TS level was measured over a period of time for fermenter number 1 (Figure 49). These results allowed a feeding schedule to be set up to maintain a fairly stable TS concentration of 400ppm in the fermenter. The bacterial numbers in the fermenter bulk solution remained almost constant in the range 10^6 - 10^7 bacteria per ml. It must be remembered that the number of bacteria measured in the bulk solution is unrepresentative of the actual bacterial population within the fermenter. This is due to the bacteria being sessile so higher numbers would be associated with surfaces within the fermenter. The fermenters were half filled with small pearlite beads to provide a large surface area within the fermenter. The highest bacterial numbers would be associated with the biofilm surrounding these beads.

The solutions transferred from the fermenter to the anaerobic cell were also monitored for TS. It was found that the TS level dropped linearly from the initial value (Figure 50) and would be zero after 165 hours (approximately 1 week). The bacterial numbers remained the same as initially measured when taking the solution from the fermenter and were in the range given above. To maintain fairly consistent TS levels in the anaerobic cell, solution was removed from the cell and fresh fermenter solution added. This was carried out every three days to four days to maintain a TS concentration between 200 and 400ppm.

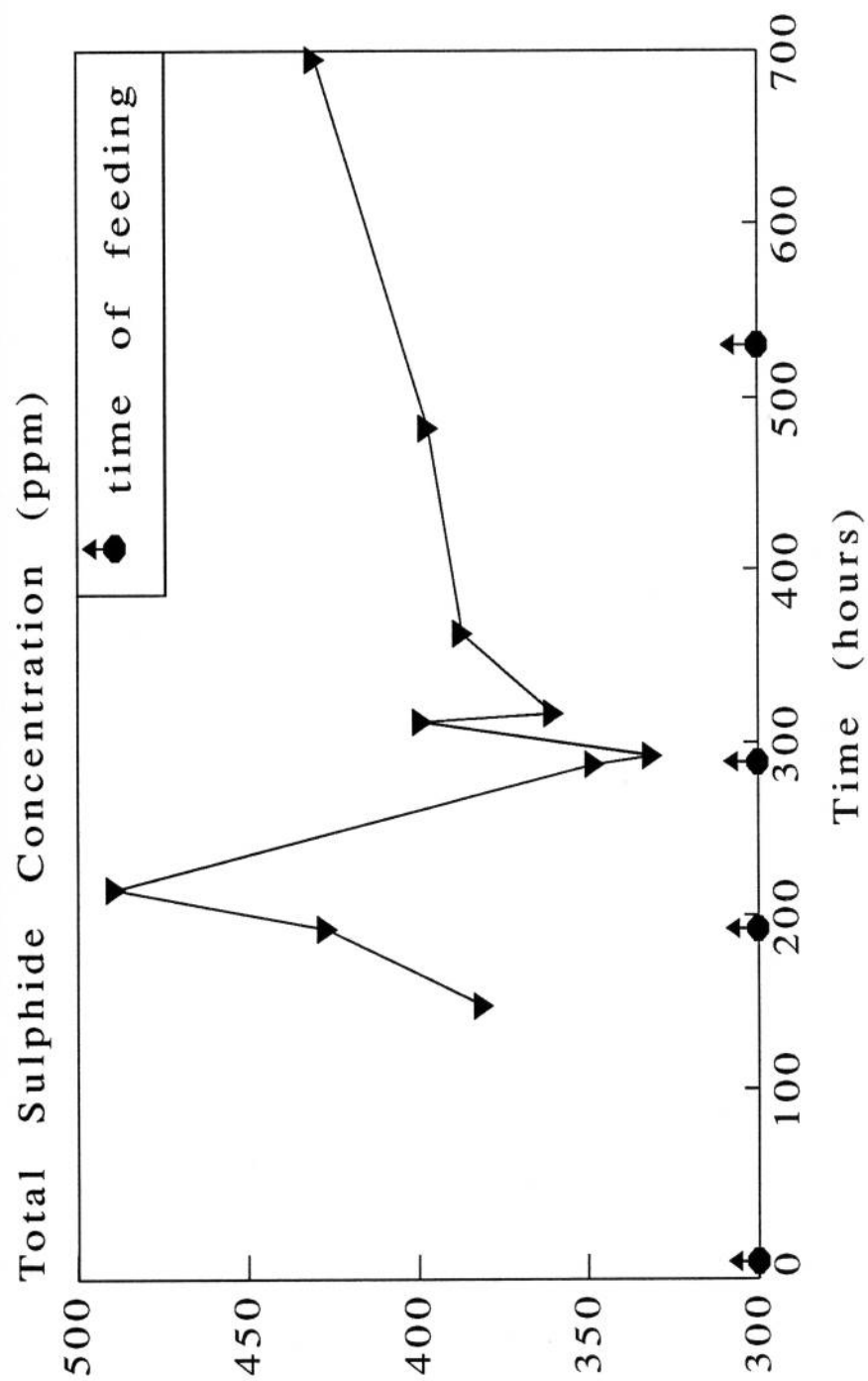


Figure 49. Variation in Bulk Total Sulphide Concentration With Time For Fermenter Number 1.

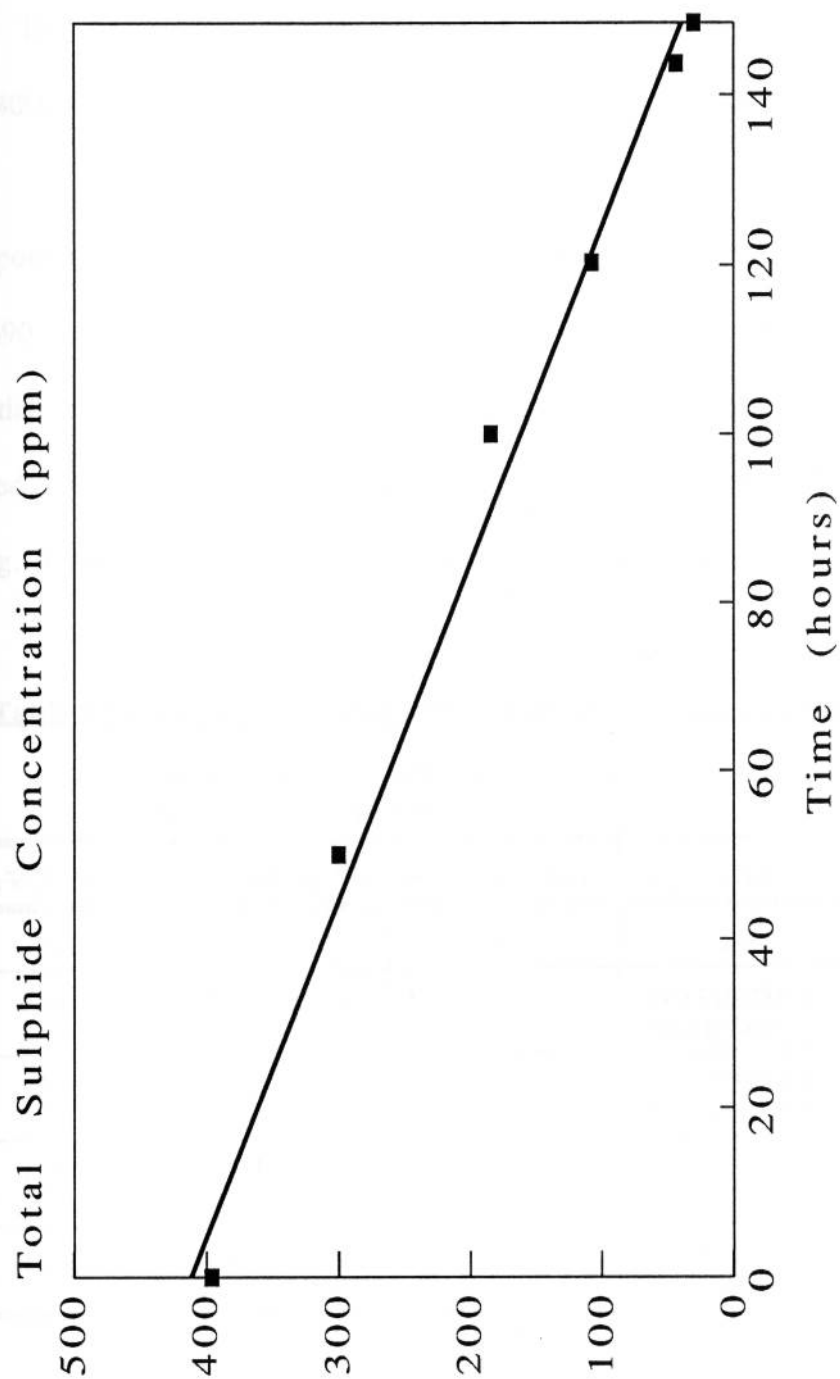


Figure 50. Variation in Bulk Total Sulphide Concentration With Time in Anaerobic Test Cell

4.4.3 BIOLOGICALLY ACTIVE SEAWATER

As described in section 4.4.1, v:K diagrams can be produced from the appropriate a:t plots. This has been carried out for the DCBs tested in biologically active seawater (200-400ppm TS, 10^6 - 10^7 SRB/ml).

At a potential of -850mV(SCE) the crack propagated 40.3mm after 625 hours in the DSE690 specimen in this more aggressive environment. Lowering of the applied potential did not cause any further crack growth until a potential of -1150mV(SCE) was reached. At this potential the crack propagated a further 29mm after 1200 hours of testing. Lowering the potential by 100mV did not result in any further crack growth.

Table 20 Summary of Threshold Values in Biologically Active Seawater

	SE500		DSE690	
mV(SCE)	K_{th} (MNm ^{-3/2})	FIGURE NO.	K_{th} (MNm ^{-3/2})	FIGURE NO.
-850	39	51	16	53
-950	NO FURTHER CRACKGROWTH	-	NO FURTHER CRACKGROWTH	-
-1050	35	52	NO FURTHER CRACKGROWTH	-
-1150	NO FURTHER CRACKGROWTH	-	10	54
-1250	NO FURTHER CRACKGROWTH	-	NO FURTHER CRACKGROWTH	-

The SE500 DCB also cracked at -850mV(SCE) in this environment. After a period of

620 hours the crack had propagated 14.7mm. Lowering the potential to -950mV(SCE) did not cause further crack propagation but at -1050mV(SCE) the crack grew a further 4mm after 1200 hours of testing. Lowering the potential to -1150 and -1250mV(SCE) did not result in further crack propagation. The threshold values obtained for each steel and the figure number for each test is summarised in Table 20.

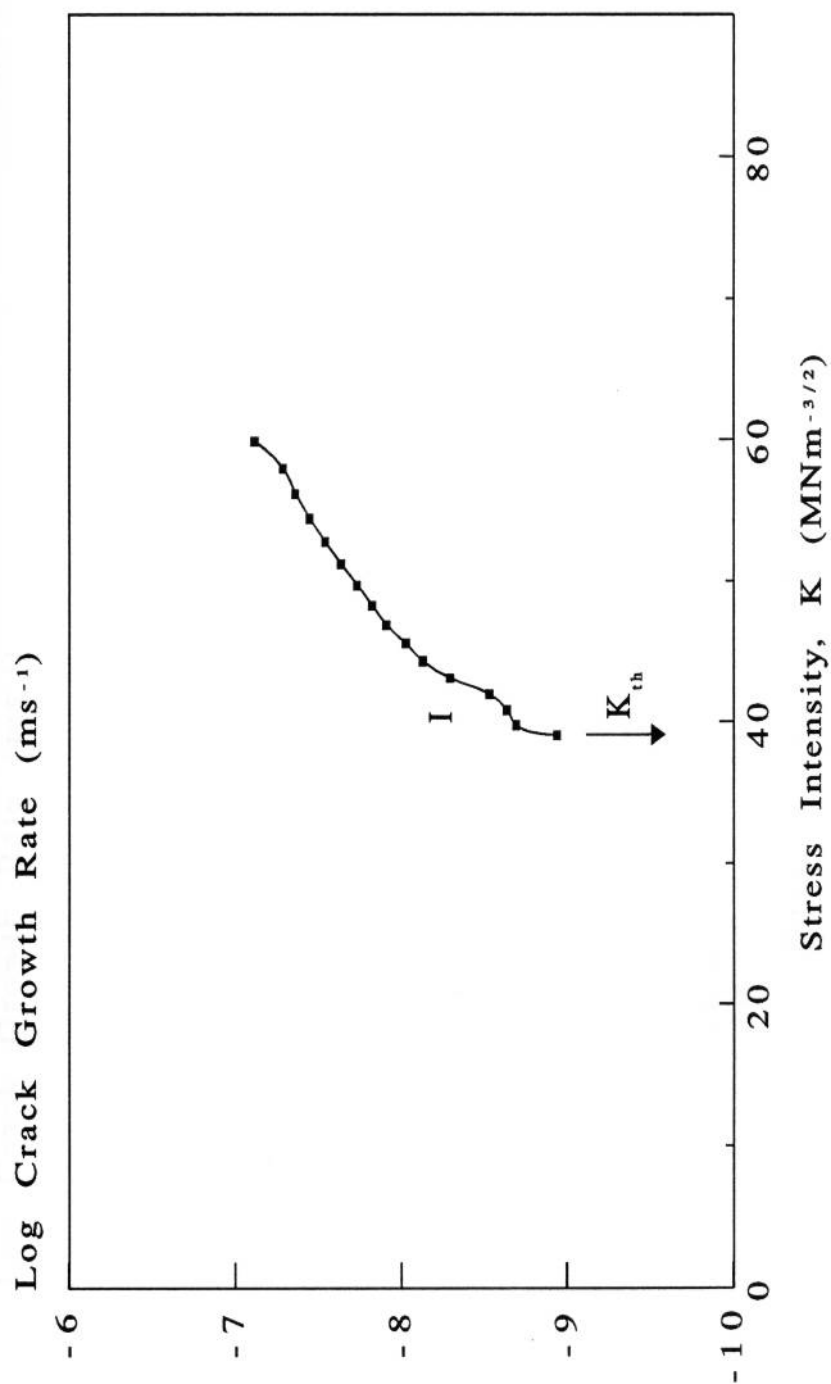


Figure 51. v:K Diagram For SE500 DCB at Cathodic Potential of -850mV(SCE) in Active Seawater

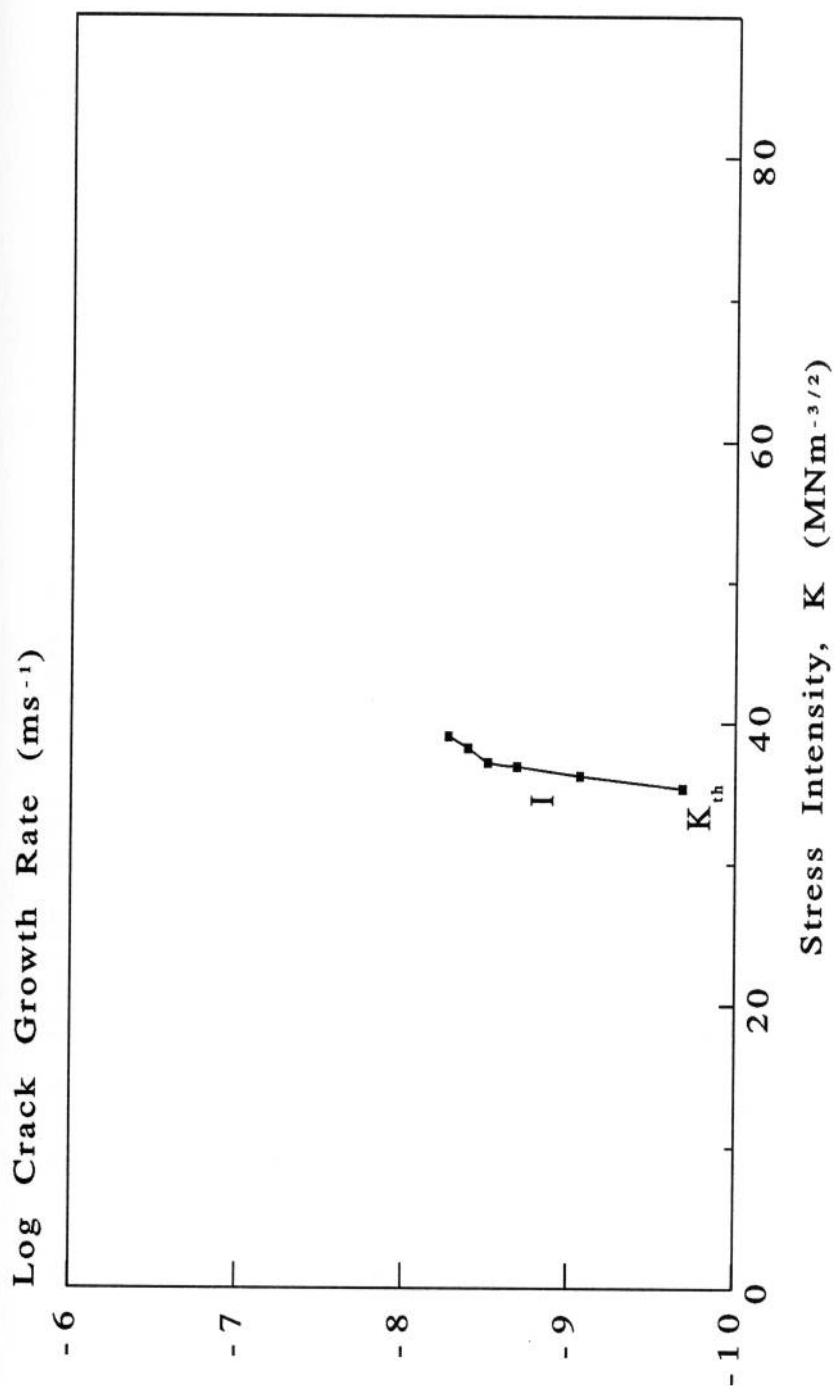


Figure 52. v:K Diagram For SE500 DCB at Cathodic Potential of -1050mV(SCE) in Active Seawater

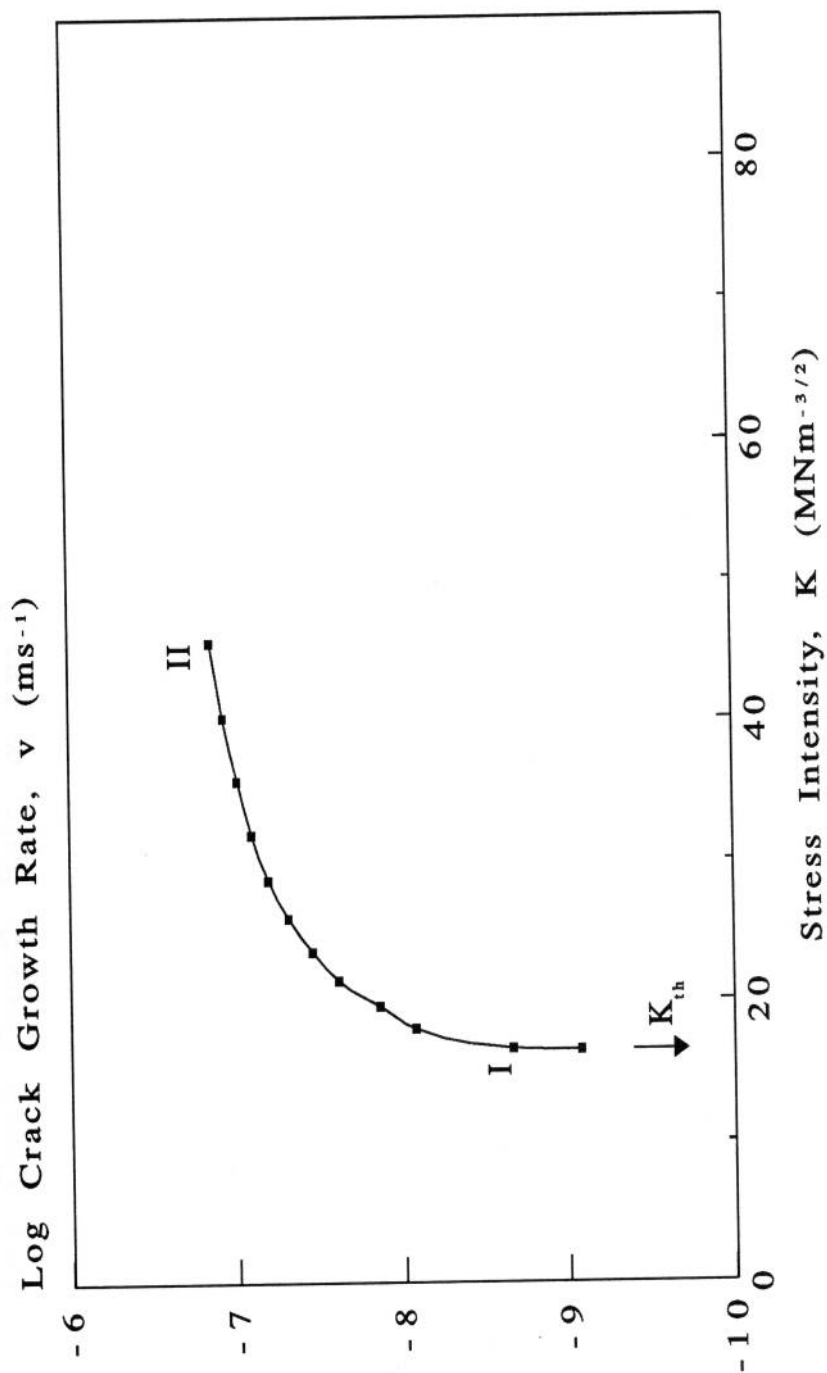


Figure 53. v:K Diagram For DSE690 DCB at Cathodic Potential of -850mV(SCE) in Active Seawater

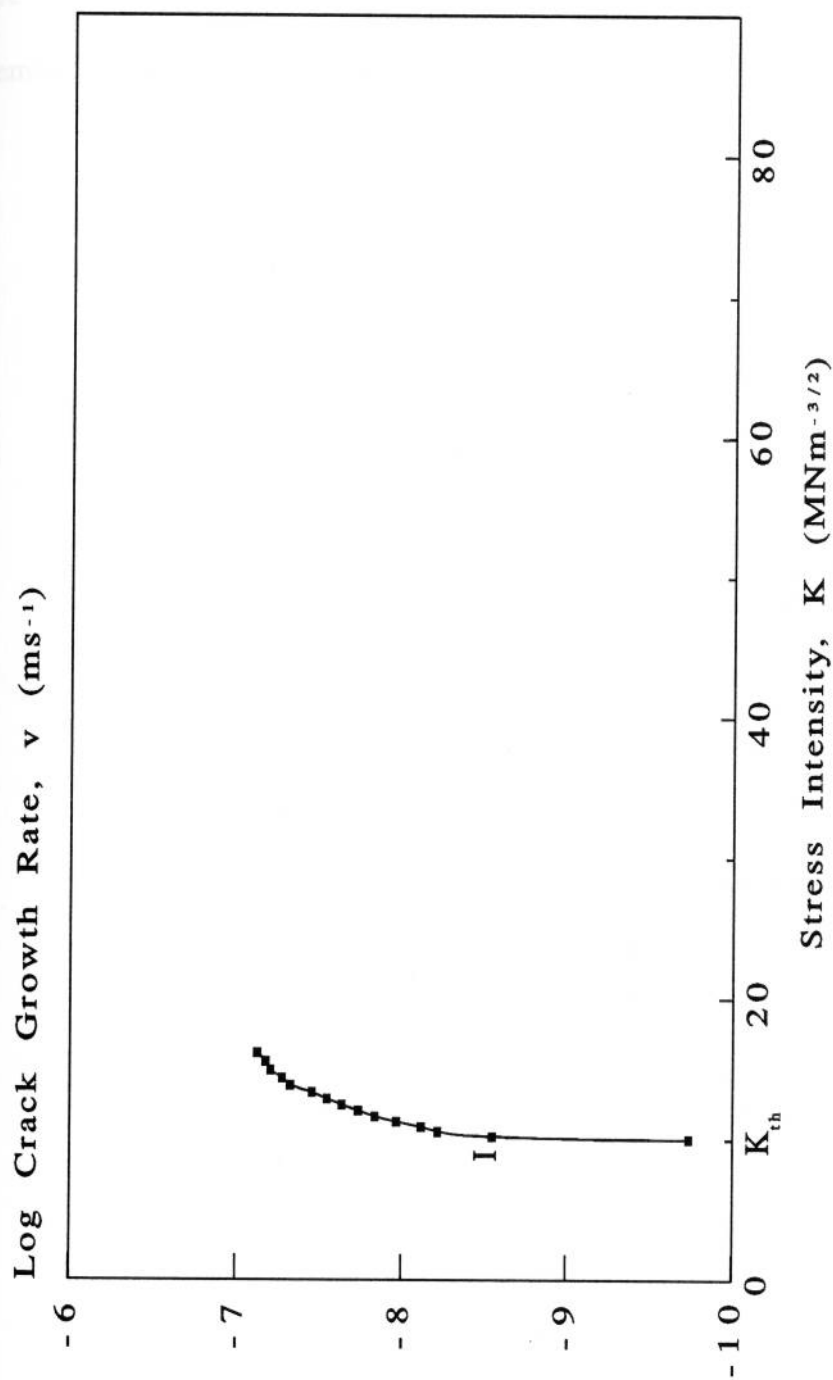
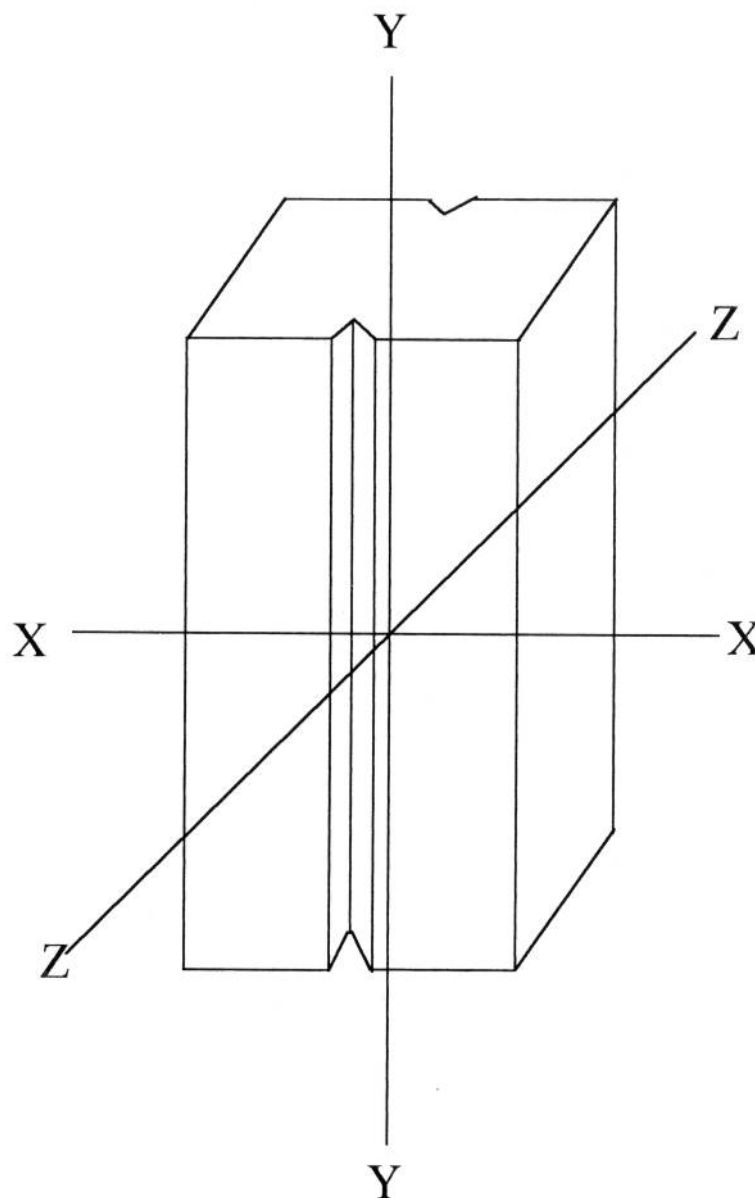


Figure 54. v:K Diagram For DSE690 DCB at Cathodic Potential of -1150mV(SCE) in Active Seawater



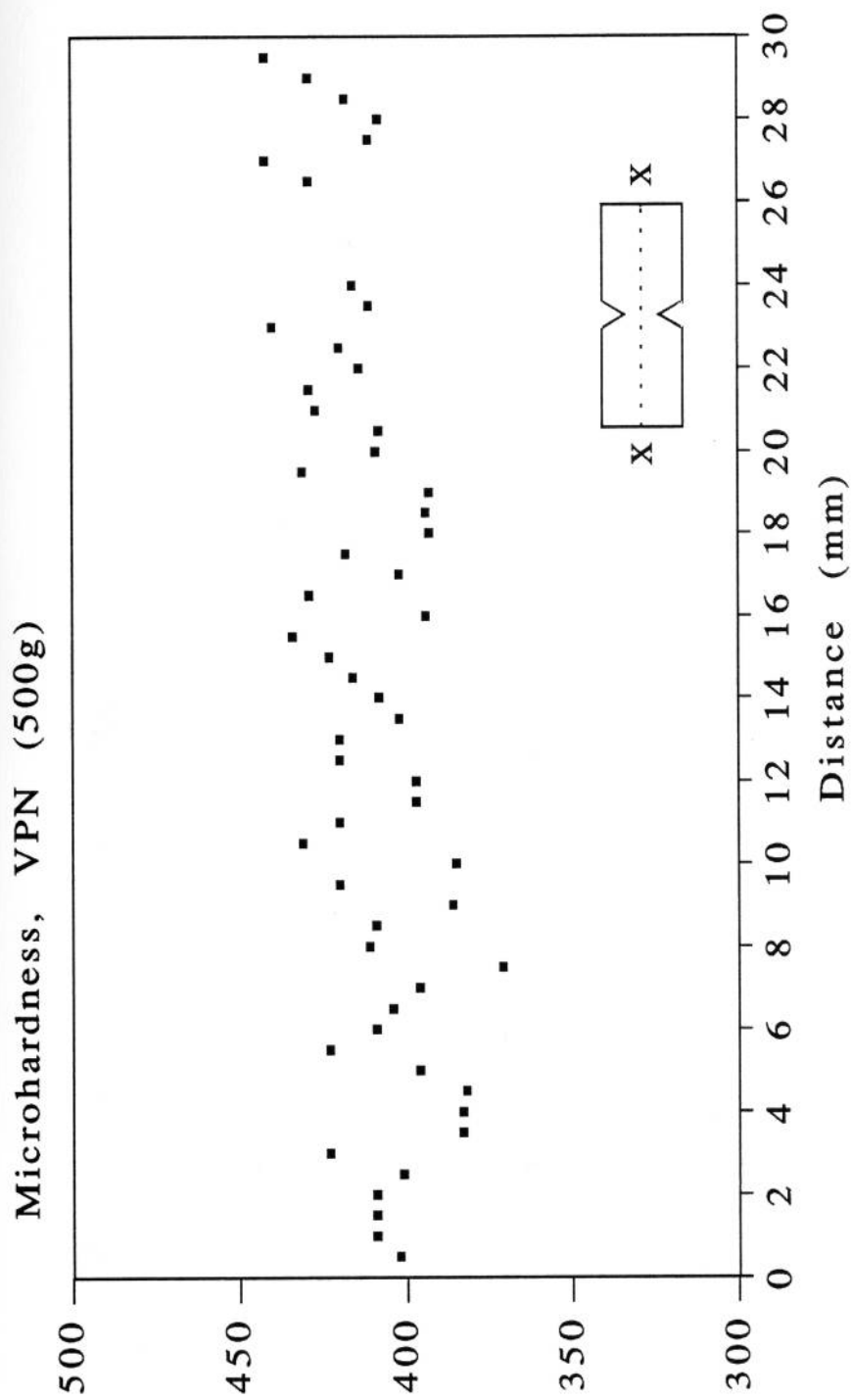


Figure 56. Variation of Microhardness Across DSE690 Steel DCB Specimen

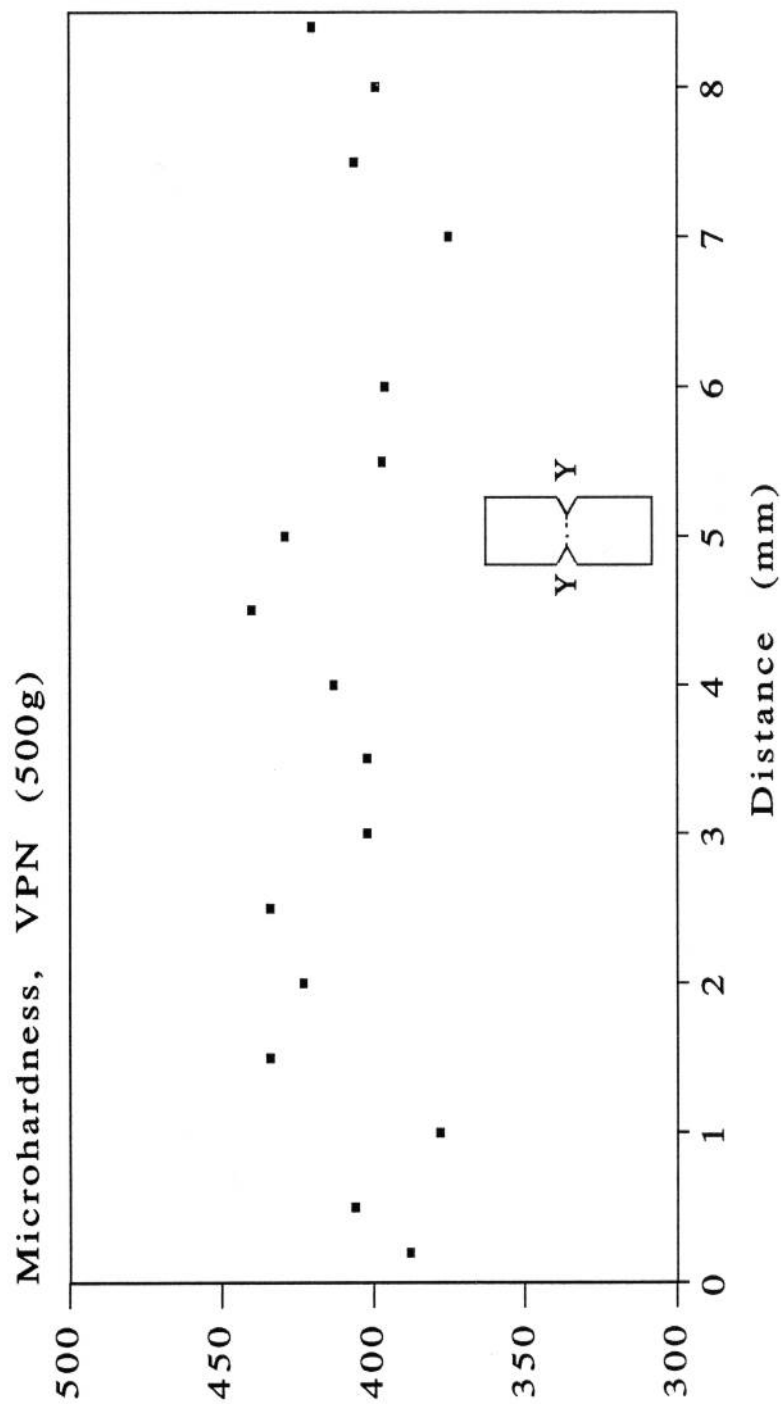


Figure 57. Variation of Microhardness Across DSE690 Steel DCB Specimen

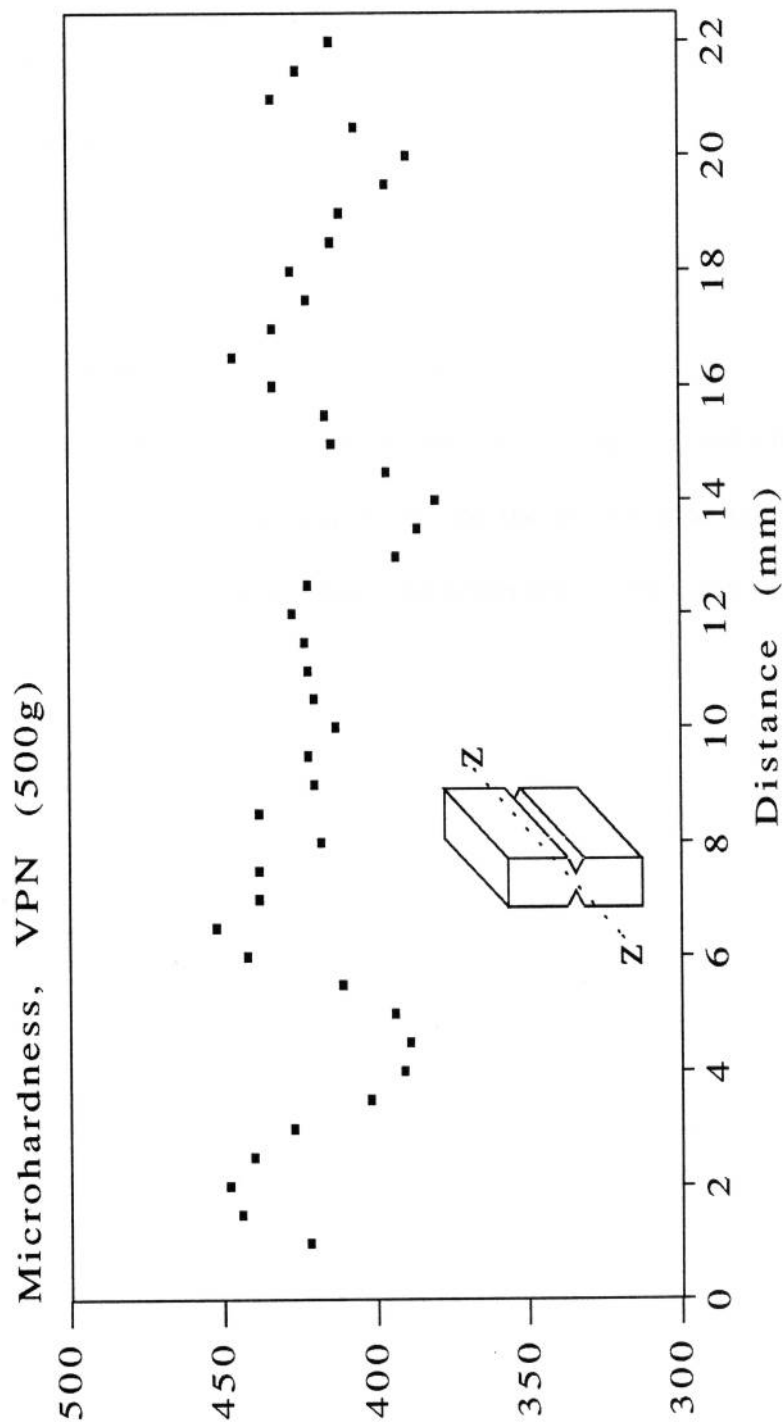


Figure 58. Variation of Microhardness Across DSE690 Steel DCB Specimen

4.5 FATIGUE TESTS

4.5.1 SETUP

When using the U8 Microgauge on the DCB specimens the device was calibrated to give direct cracklength readings. This was also true for unloaded fatigue specimens. Unfortunately, once the specimen was loaded there was a dramatic change in the readings obtained from the microgauge. As this occurred at the start of the test it was not possible to reset values so optical measurements were taken to allow calibration of the microgauge. The calibration curves obtained for the tests are summarised in Figure 59. As a linear relationship was found for the air and free corrosion tests, optical readings were only taken at the start and finish for the remaining tests.

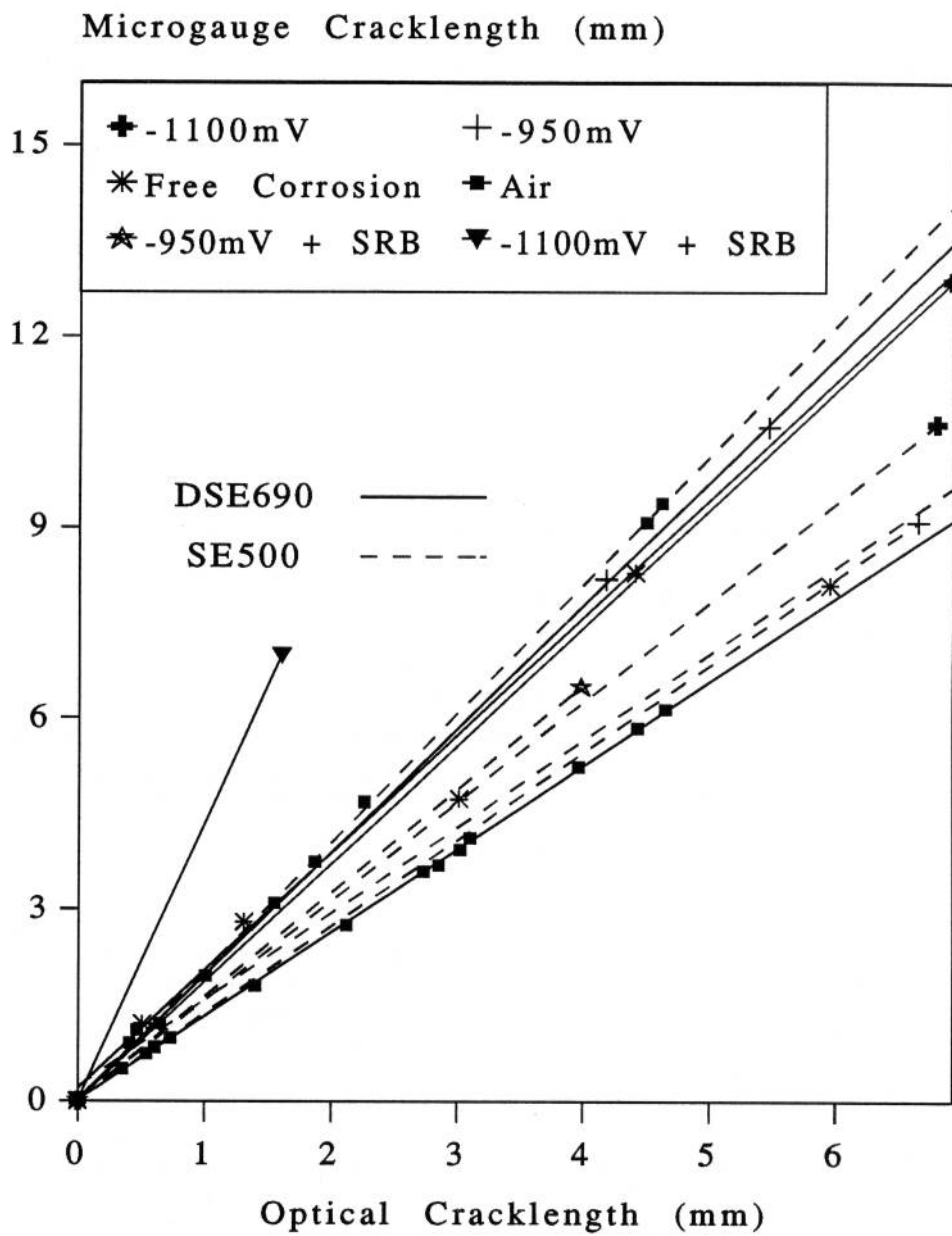


Figure 59. Calibration Plot For Optical & Microgauge Fatigue Cracklength Measurements

4.5.2 FATIGUE RESULTS

The biologically active solution for the fatigue tests was circulated through the test cell from fermenter 2. This solution had a measured TS in the range 331 to 410ppm and bacterial numbers in the range 10^5 to 10^6 (Table 24). It must be remembered that the number of bacteria measured in the bulk solution is unrepresentative of the actual bacterial population within the fermenter. This is due to the bacteria being sessile so higher numbers would be associated with surfaces within the fermenter.

Table 21 Summary of Final Cracklengths (a) and Total Number of Cycles (N) For Fatigue Tests

Test Condition	SE500		DSE690	
	a (mm)	N/1000	a (mm)	N/1000
Air	4.6	208	4.7	224.5
Free Corrosion	5.9	168	4.4	152.5
-950mV(SCE) (Sterile)	6.1	48	5.5	60.5
-1100mV(SCE) (Sterile)	6.8	36	6.9	36
-950mV(SCE) (Active)	3.9	15	1.8	14
-1100mV(SCE) (Active)	3.9	8	1.6	8.5

The final cracklength and total number of fatigue cycles are summarised for both steels for each test condition in Table 21. For each test a da/dN versus ΔK plot has been constructed and the corresponding figure number is given in Table 22. During the fatigue tests carried out under free corrosion conditions the variation in the potential of

the fatigue specimens was monitored. The results are shown in Figures 62 (SE500) and 69 (DSE690).

Table 22 Summary of Fatigue Figure Numbers

CATHODIC POTENTIAL [mV(SCE)]	FIGURE NUMBER	
	SE500	DSE690
AIR	60	67
FREE CORROSION	61	68
-950 (Sterile)	63	70
-1100 (Sterile)	64	71
-950 (Active)	65	72
-1100 (Active)	66	73

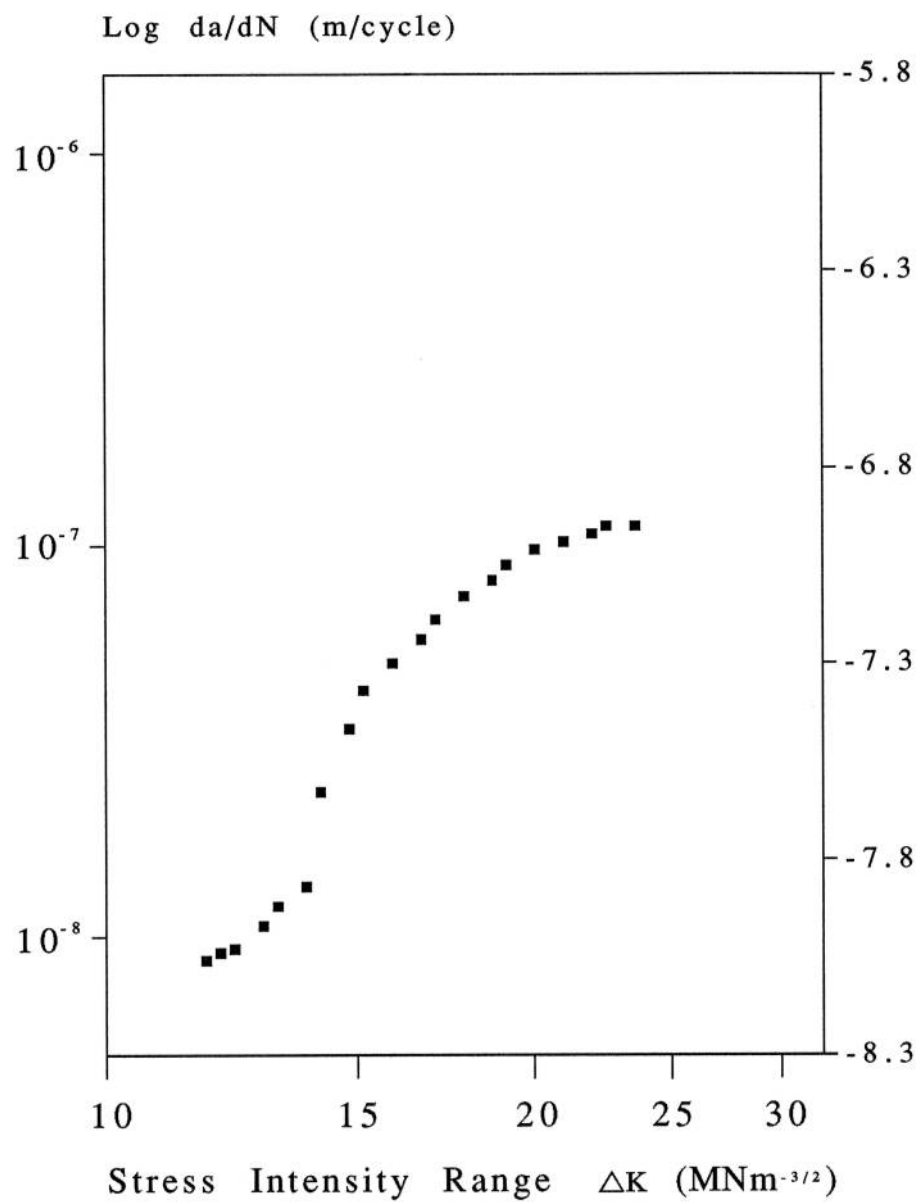


Figure 60. Air Fatigue Data For SE500
Tested at 0.5Hz & R=0.6

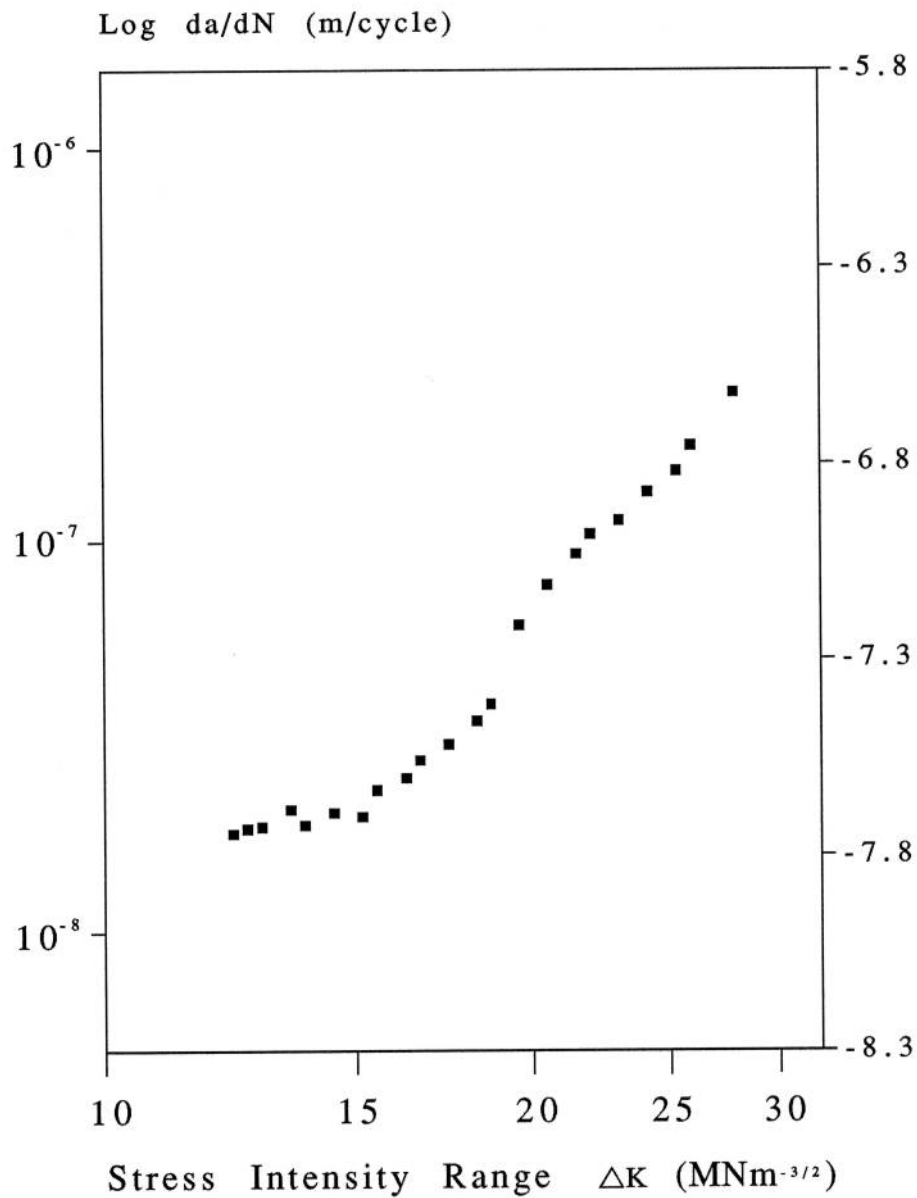


Figure 61. Free Corrosion Fatigue Data For SE500
Tested at 0.5Hz & R=0.6

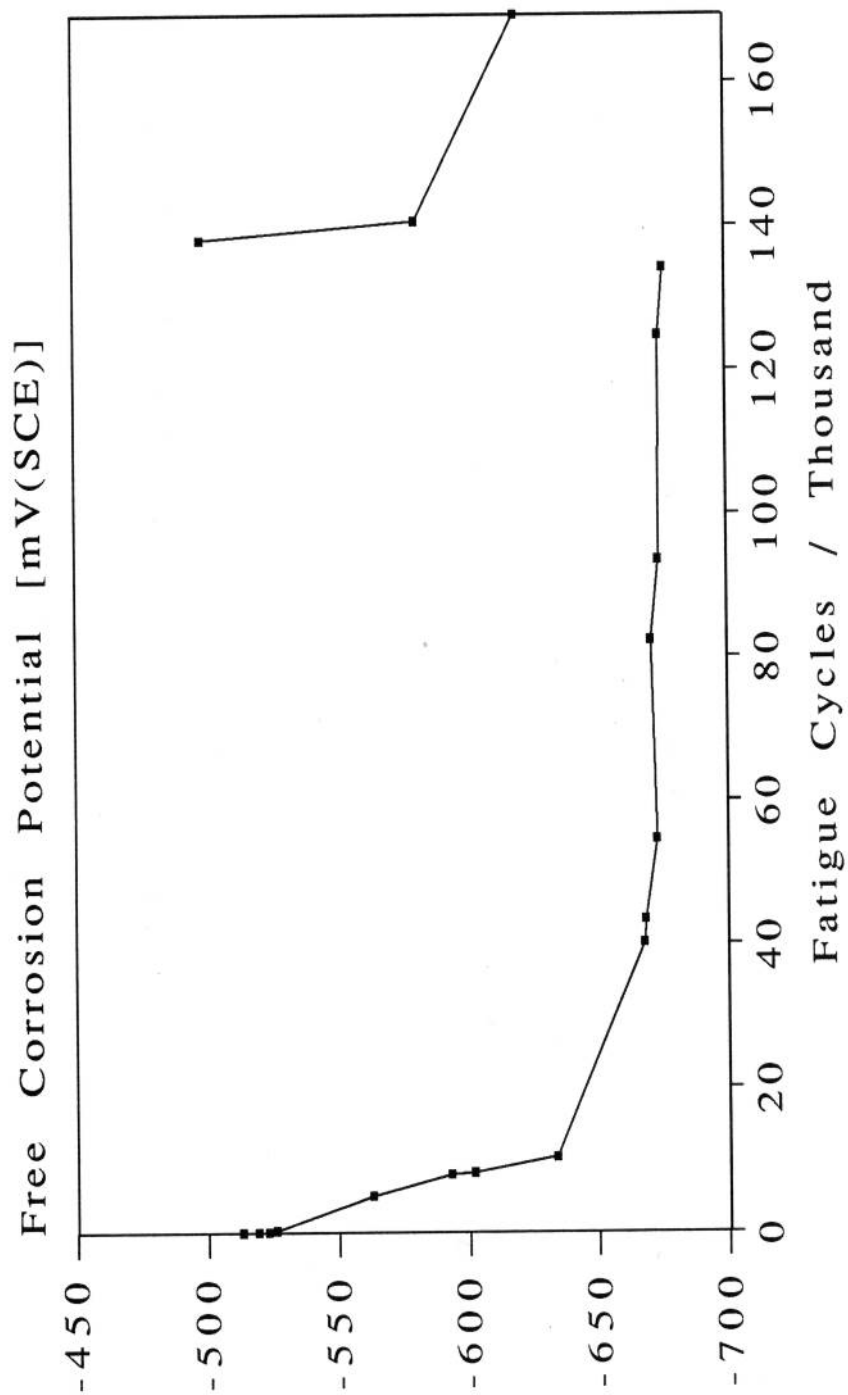


Figure 62. Variation of Free Corrosion Potential of SE500 Fatigue Specimen During Testing

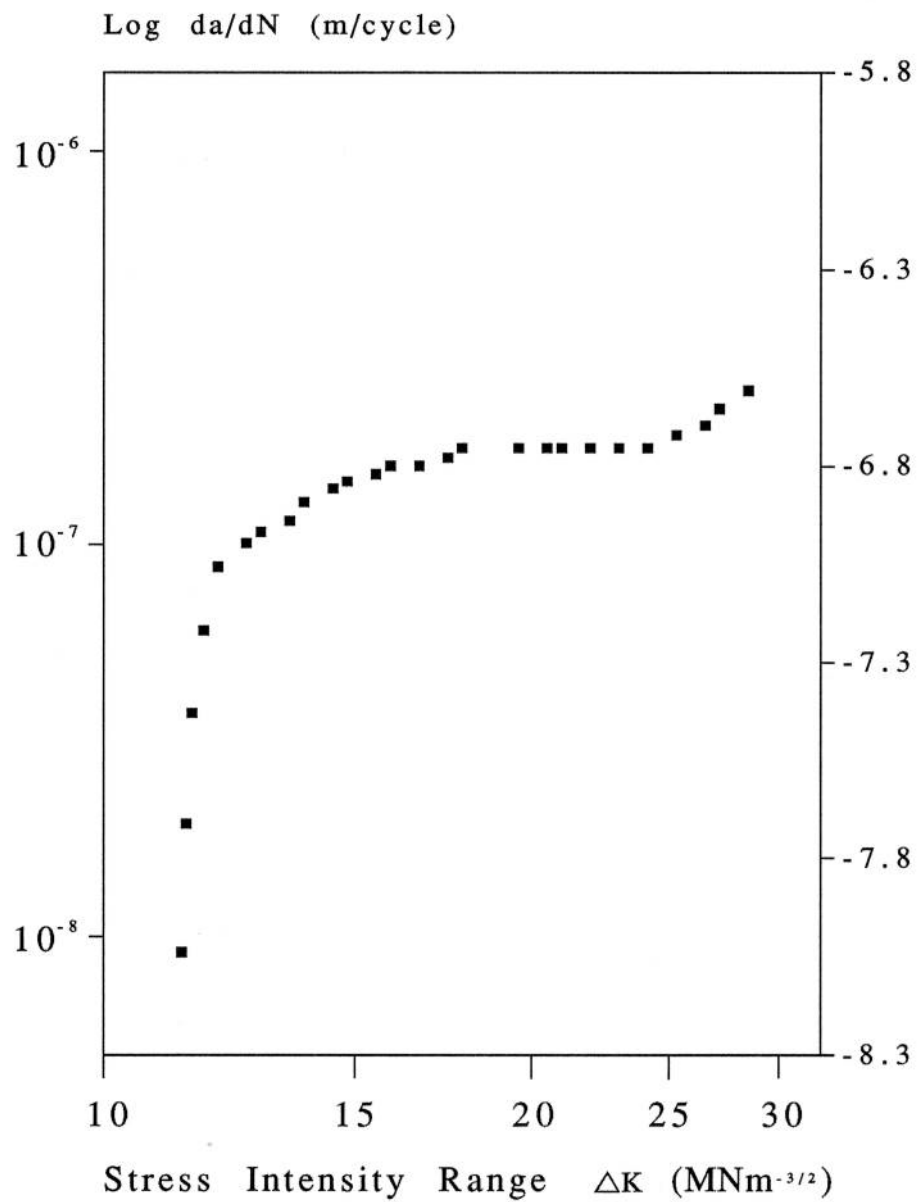


Figure 63. Corrosion Fatigue Data For SE500 at -950mV(SCE), Tested at 0.5Hz & R=0.6

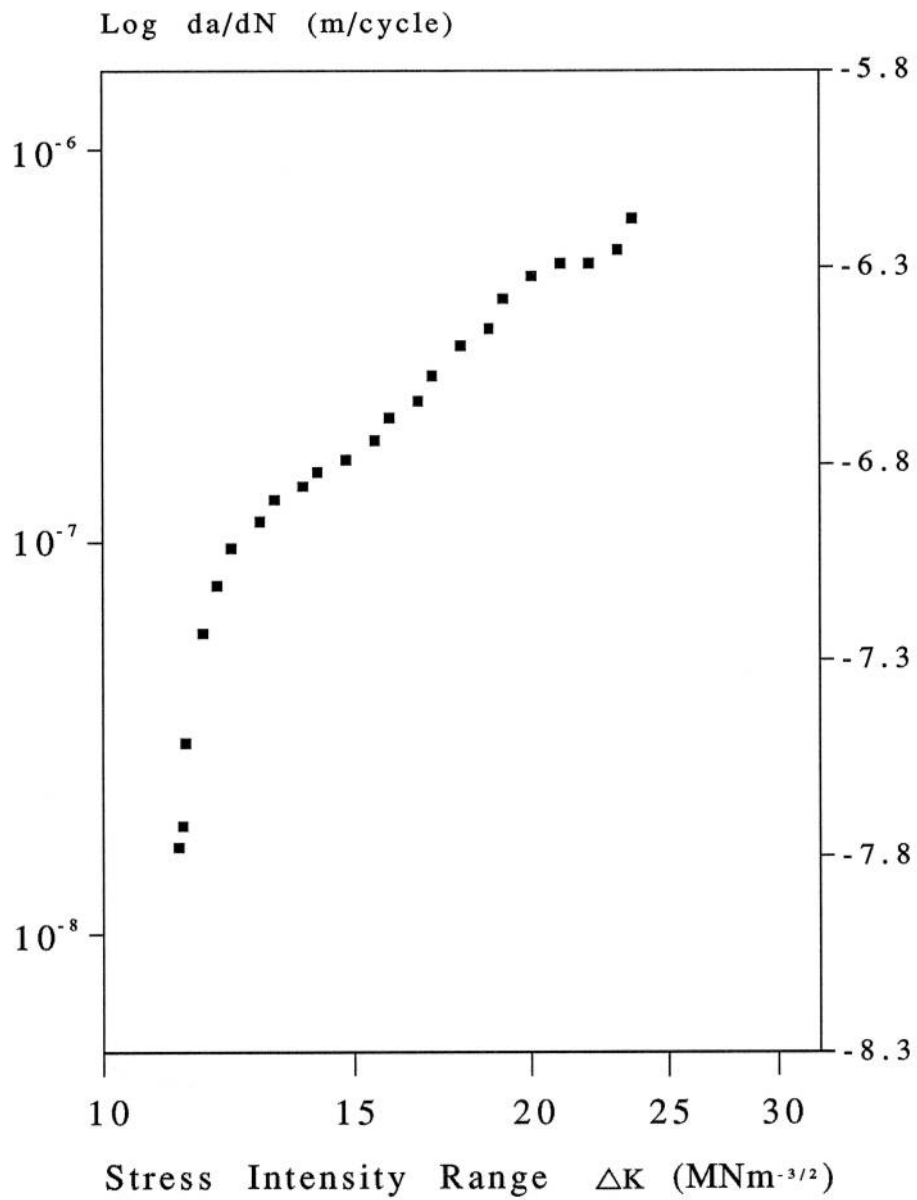


Figure 64. Corrosion Fatigue Data For SE500 at -1100mV(SCE), Tested at 0.5Hz & R=0.6

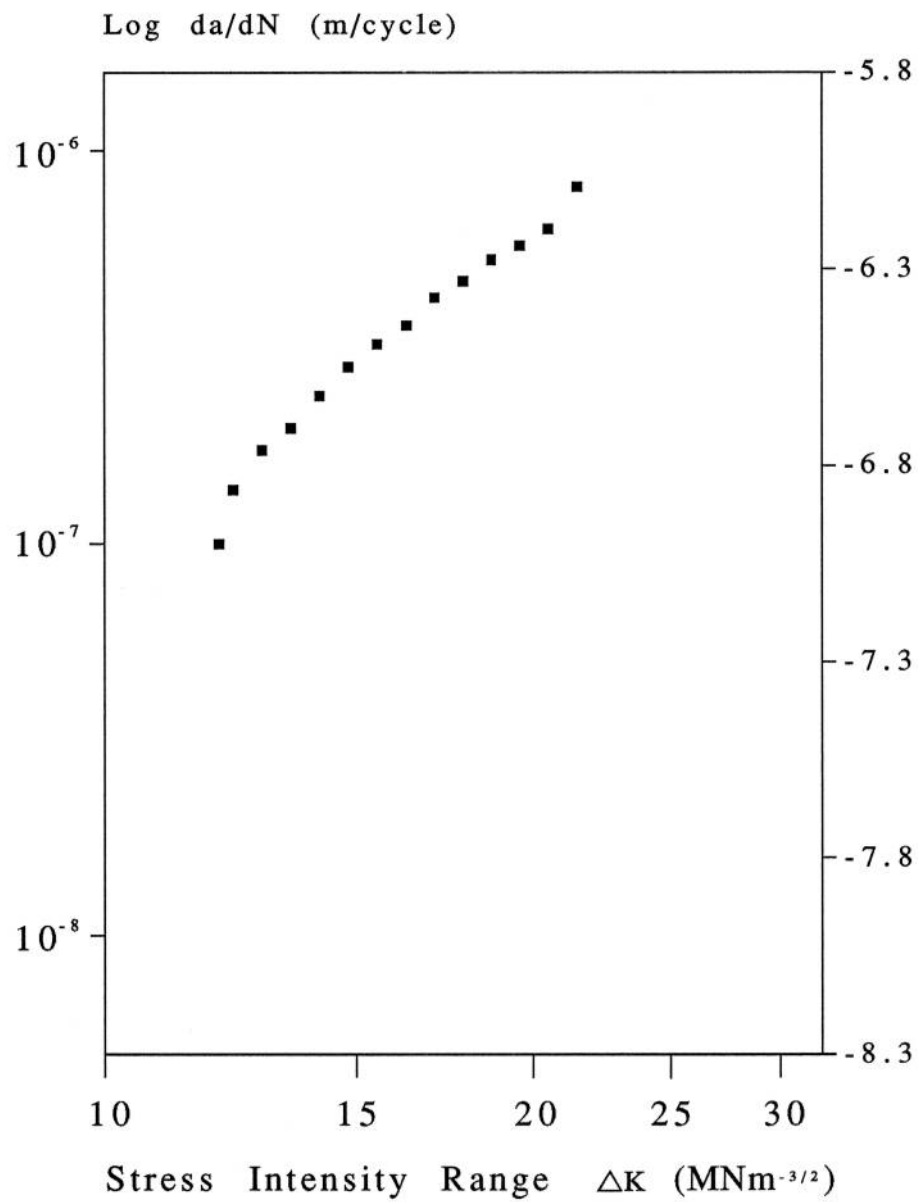


Figure 65. Corrosion Fatigue Data For SE500 at -950mV(SCE) in Active Seawater, 0.5Hz & R=0.6

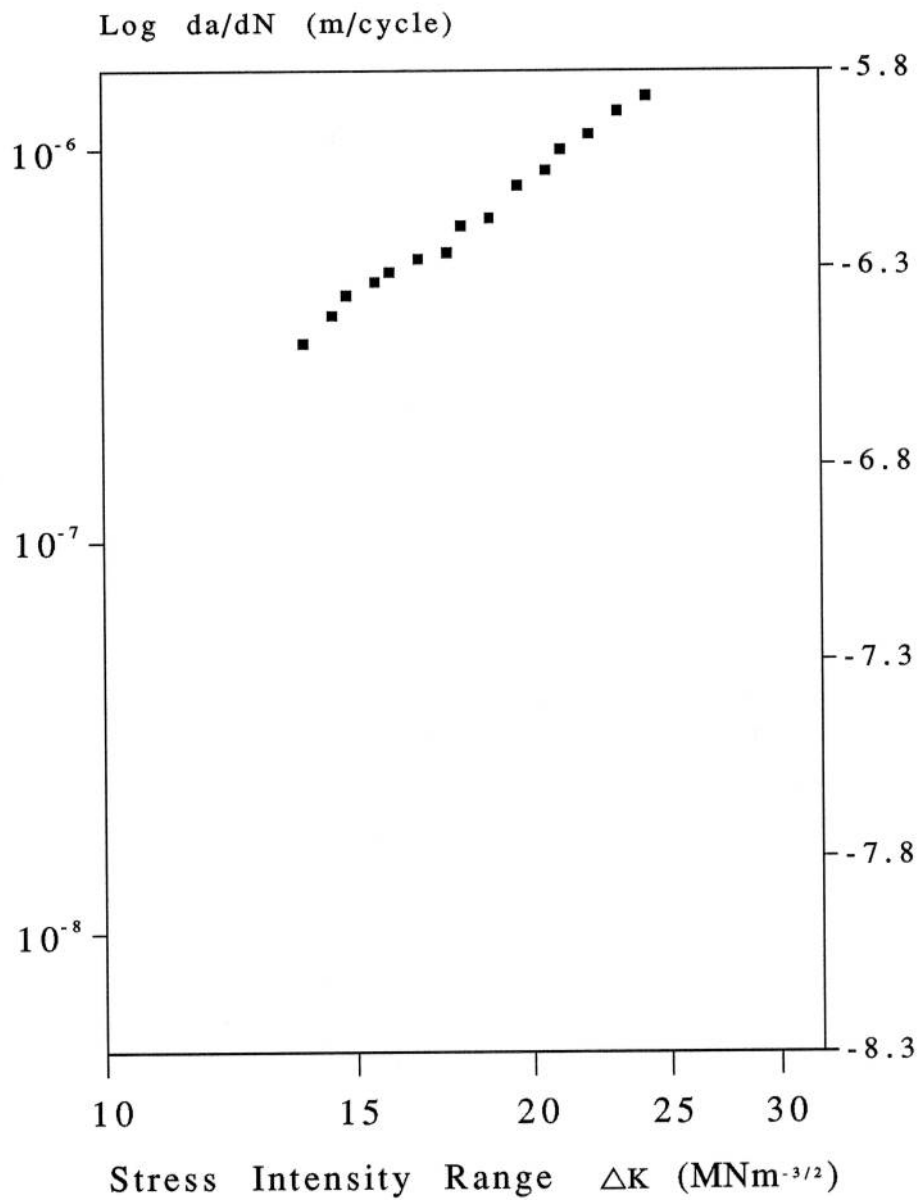


Figure 66. Corrosion Fatigue Data For SE500
at -1100mV(SCE) in Active Seawater, 0.5Hz & R=0.6

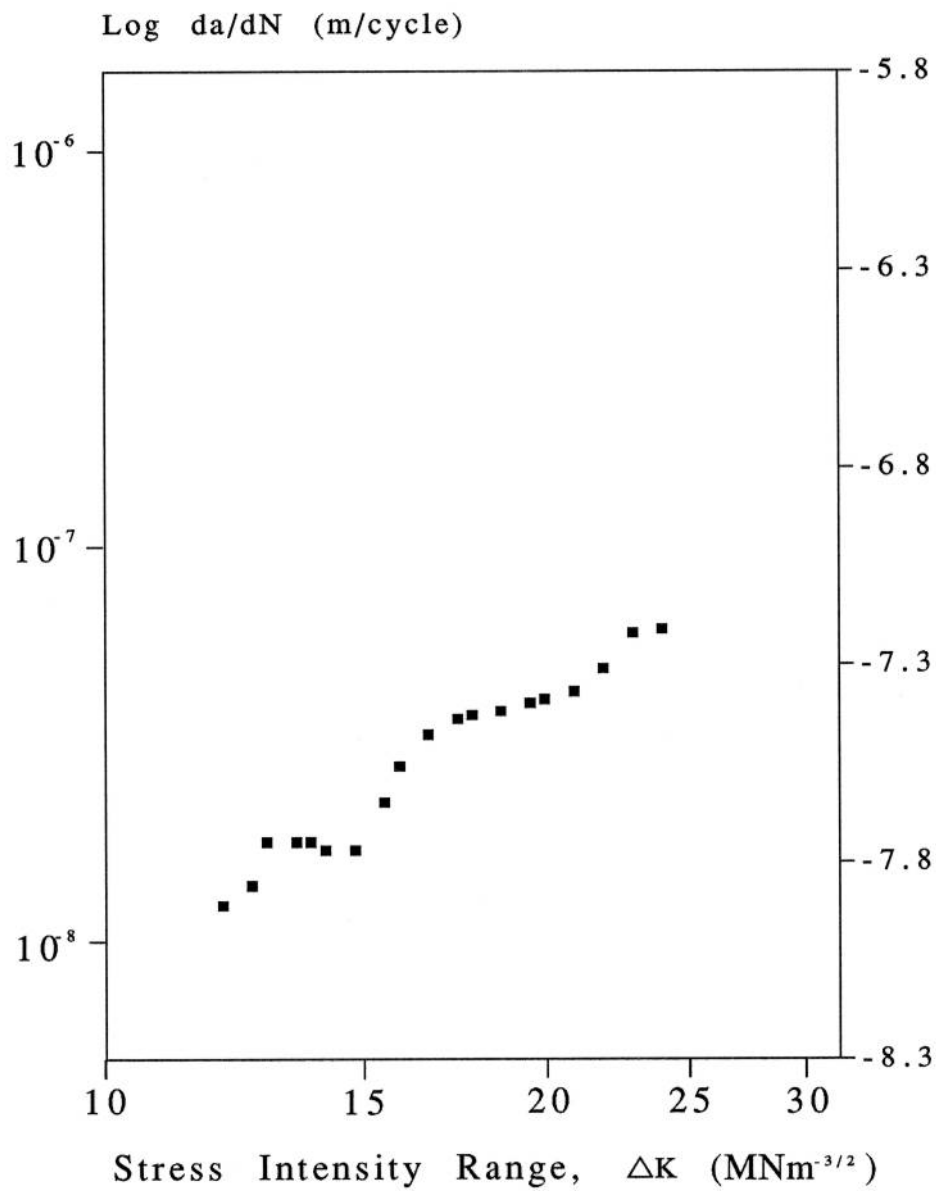


Figure 67. Air Fatigue Data For DSE690
Tested at 0.5Hz & R=0.6

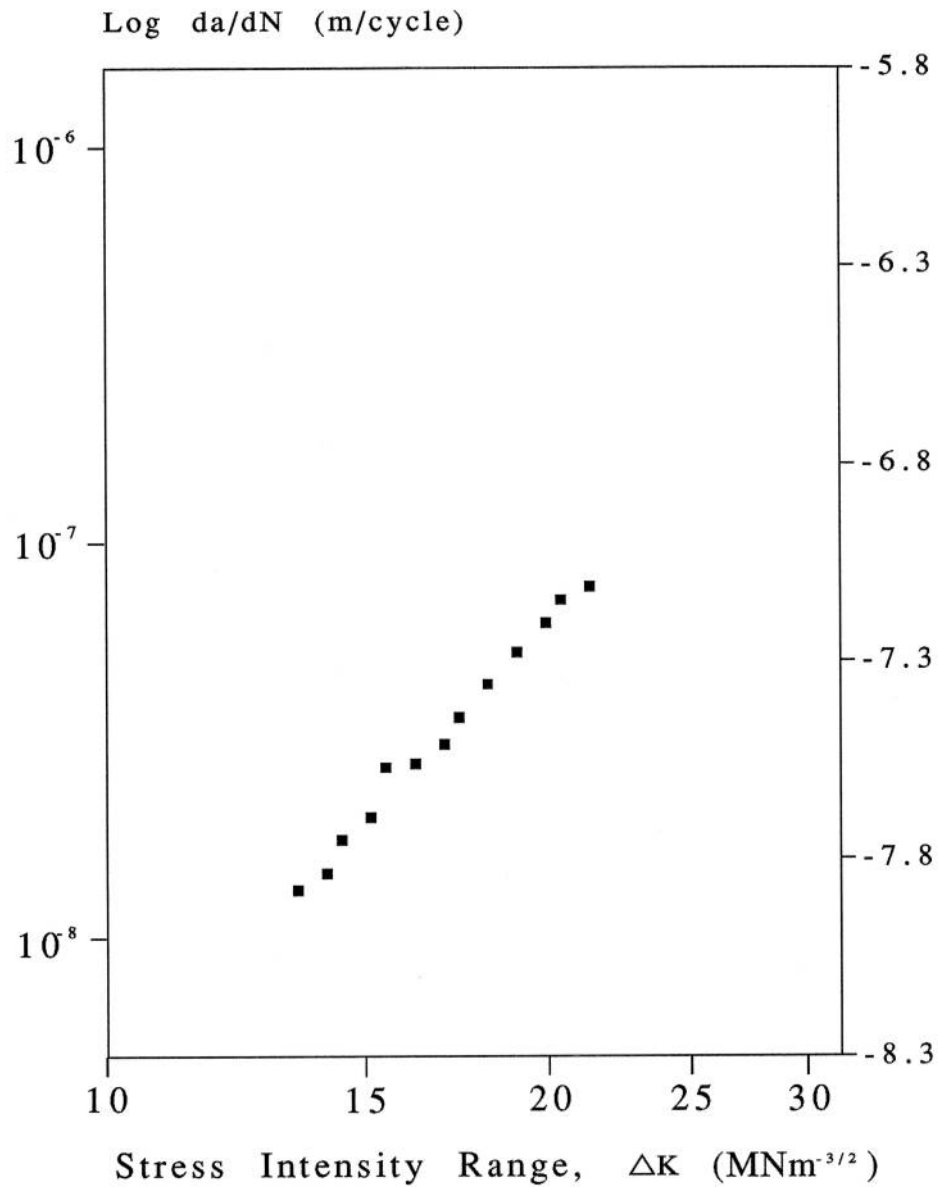


Figure 68. Free Corrosion Fatigue Data For DSE690
Tested at 0.5Hz & R=0.6

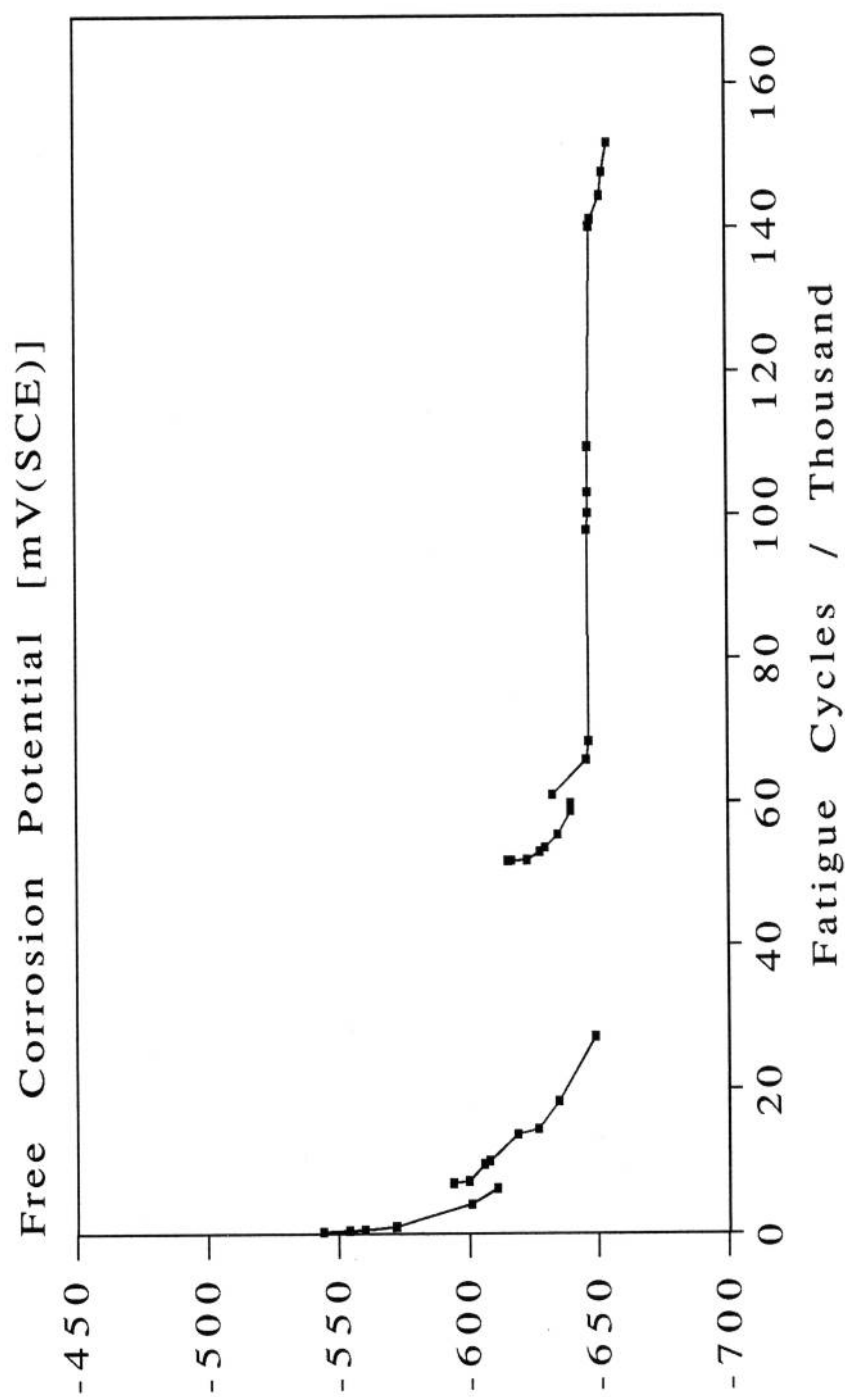


Figure 69. Variation of Free Corrosion Potential of DSE690
Fatigue Specimen During Testing

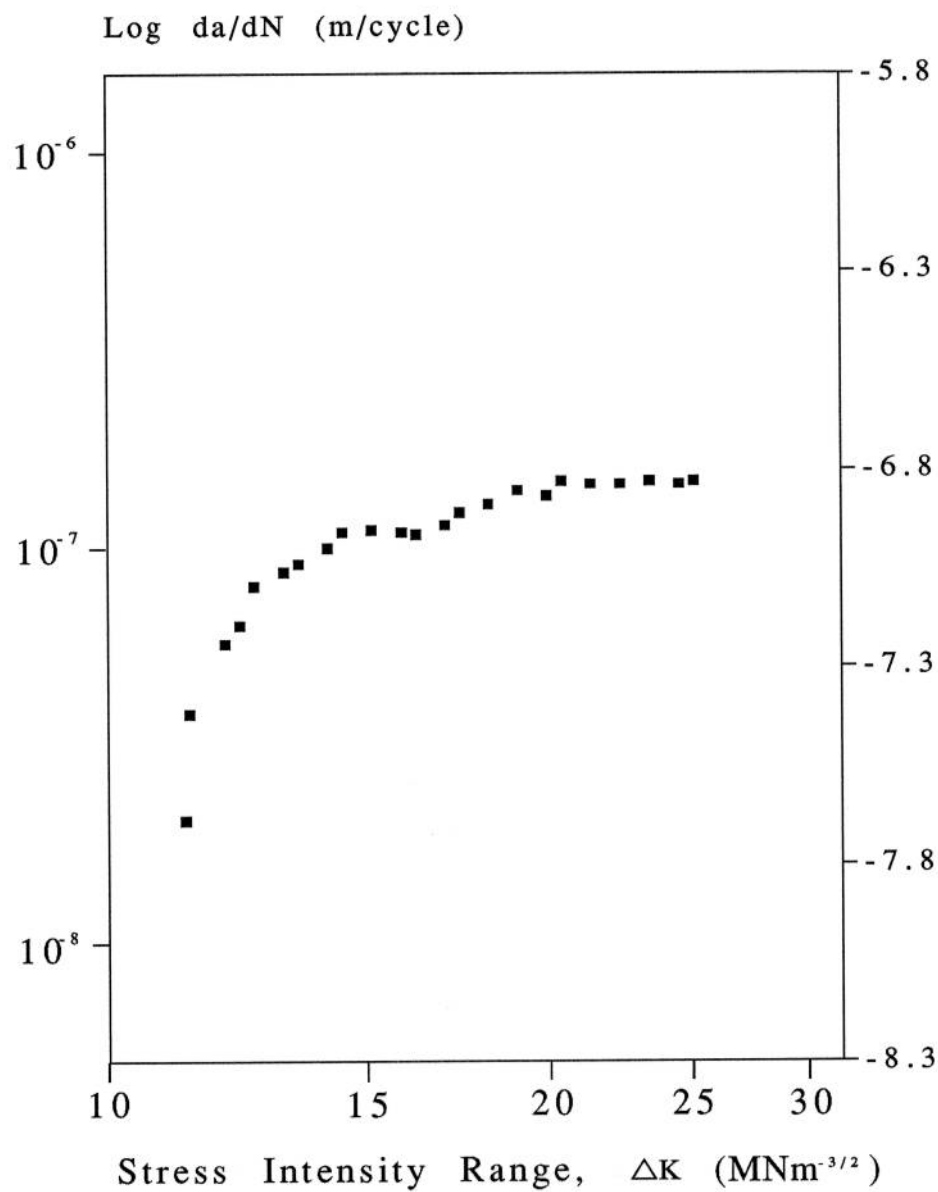


Figure 70. Corrosion Fatigue Data For DSE690
at -950mV(SCE), Tested at 0.5Hz & R=0.6

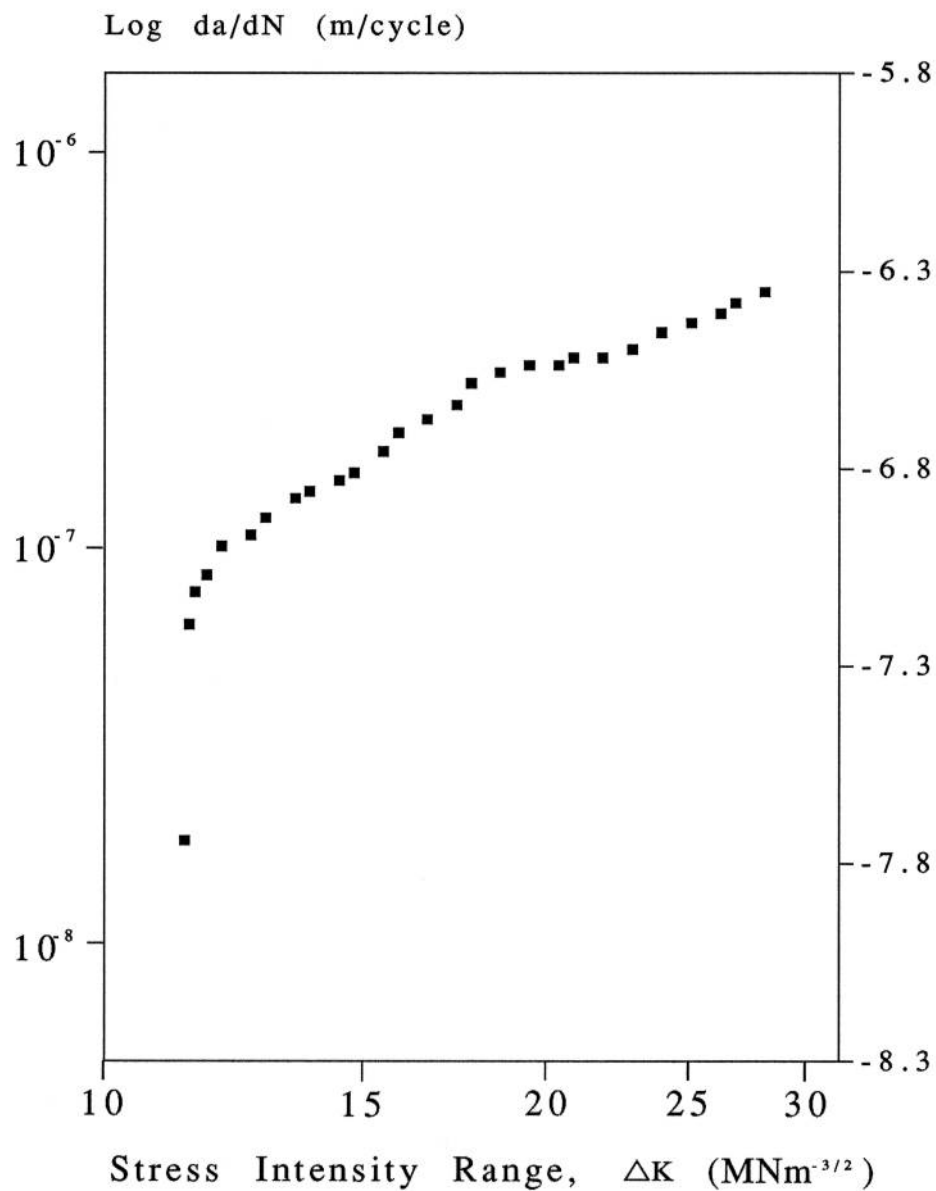


Figure 71. Corrosion Fatigue Data For DSE690
at -1100mV(SCE), Tested at 0.5Hz & R=0.6

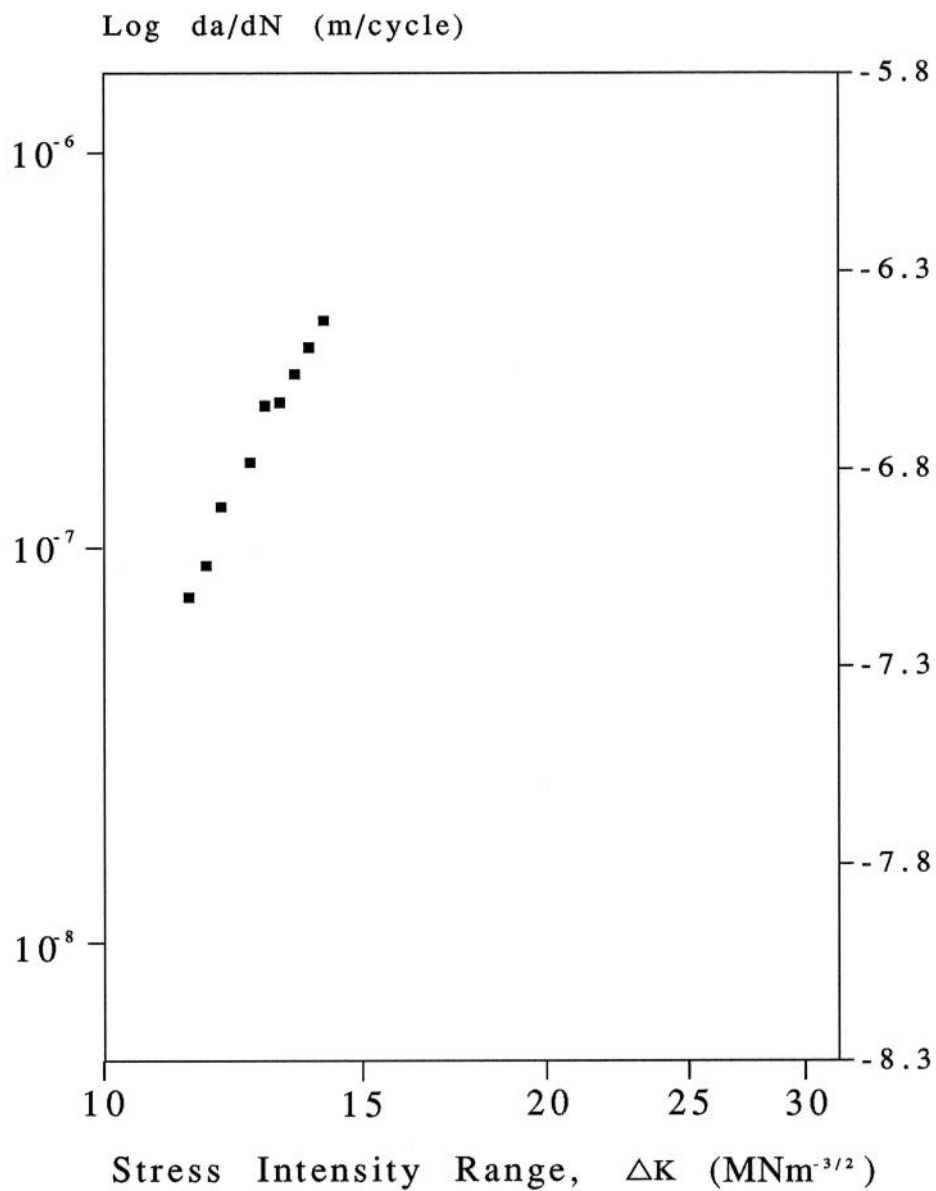


Figure 72. Corrosion Fatigue Data For DSE690 at -950mV(SCE)in Active Seawater, 0.5Hz & R=0.6

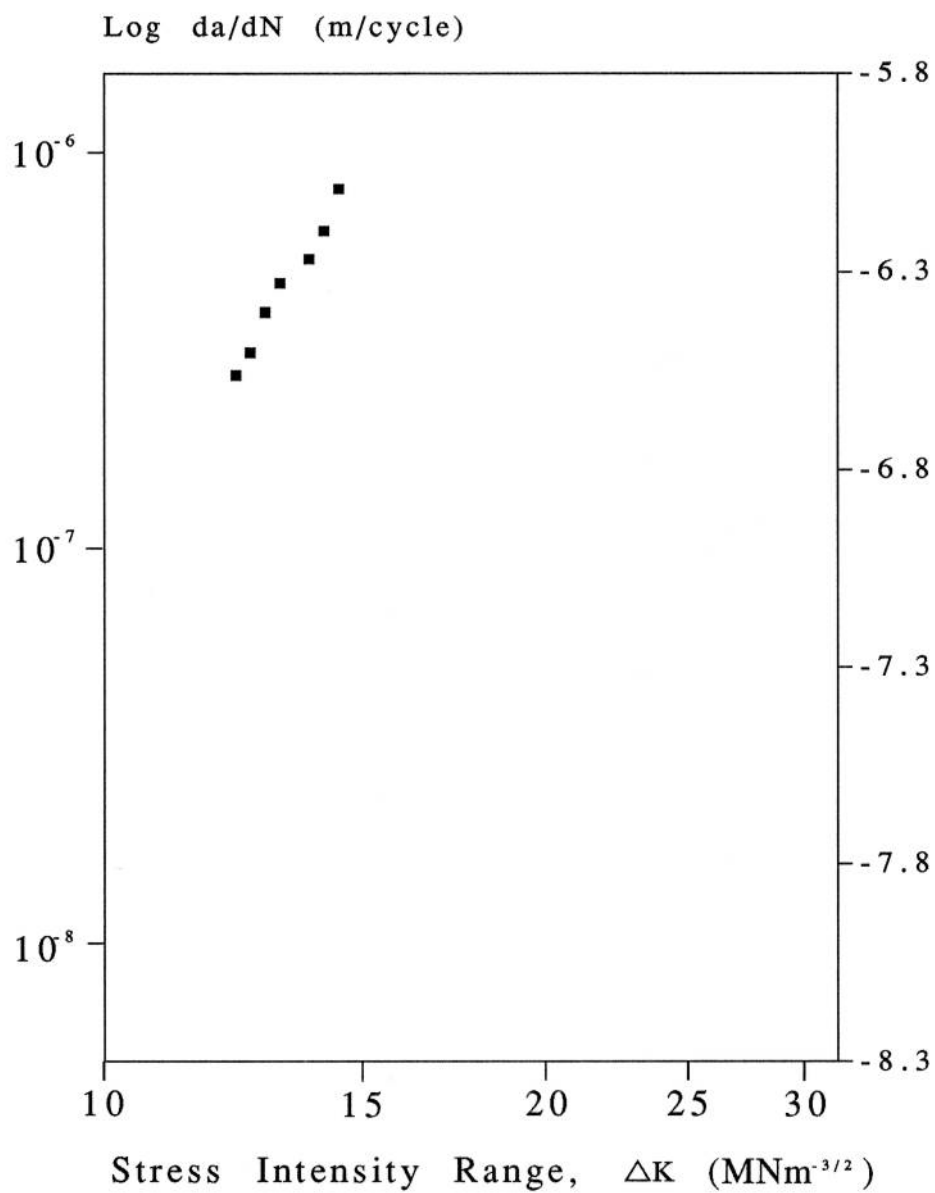


Figure 73. Corrosion Fatigue Data For DSE690
at -1100mV(SCE)in Active Seawater, 0.5Hz & R=0.6

4.6 HYDROGEN PERMEATION MEASUREMENTS

4.6.1 DOUBLE CANTILEVER BEAM SPECIMENS

The surface hydrogen concentrations (C_o) measured for each applied potential during the DCB testing in sterile and biologically active seawater are given in Table 23. The values are also shown in the form of a bar graph in Figure 74.

Table 23 Summary of Hydrogen Permeation Measurements

Potential [mV(SCE)]	Co (ppm)	
	Sterile	Active
-850	0.0181	0.454
-950	0.0460	0.646
-1050	0.1268	0.747
-1150	0.1963	0.998
-1250	0.3478	1.130

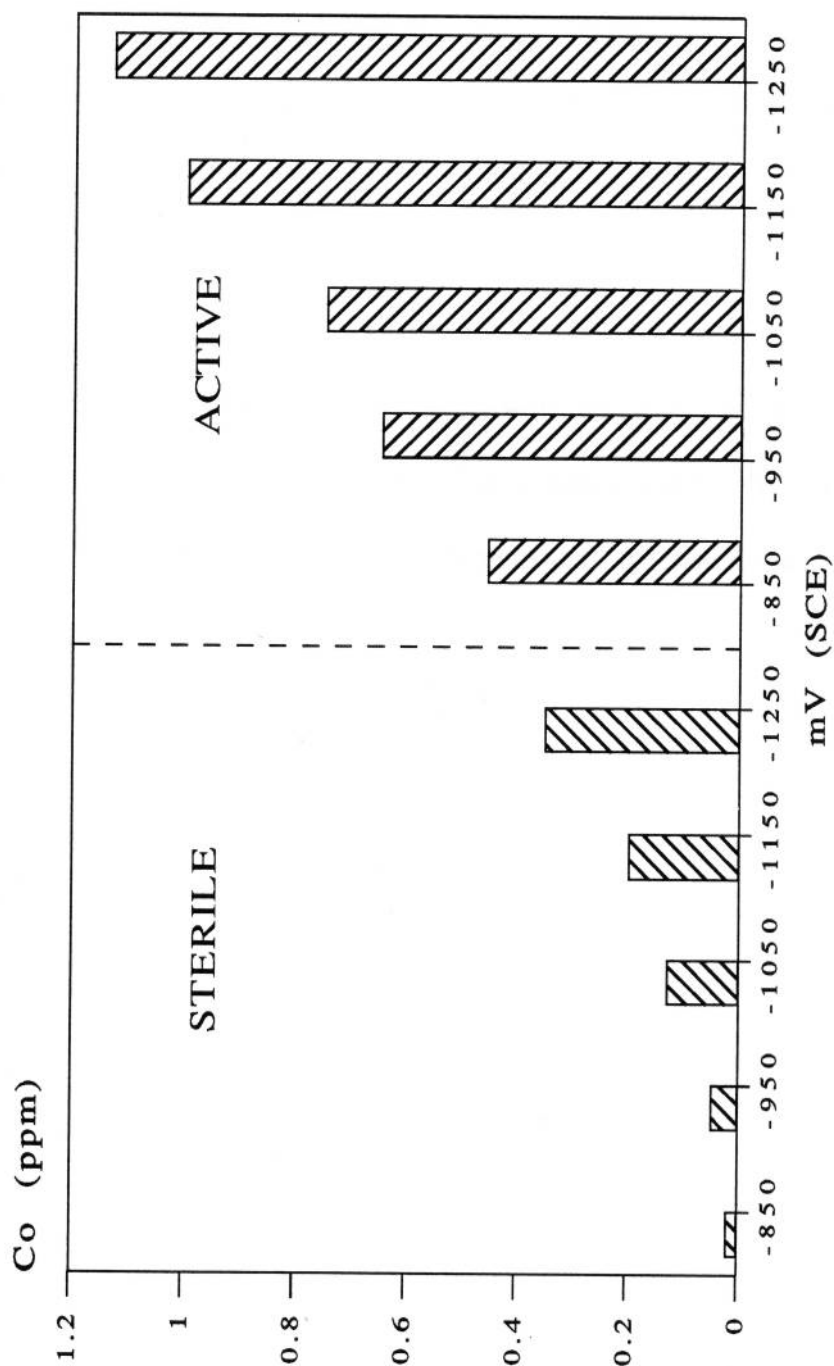


Figure 74. Comparison of Co Values For Sterile & Active Seawater Obtained Over a Range of Applied Potentials During DCB Testing

4.6.2 FATIGUE SPECIMENS

Measurements of C_o were carried out with a hydrogen detector cell placed in the test solution flow line near to the fatigue cell containing the fatigue specimen under test. Reliable results were difficult to obtain as the fatigue tests in sterile seawater were stopped for short periods during testing. Initial results matched those obtained with the DCB specimens.

Tests in the biologically active solution were too short for the hydrogen permeation transient to reach J_{∞} and therefore reliable data could not be obtained. As with the sterile seawater test the initial part of the transients matched those obtained under similar conditions with the DCB specimens.

4.6.3 SEDIMENT CELL

The cell containing sediment from the River Mersey gave C_o values of 0.16ppm for the applied potential of -850mV(SCE) and 0.27ppm for -950mV(SCE). The cell containing sediment collected from the base of a North Sea offshore platform gave similar C_o values of 0.15ppm for -850mV(SCE) and 0.28ppm for -950mV(SCE).

4.6.4 DOUBLE HYDROGEN PERMEATION

Figure 75 shows a plot of C_O and TS against time for tests carried out with the biologically active solution at a potential of -850mV(SCE). At time zero fresh test solution from fermenter 2 (Table 24) is added to the charging cell and the CP applied. The initial high TS level is observed to decline over the next 50 hours. Fresh solution is then added and the TS level is increased. This process is repeated once more before the TS levels are allowed to drop to 100ppm over a period of 140 hours. After which, the solution is changed a further three times as signified by the peaks in TS. It appears that measured C_O values are affected by the TS levels present in the bulk solution.

Table 24 Comparison of TS and SRB Numbers Measured For
Each Environment (Sediment Values Expressed Per Gram (Wet)
& Fermenters Per ml).

ENVIRONMENT	TOTAL SULPHIDE (ppm)	SRB NUMBERS	
		LIQUID	SEMI-SOLID
North Sea Sediment	68	$>2.5 \times 10^7$	$>6 \times 10^7$
Mersey Sediment	109	1000 - 2000	330 - 3300
Fermenter 1	330 - 491	$10^6 - 10^7$	-
Fermenter 2	331 - 410	10^5	$10^5 - 10^6$
	572 - 654*	10^6	10^6
	528*	$10^6 - 10^7$	10^6
	20	10^4	-

* Fed Nutrient Solution Without Thioglycollate

Similar tests were carried out with potentials of -850 and -950mV(SCE) in biologically active seawater and in the prepared sodium sulphide solution. The test parameters and corresponding figure numbers for the test results are given in Table 25.

Table 25 Summary of test conditions

FIGURE NUMBER	POTENTIAL [mV(SCE)]	TEST SOLUTION	TOTAL SULPHIDE (ppm)
75	-850	Fermenter 2	0 - 549
76	-950	Fermenter 2	0 - 528
77	-950	Fermenter 1	0 - 20
78	-950	Fermenter 1	0 - 125
79	-850	Sodium Sulphide	0 - 400
80	-850	Sodium Sulphide	0 - 20

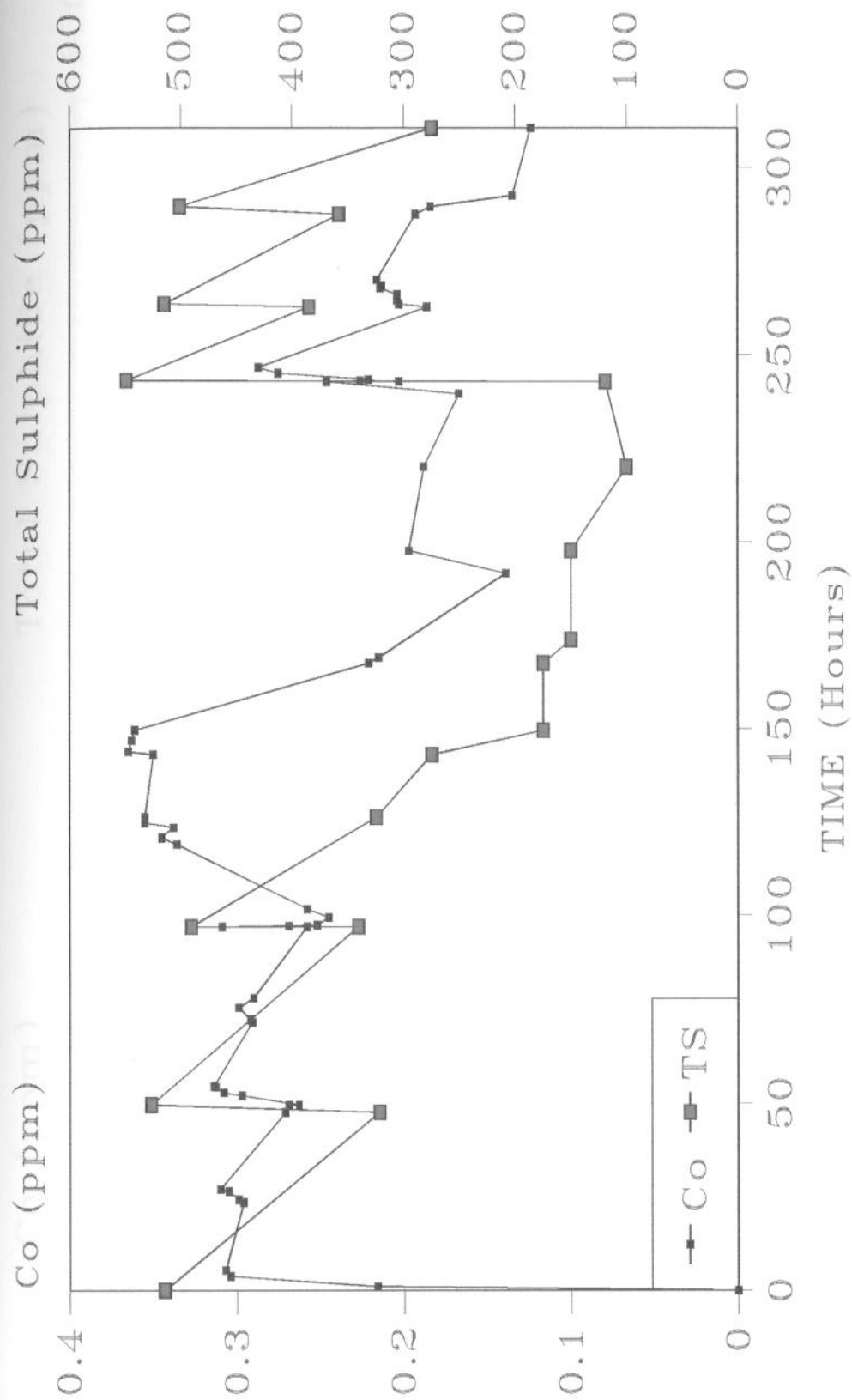


Figure 75. Total Sulphide & Co v Time in Fermenter Solution at $-850\text{mV}(\text{SCE})$ & 21°C

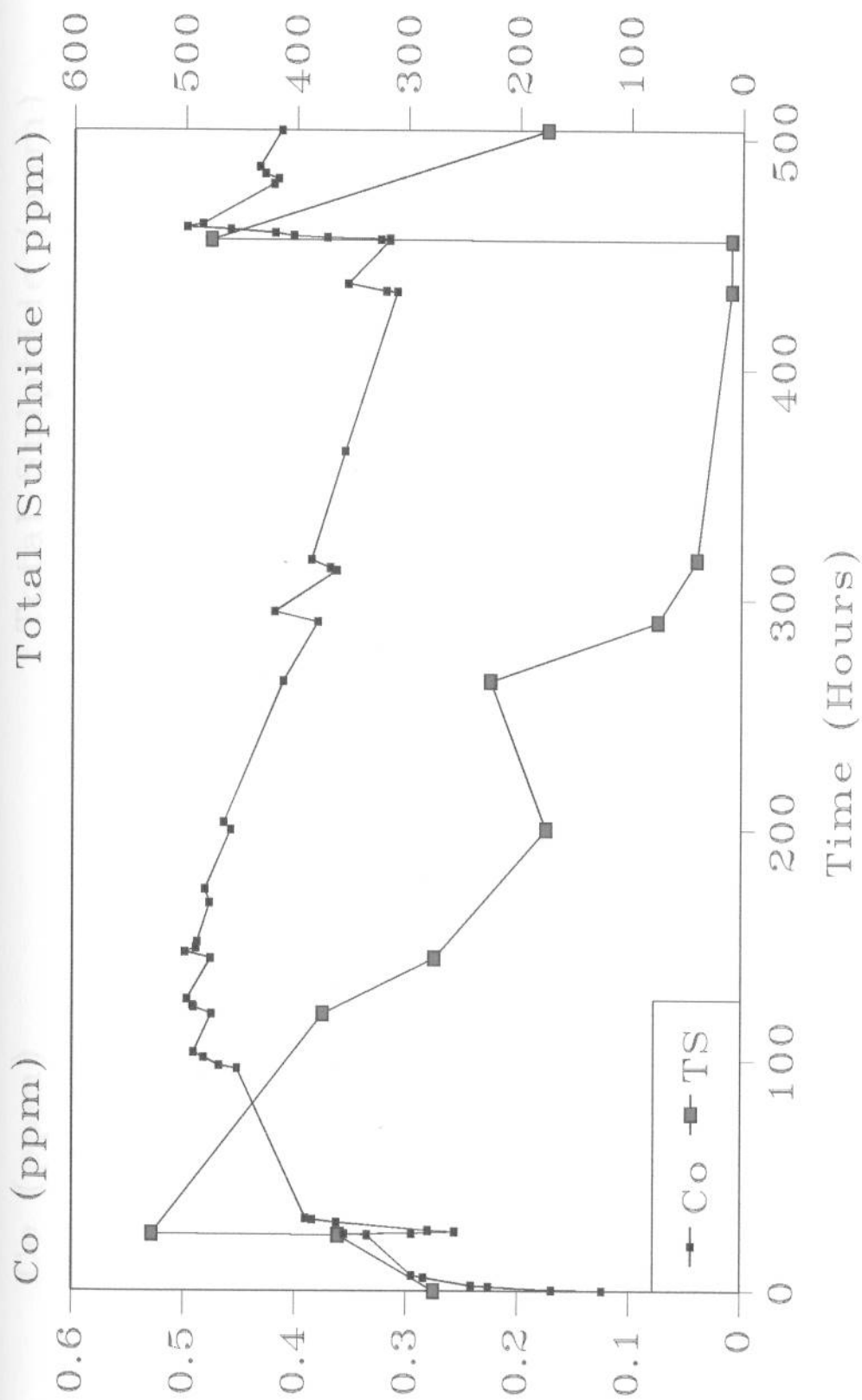


Figure 76. Total Sulphide & Co v Time in Fermenter Solution at $-950\text{mV}(\text{SCE})$ & 21°C

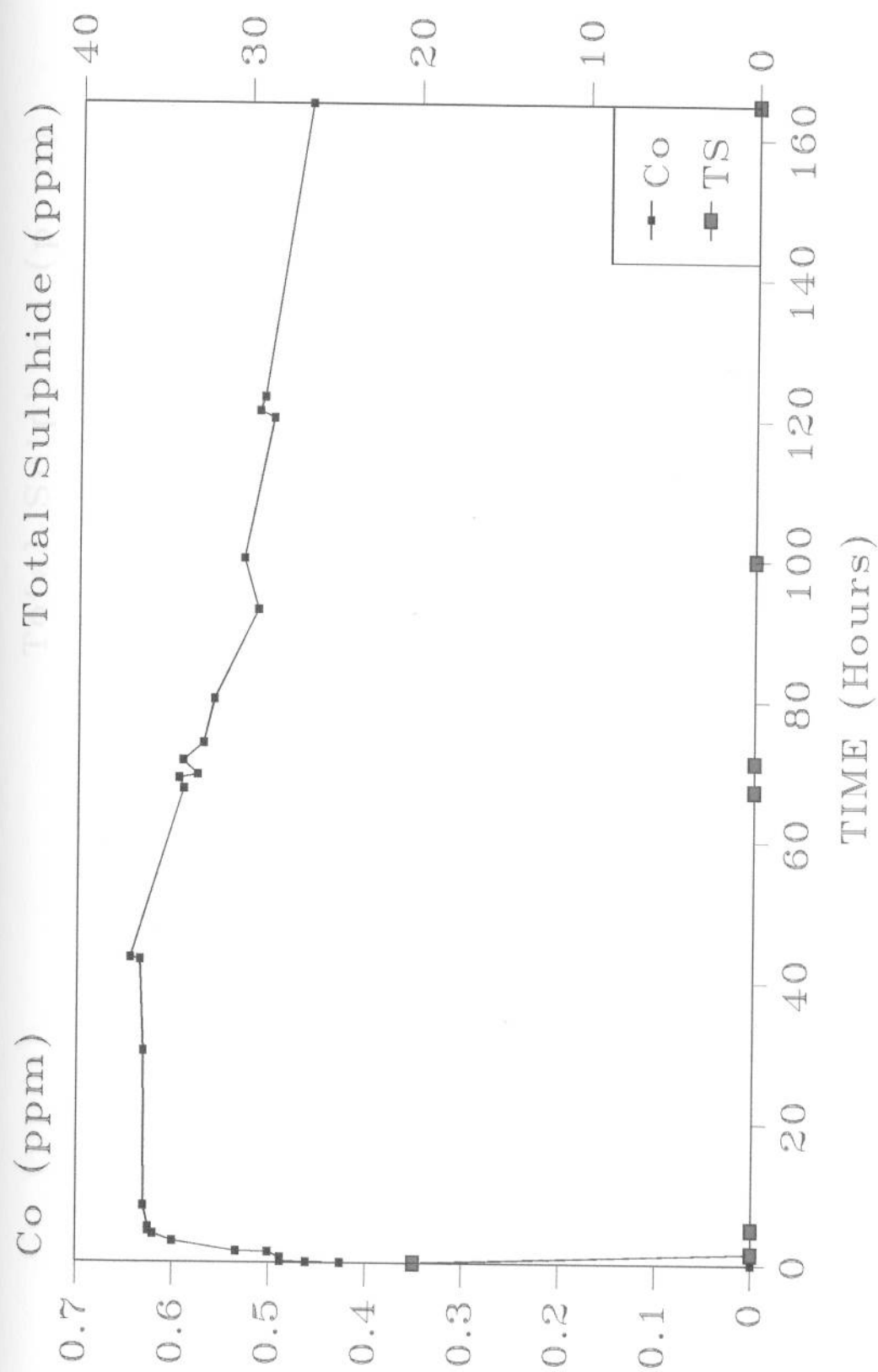


Figure 77. Total Sulphide & Co v Time in Fermenter Solution at $-950\text{mV}(\text{SCE})$ & 21°C

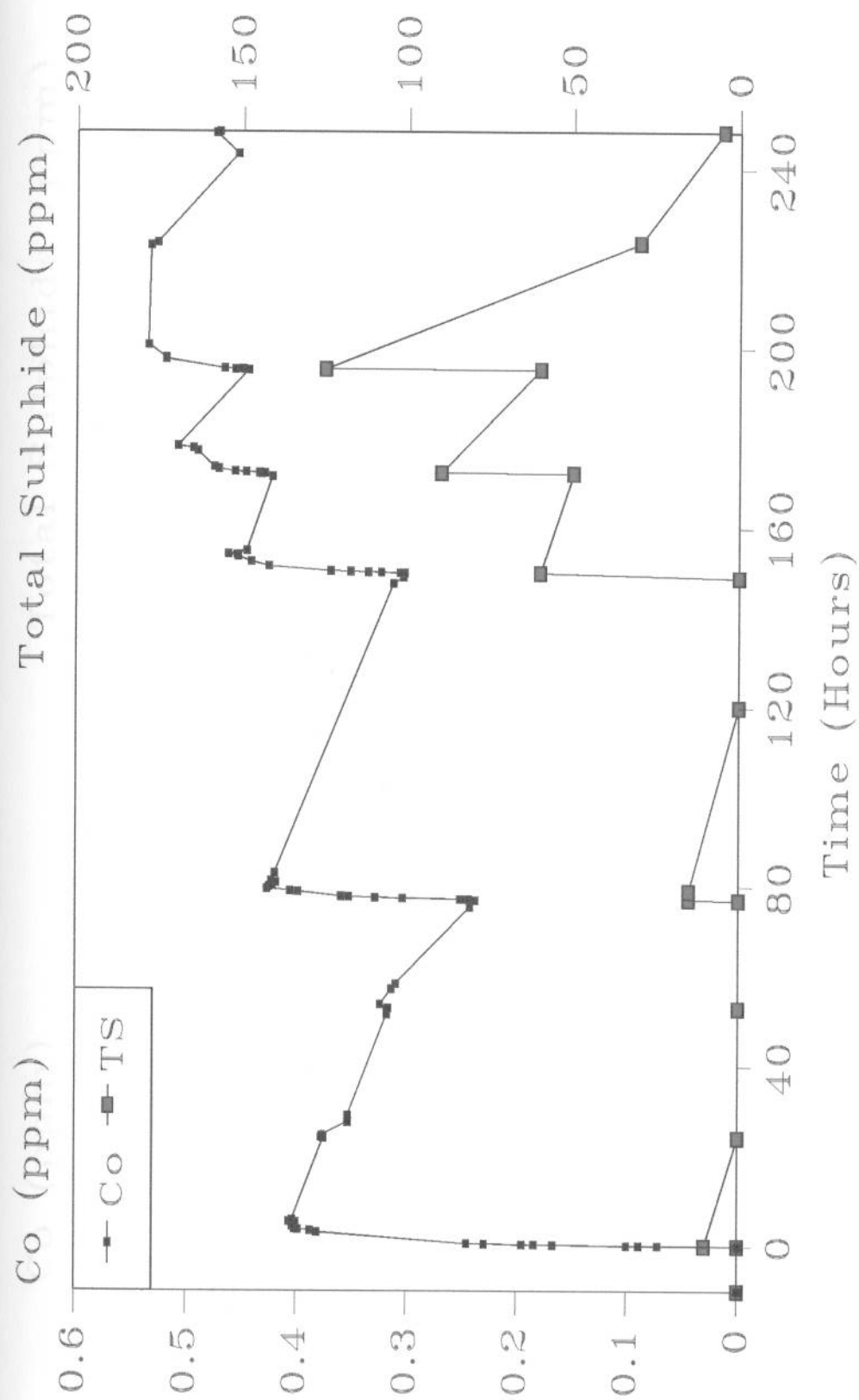


Figure 78. Total Sulphide & Co v Time in Fermenter Solution at -950mV(SCE) & 21°C

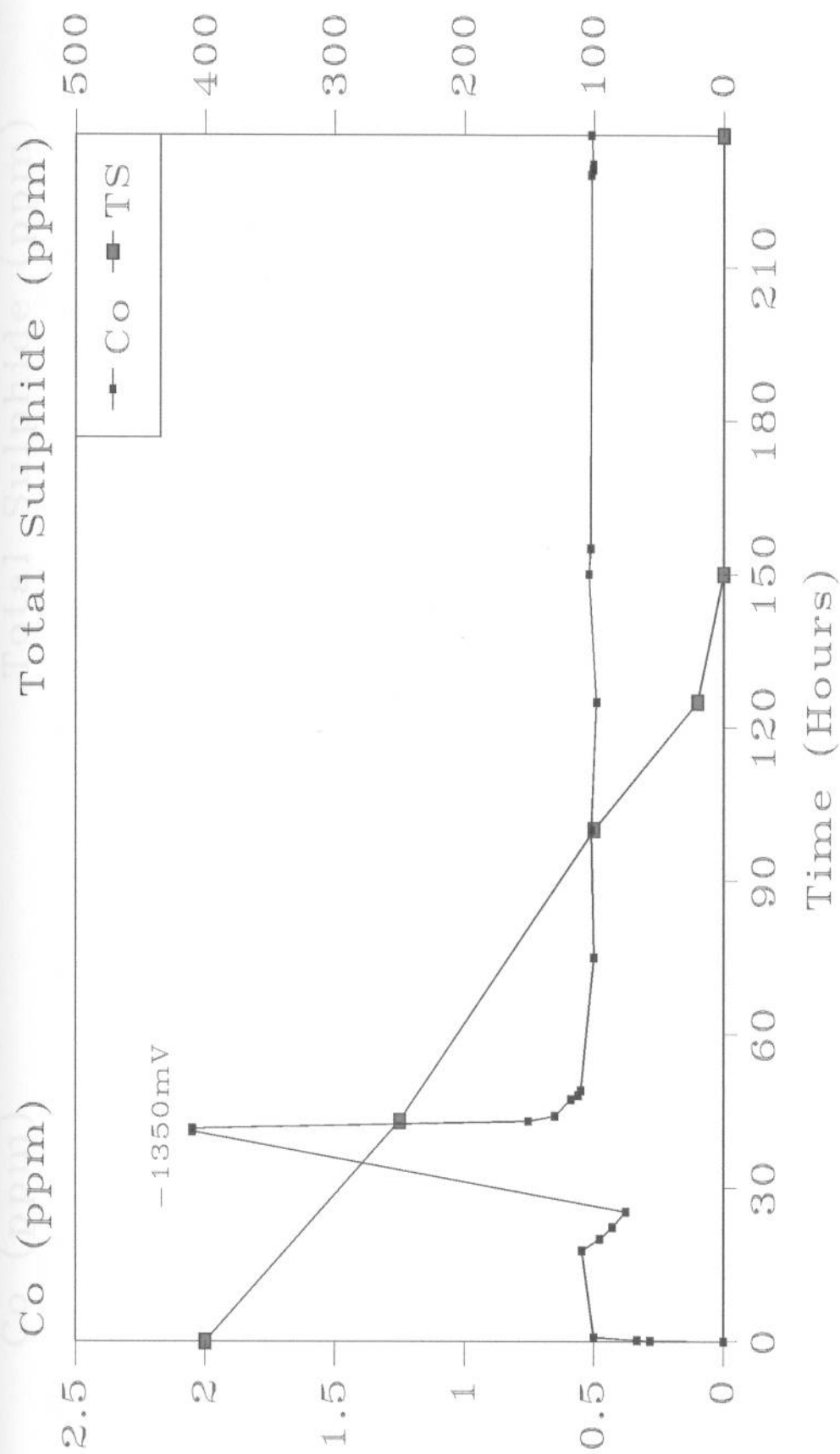


Figure 79. Co & Total Sulphide v Time For Sodium Sulphide Solution at $-850\text{mV}(\text{SCE})$ & 21°C

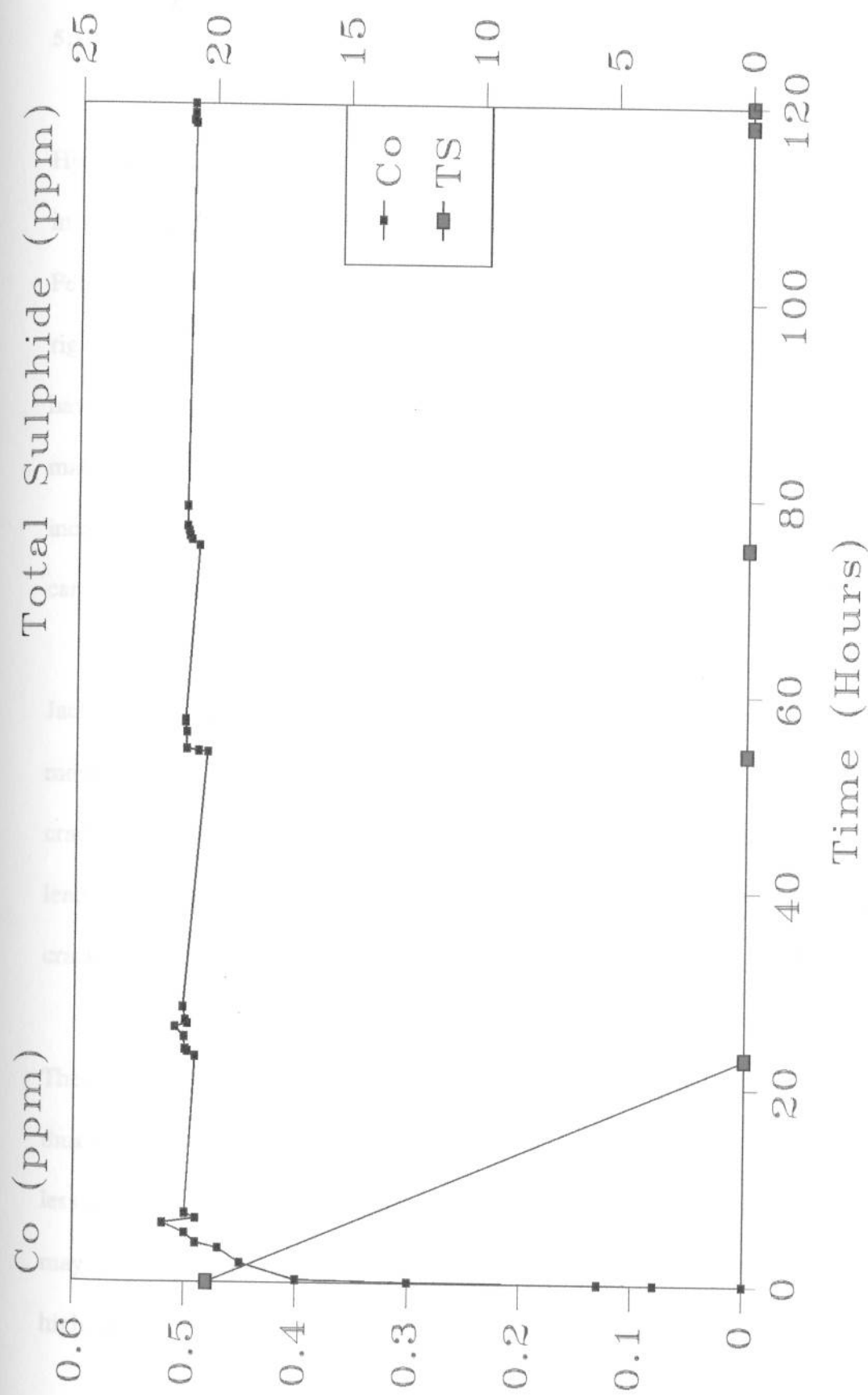


Figure 80. Total Sulphide & Co v Time For Sodium Sulphide Solution at $-850\text{mV}(\text{SCE})$ & 21°C

5.0 DISCUSSION

5.1 WELDING, HEAT TREATMENT AND MATERIAL PROPERTIES

Hydrogen assisted cracking in certain steels used in jack-ups has been reported⁽¹⁾. Early in 1988 cracking was found in two rigs during routine surveys^(1,273), and by the end of February 1989 cracking of the spud cans and legs had been found in a total of eleven rigs of five different types⁽²⁷³⁾. In current jack-up units the steels used for the leg chords have yield strengths in the range 485 to 690MPa, and it has been suggested that chord materials for the next generation will be in the range 760 to 900MPa⁽²⁷³⁾. Such an increase in strength would increase the risks of HE, especially in the HAZ of welds carried out on such material⁽⁵⁾.

Jack-up structures are vulnerable to fatigue damage due to their sensitivity to sway motions created by wave loading. In addition to fatigue damage sustained on site, cracking has been reported in the legs after long tows where rolling of the vessel has lead to a large numbers of fatigue cycles in the raised legs⁽²⁷³⁾. As a result fatigue cracking in the legs and jacking system has occurred, requiring expensive repairs⁽²⁷³⁾.

The composition of the steels used in jack-ups are normally tailored to their application, thus allowing savings to be made on expensive alloying elements. If the steel contains less of the expensive alloying additions chromium and molybdenum, the hardenability may be compensated for by an increase in the carbon content. This would result in a high carbon equivalent and thus the HAZ hardness would be particularly sensitive to

welding conditions⁽²⁷³⁾.

A steel's hardness is a major indication to the degree of its susceptibility to hydrogen embrittlement (with susceptibility increasing with greater hardness values)⁽⁶⁾. In this work, the aim of welding with a low heat input of 1.5kJmm^{-1} was to create harder HAZs compared to those which would be obtained with higher heat inputs. Heat treatments were based on the hardness and microstructure obtained in BOP tests. The single weld pass used in the BOP test represented the worst case as a multipass weld (as used for the fatigue specimens) has some tempering of the HAZ.

It could be argued that by ensuring that welding is carried out with higher heat inputs, together with postweld heat treatment, that the susceptible microstructure could be avoided in the first place. Unfortunately, using higher heat inputs for the welding may not be possible as it could result in undesirable properties. Also, higher heat inputs do not guarantee that hard microstructures will be avoided. Macrohardness measurements (effectively a mean hardness) have shown low heat input multipass welds on SE500 have a harder microstructure than higher heat input welds, but when microhardness measurements are made the picture is not so clear (Table 26)⁽²⁵³⁾. The range of microhardness values found for welds at higher heat inputs overlap and demonstrate that 6kJmm^{-1} welds can have regions of hardness which exceed the values found in a 1.5kJmm^{-1} weld⁽²⁵³⁾.

It is clear that hard microstructures are undesirable from a HE viewpoint. The proposed

use of higher strength steels in the construction of jack-ups will increase the risk that unacceptably high hardnesses will be produced in the HAZ of welds carried out on these materials. Welding procedures must be developed which avoid producing excessively hard regions in the HAZ. Material selection and welding procedures need to be considered in view of the CP system type to be used, proposed applied CP potential and the local environments that will be encountered. Research into the effects of the various environments encountered offshore on HE of higher strength steels needs to be carried out using realistic conditions.

**Table 26 Measured Hardness of SE500 Multipass Weld HAZs Created
With Different Heat Inputs⁽²⁵³⁾ (Weld Parameters as Table 5).**

HEAT INPUT (kJ/mm)	HARDNESS (VPN)	
	MACRO (5kg)	MICRO (50g/10g)
Parent plate	210	162-299
1.5	296	271-299
3.0	279	246-341
6.0	264	254-332

5.2 TEMPERATURE EFFECTS ON C_o

It has been observed in this work that C_o values calculated from measurements made using the electrochemical technique were temperature dependent. Changes in temperature during hydrogen permeation measurements were reflected by changes in the value of J_{∞} recorded and thus the C_o values calculated. It was assumed that C_o was independent of temperature and that the changes in J_{∞} with temperature were the result of changes in the diffusion coefficient, D . In reality, the changes in J_{∞} are caused by the temperature variation of both D and C_o as this is also temperature dependent, as it can be affected by the kinetics of the surface reactions. The relationship between C_o and temperature (T) has the basic form^(8,70,193,275),

$$C_o = A_c P_H^{1/2} \exp (-Q_c / R_U T) \quad (73)$$

where A_c and Q_c are constants for a given material, R_U is the Universal Gas Constant, T is measured in Kelvin and P_H is hydrogen gas pressure.

The diffusion coefficient (D) for steel is known to be very temperature dependent and is related to temperature (T) as shown in equation 74.

$$D = A_D \exp (-Q / R_U T) \quad (74)$$

where A_D and Q are constants.

Turnbull and Carrol⁽²⁷²⁾ carried out permeation measurements with martensitic stainless steel in acidified sodium chloride solutions containing hydrogen sulphide and found that D and C_o changed with temperature. If C_o was assumed to be constant then D increased

by a factor of two when the temperature was increased from 23 to 77°C. When the actual increase in C_0 value obtained at the elevated temperatures was considered also, the increase in hydrogen charging was by an order of magnitude.

Other work⁽²⁷⁵⁾ in unstrained 4135 steel has also shown that C_0 increases with temperature. Increasing the temperature from 280 to 345K caused C_0 to increase by an order of magnitude. This variation was shown to be affected by the loading condition of the specimen. As the level of specimen strain was increased the temperature dependence of C_0 diminished and then the relationship reversed such that C_0 decreased with increasing temperature. The diffusion coefficient was again found to vary with temperature and this was affected by the level of specimen strain. In unstrained material the diffusion coefficient increased by a factor of 2 with a temperature increase from 280 to 345K. When a strain of 30% was applied to the specimen the diffusion coefficient increased by an order of magnitude for the same increase in temperature.

The effect of tensile stress on cathodic hydrogen charging of iron specimens has been investigated by Beck et al⁽⁷³⁾. It was found that strain increased the concentration of absorbed hydrogen. This was suggested to be caused by the dilation of the interstitial lattice sites where hydrogen lodges. The diffusion coefficient did not change from the unstressed to the stressed condition. The increase in permeability (product of solubility and diffusivity) measured was considered to be due solely to the increase in solubility.

It is proposed that the hydrogen concentration, C_σ , in material under tensile stress, σ , is

given by⁽¹⁹³⁾;

$$C_{\sigma} = C_0 \exp (6\sigma^2 V_H / 2\sigma_{ys} R_U T) \quad (75)$$

where C_0 is the hydrogen concentration in the absence of stress, V_H is the partial molar volume of hydrogen and σ_{ys} is the yield strength. The factor of 6 comes from the coordination of octahedral interstitial sites and the term $\sigma^2 / 2\sigma_{ys}$ represents the elastic strain energy. Beck et al⁽⁷³⁾ subjected specimens of high strength steel to static tensile stress during hydrogen charging. The increases in hydrogen concentration measured during the work closely agreed with the concentration that would be predicted from equation 75.

It is thought that in the present work, the kinetics of the hydrogen evolution reaction were not significantly temperature dependent. Jelinek and Neufeld⁽²⁷⁴⁾ have demonstrated that the hydrogen formation rate on mild steel in anaerobic water was independent of temperature over the range 60 to 90°C. It was concluded that hydrogen formation was probably independent of temperature over a much wider range. Such a dependence would be expected to differ as the test environment changed, but the calibration lines obtained in this work (Figure 43) for all test in differing environments appear to have similar slopes.

As the variation with temperature of D and C_0 was not measured directly during the work it is difficult to comment on their temperature variations in detail. Their combined temperature variation in this work was found to change by a factor of approximately three for a change of 13°C (Figure 43). If this temperature range was extended to cover

a similar one to those given above then the change is approximately an order of magnitude which compares favourably with the reported variations given above.

As the temperature variation of C_o and D were not measured directly, calibration curves obtained (Figure 43) were the only method of correcting for temperature and appeared to be linear following the relationship below;

$$\ln C_o = G / T + C \quad (76)$$

where G and C are constants. The mean of the gradients obtained for all environments tested (Table 18) in the experiments gave the relationship;

$$\ln C_o = -5550 / T + C \quad (77)$$

5.3 DOUBLE CANTILEVER BEAM TESTING

5.3.1 DOUBLE CANTILEVER BEAM TESTING

The crack tip stress intensity was assumed to have reached a threshold value when the cracks velocity (v) had fallen below 10^{-10} ms^{-1} . It was important to ensure that this velocity was limited by crack tip stress intensity alone and not by the crack propagating into steel containing lower hydrogen concentrations. The dominant site of hydrogen entry (crack tip versus external surfaces) with regard to hydrogen embrittlement is still a topic for debate. It has been suggested that the dominant charging site can change depending on the level of applied cathodic potential⁽²³⁷⁾ and the nature of both the bulk and local crack environments. It would take longer for hydrogen to diffuse to the crack region from external surfaces than from the crack tip (if both these charging sites were operating). To be confident that the time calculated for a constant hydrogen concentration to be reached throughout the specimen is correct, the slower external surface charging condition is assumed to operate by default. Using this assumption it can be shown quite simply that for a DCB specimen, 12.5mm in thickness, the hydrogen would reach an essentially uniform concentration after approximately 27 days (Figure 81)⁽²⁶⁴⁾.

$$Dt / l^2 = 1.5 \quad (78)$$

where D = Diffusion coefficient ($2.5 \times 10^{-7} \text{ cm}^2\text{s}^{-1}$), t is time (sec) and l is half distance (cm). Provided the duration of the test exceeded 27 days (648 hours) then one can be confident that the results were not influenced by hydrogen concentration gradients.

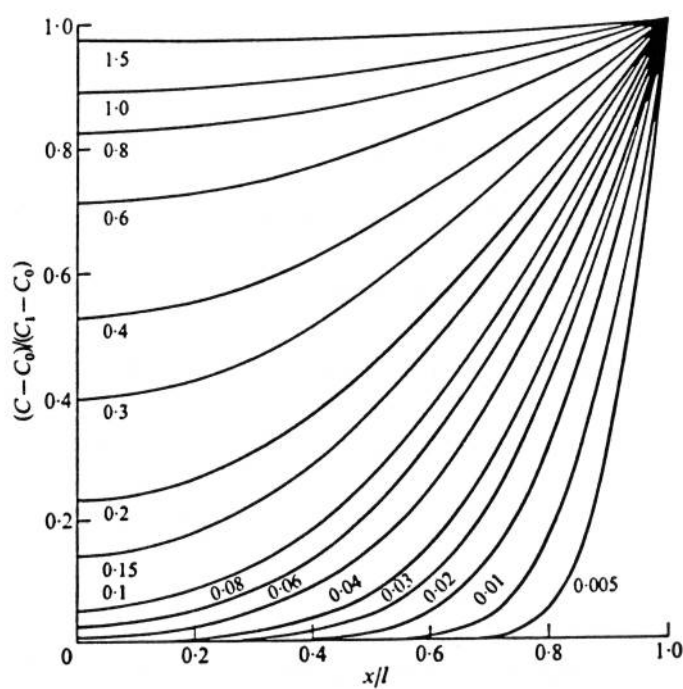


Figure 81. Concentration Distributions at Various Times. Numbers on Curves are values of Dt/l^2 (264)

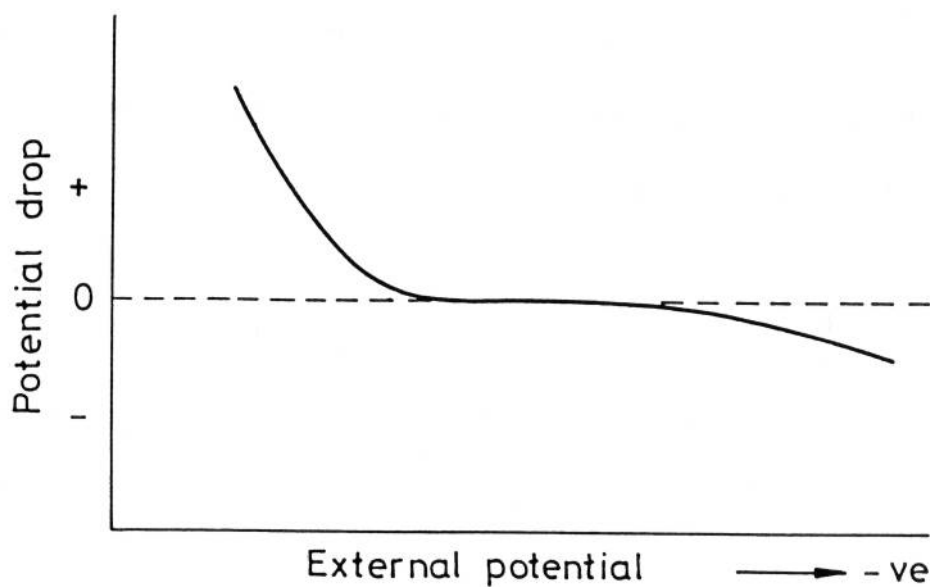


Figure 82. Schematic Illustration of the Variation of the Potential Drop at the Crack Tip With Applied External Potential (231)

The time required to reach a uniform concentration across the specimen region where crack propagation occurs, may be less than that calculated above. It must be remembered that the DCB specimens were sidegrooved to keep the crack in the centre of the specimen and reduce crack front bowing. The sidegrooves were machined to a depth of 2mm on each side, which meant that the DCB specimen was 8.5mm thick around the crack tip region. If the above analysis (equation 78) is used for a value of 8.5mm then the lower time of 2.5 days (300 hours) is required for a uniform concentration across this section.

In addition, the discussion in the previous section (5.2) demonstrates that applied stresses can affect both C_o and D . Thus, if in the strained specimen one or both of these parameters were increased the resulting increase in permeability would further decrease the time taken for a uniform concentration to be achieved across the specimen.

The above assumption, that external surface charging dominates, becomes more valid as C_o increases. For high C_o values produced by large applied cathodic potentials and/or hydrogen recombination poisons, the crack tip is more alkaline⁽²³¹⁾ due to reduced mixing and at a less negative potential compared to the external surfaces (Figure 82), so crack tip charging would be of less consequence. The threshold hydrogen concentration for embrittlement is controlled by bulk charging and a $C_o - K_{th}$ correlation should be valid⁽⁶⁵⁾.

In contrast it has also been suggested⁽⁶⁵⁾ that for low C_o values, typical of neutral

electrolytes and small applied cathodic potentials, bulk charging may have little effect on embrittlement and a $C_0 - K_{th}$ correlation could be inaccurate if the crack tip hydrogen concentration exceeds that calculated from permeation measurements. In this work it is believed that crack tip charging did not create diffusible hydrogen concentrations higher than C_0 in the DCB, but no real conclusions can be drawn about the dominant charging site. All specimens were tested to give K_{th} values at constant hydrogen concentrations throughout the specimen, so if the dominant charging site altered during propagation of the crack, it is of no consequence to the threshold value obtained.

It is worth noting that in each environment the DCB testing was carried out as a continuous test. The potential applied to the specimen was changed by 100mV after a K_{th} value had been obtained. Therefore, at this initial stage the concentration of hydrogen in the specimen was equal to the C_0 value obtained for the previous potential. If bulk charging was dominating it is possible for hydrogen produced in the crack tip region to have an effect. The smaller amount of hydrogen produced in the crack tip could still cause renewed crack propagation by reaching the critical concentration required to cause the crack to restart before hydrogen absorbed at external surfaces had reached the crack tip region. It is assumed that the concentration of hydrogen required to restart the crack propagating is less than the concentration that exists at the crack tip region when the crack stops propagating at K_{th} .

The presence of residual stresses in the DCB specimens were not thought to create a problem during testing. During heat treatment of the DCB specimens it is probable that

residual stresses were created in the specimen. The presence of residual stresses, if large, could affect the cracking observed in the DCB specimens by changing the local stress fields. As the DCB specimens were relatively thin and some bowing of the DCB specimens was observed after quenching it is thought that some, if not the majority, of these stresses were relieved. It is however, not possible to quantify the scale of such stresses and therefore, comment on their effect on the K_{th} values apart from noting that they would affect the results obtained. Residual stresses would be expected to be creating by welding, so their presence does not create an unrealistic situation.

5.3.2 THRESHOLD STRESS INTENSITIES - STERILE SEAWATER

The effects of stress intensity on the crack velocity for DSE690 in sterile seawater are compared for each applied CP potential in Figure 83. At high (stage II) stress intensities the crack propagates at approximately 10^{-8} ms^{-1} , (close to 1mm/day) although the values differ slightly between each potential. K_{th} is the most important parameter for design and failure prevention where hydrogen related cracking is concerned because the stage II crack growth rates in hydrogen are so fast as to be intolerable in most practical situations⁽²⁷⁶⁾. It has been suggested that hydrogen induced crack growth is only observed at stress intensities above K_{th} since the distance over which a critical combination of stress and hydrogen concentration is exceeded increases with increasing stress intensity⁽²⁷⁶⁾.

At -850mV(SCE) the measured crack tip K_{th} was $51 \text{ MNm}^{-3/2}$ but it must be noted that this level of CP is very conservative. This K_{th} value is too high to be of practical concern under normal loading conditions, which is demonstrated by the following analysis of the critical flaw size, a_c , required for a crack to propagate from a semicircular surface opening⁽²⁶³⁾.

$$K_I = 1.12 M_K \sigma (\pi a / Q_C)^{1/2} \quad (79)$$

where M_K is the front free-surface correction, σ is tensile stress, a is crack length (flaw size) and Q_C is the flaw shape parameter and is calculated as follows;

$$Q_C = (\Phi^2 - 0.212\sigma^2 / \sigma_{ys}^2) \quad (80)$$

where σ_{ys} is the yield strength and

$$\Phi = 3\pi / 8 + \pi a^2 / 8c^2 \quad (81)$$

where c is defined in Figure 82. For a semicircular flaw a equals c , M_K is unity and $\Phi = \pi/2$. Equation 79 is expressed in terms of cracklength (a) below. This value is the critical cracklength, a_c , for a flaw, if K_I is K_{th} .

$$a_c = K_{th}^2 Q_C / 1.25 \pi \sigma^2 \quad (82)$$

Figure 84 employs equation 82 to plot a_c against applied stress, σ , for a range of K_{th} values. The line obtained for a K_{th} of $50\text{MNm}^{-3/2}$ shows that the critical size of a semicircular crack in material of yield strength 690MNm^{-2} loaded to a tensile stress of 350MNm^{-2} would be approaching 8mm. This is larger than the size of microstructural features expected in the steel (<1mm).

Reducing the potential to -950mV(SCE) caused the crack to propagate further and give a new lower K_{th} value of $45\text{MNm}^{-3/2}$. This decrease in K_{th} is caused by the increase in hydrogen produced at the specimens external surfaces or crack region by the application of the more negative potential^(158,159). In a fixed environment the surface coverage of hydrogen is controlled by the potential and therefore, as the potential becomes more negative, the hydrogen coverage increases and increased hydrogen absorption is measured. As would be expected, at -1050mV(SCE) the crack again began to propagate to give the lower K_{th} value of $30\text{MNm}^{-3/2}$. A line corresponding to the threshold value of $30\text{MNm}^{-3/2}$ is shown in Figure 84.

At -1150mV(SCE) there was no further crack growth observed. There was an increase

in the hydrogen concentration in the DCB specimen due to the lower applied potential (Figure 74), but the effect of the local crack stresses are more important. It has been proposed that the effect of stress on concentrating hydrogen in the crack tip region is given in the following equation^(65,275) which is similar to equation 75;

$$C_{\sigma} = C_0 \exp (\sigma_h V_H / R_U T) \quad (83a)$$

where C_{σ} is the hydrogen content at the stressed crack tip region, C_0 is the hydrogen content in the stress free iron, σ_h is the hydrostatic stress and V_H is the partial molar volume of hydrogen. Bockris⁽²⁷⁷⁾ expressed the above relationship with σ_h equal to $\sigma/3$ where σ is the tensile stress and is negative.

$$C_{\sigma} = C_0 \exp (-\sigma V_H / 3 R_U T) \quad (83b)$$

A number of models have been proposed that state that cracking occurs when the combination of hydrogen concentration and stress reach a critical value ahead of the crack tip⁽²⁷⁶⁾. Equation 83b shows that the hydrogen concentration at the crack tip, C_{σ} , can be increased to reach the critical value required for cracking by increases in C_0 and the crack tip stresses. As K values are proportional to the applied stress it can be seen from equation 83b why C_0 is proportional to $\log K_{th}$, as found experimentally in equations 3 to 5. Equation 83b demonstrates that at a high applied stress (and thus high K) a small change in C_0 is reflected as a large increase in C_{σ} . Conversely at low applied stress (low K) the effect of a small increase in C_0 is reflected in a much smaller increase in C_{σ} . Thus, to give the same C_{σ} as the high K situation a very large increase in C_0 is required.

During the DCB tests, initially at high K values, changes in C_0 are extremely important

in crack propagation. C_o was found to be related linearly to the applied potential (Figure 74). During the tests the applied potential was made more negative, resulting in an increase in C_o and thus a decrease in K as a result of crack propagation. As the value of K decreased there must come a point where the increase in C_o caused little change in C_o , whereas the local stress becomes sensitive to the variations in the steels microstructure, hardness and the presence of residual stresses. A slight reduction in K would outweigh the effect of the increased hydrogen concentration and crack propagation would not occur. It has been shown that the microhardness varied through the steel (Figures 56 to 58) and it is proposed that at low K_{th} values these differences became important and the small changes that occurred in hydrogen content became less important in controlling the K_{th} value.

At -1250mV(SCE) the crack propagated again due to the increased hydrogen content. The threshold value is much lower, $27\text{MNm}^{-3/2}$, and demonstrates the risks of cathodic overprotection. The threshold stress intensity values obtained for DSE690 in sterile seawater are plotted against the applied CP potential in Figure 85. It is clear that CP has an important influence on the susceptibility to hydrogen assisted crack growth in this steel. As the applied potential becomes more negative the concentration of hydrogen is increased and the K_{th} is decreased.

In contrast the lower strength steel, SE500, did not crack in the sterile seawater at the applied cathodic potentials used in the test. This demonstrates the lower susceptibility to HE usually associated to microstructures with lower hardness. Crack tip elastic

stresses and strains, the size of the plastic zone and the location of peak elastic-plastic stresses are proportional to $K^{(65)}$. K_{th} may be related to the hardness of the steel as the crack tip stresses are dependent upon yield stress⁽²⁷⁶⁾. In equation 83a, σ_h is proportional to the yield stress of the material and therefore, controls the maximum stress which in turn controls the maximum concentration of hydrogen ahead of the crack tip.

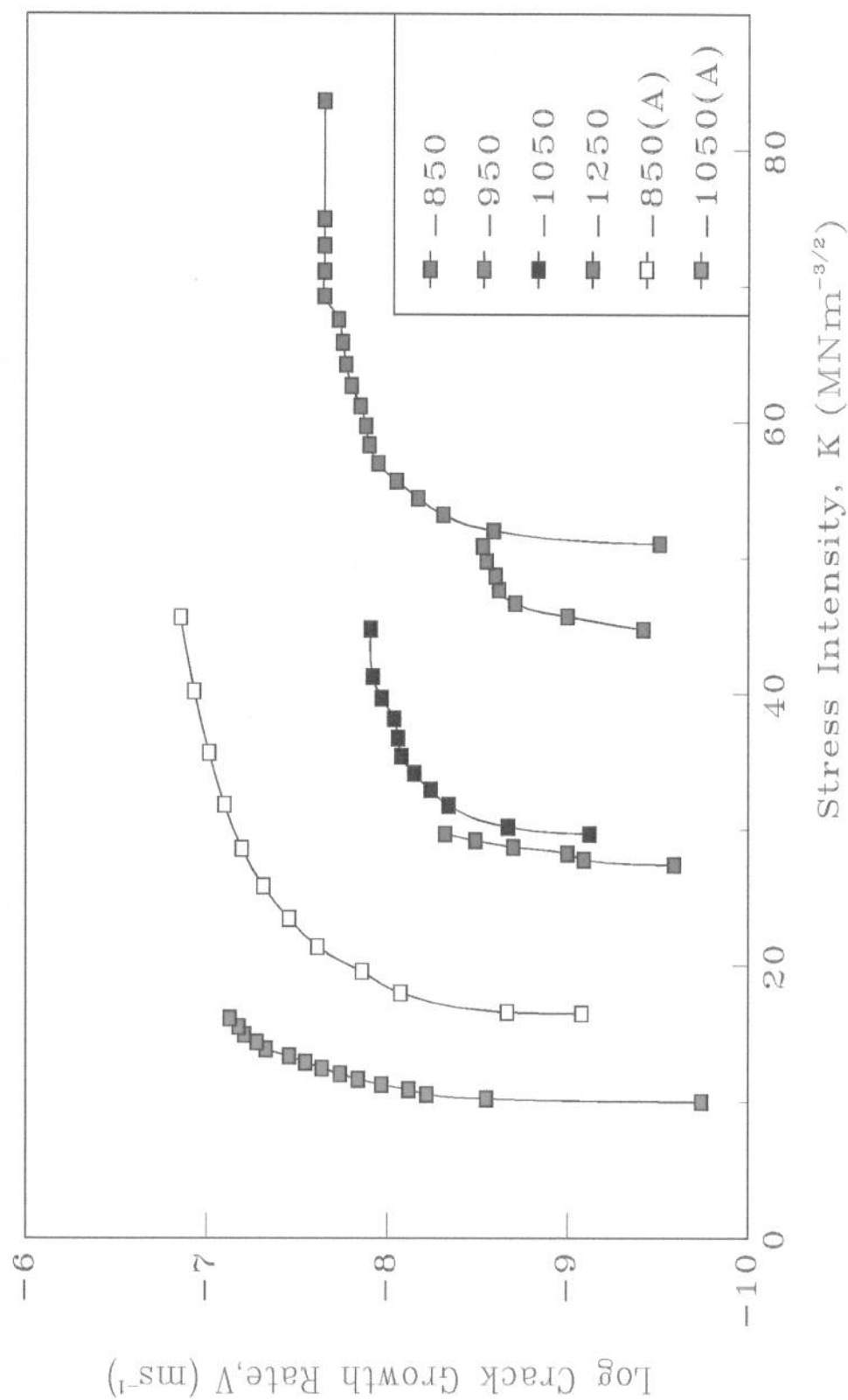


Figure 83. v:k Diagram For DSE690 in Sterile & Biologically Active
(A) Seawater at Indicated Applied Cathodic Potentials [mV(SCE)]

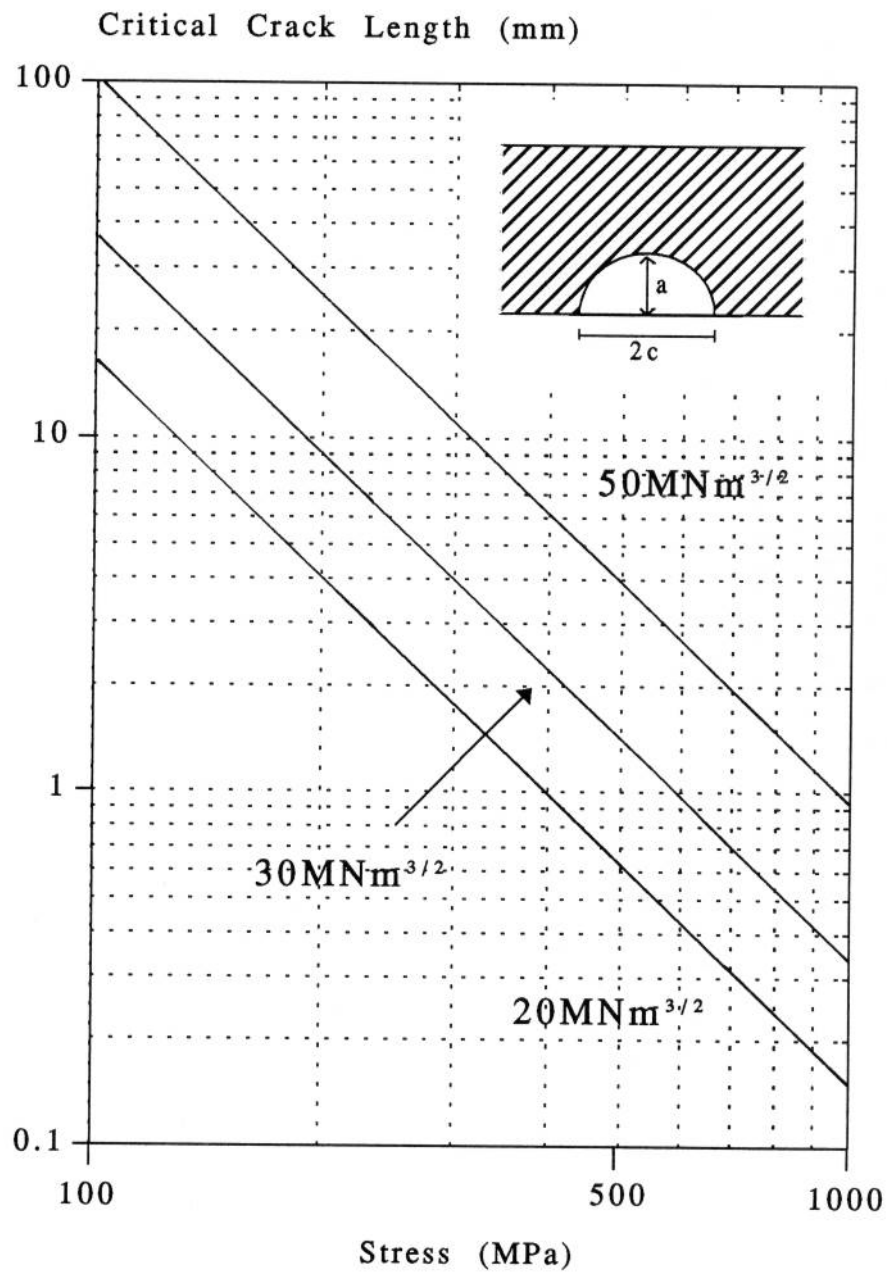


Figure 84. Critical Crack length Versus Stress For Steel With 690MPa Yield Strength

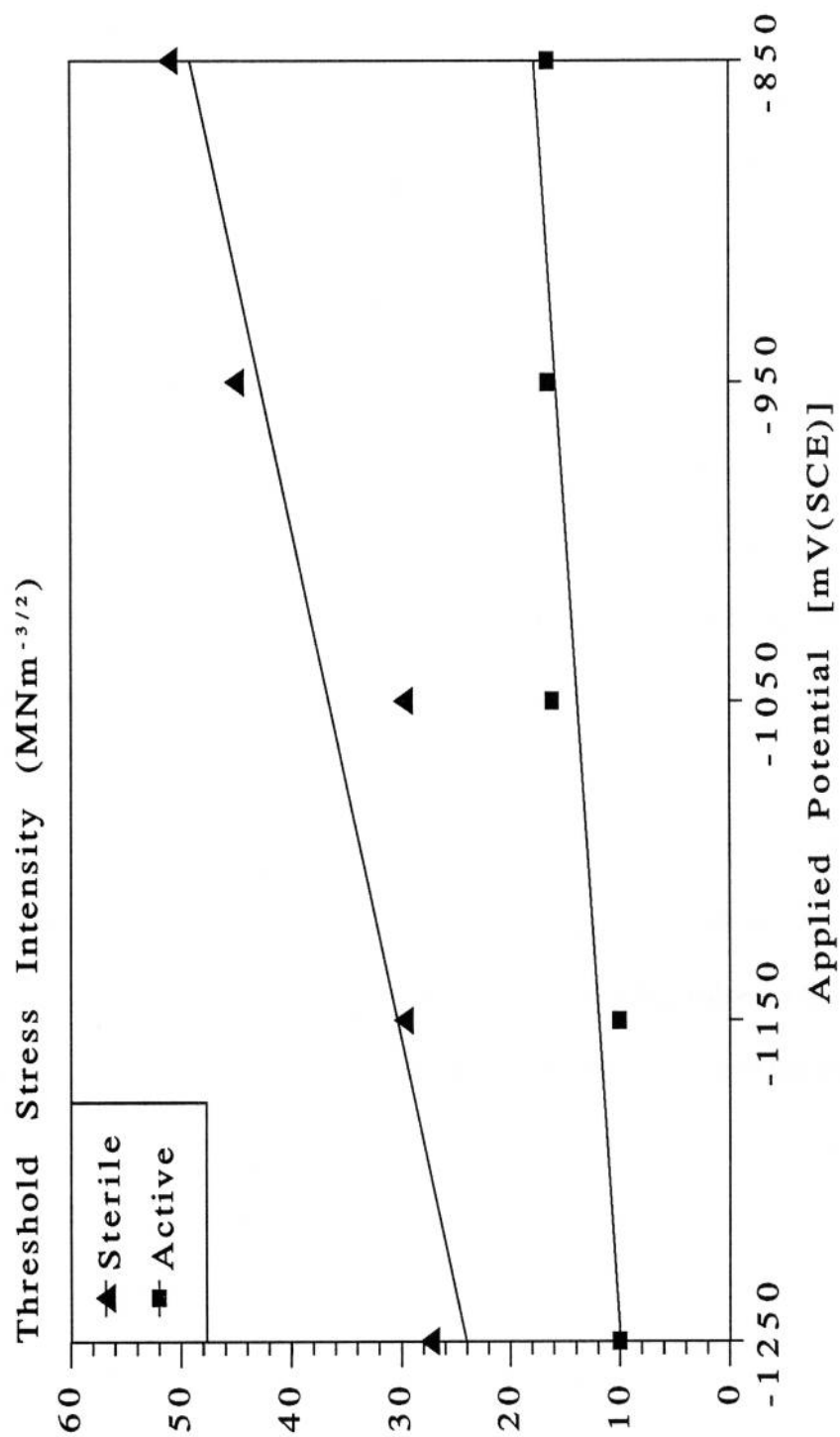


Figure 85. Threshold Stress Intensity Against CP Potential For DSE690 in Sterile and Biologically Active Seawater

5.3.3 THRESHOLD STRESS INTENSITIES - BIOLOGICALLY ACTIVE SEAWATER

The $v:K$ plots for DSE690 in biologically active seawater are shown in Figure 83. At -850mV(SCE) the crack propagated to give a K_{th} value of $16\text{MNm}^{-3/2}$. This very low value demonstrates the effect that active SRB environments have on hydrogen absorption and thus HE. The value obtained in sterile seawater at -850mV(SCE) is reduced by nearly 70% by the presence of active SRB. The stage II crack velocity ($\sim 11\text{mm/day}$) was an order of magnitude greater than that found in sterile seawater. The component of the SRB containing environment that causes the increased hydrogen absorption is discussed in a later section, but it is worth noting that the SRB numbers in this solution remained fairly constant throughout testing (Table 24).

The threshold stress intensity values obtained for DSE690 in biologically active seawater are plotted against the applied CP potential in Figure 85. It can be seen that the SRB have the effect of moving the line obtained to lower K_{th} values when compared to the sterile seawater. Figure 85 clearly indicates that when assessing the risk of HE from CP overprotection, the local environment can be by far the most critical parameter.

The cathodic potential was lowered further to -950 and -1050mV(SCE) with no further crack propagation. It is thought that this was due to the reasons given before that at such low K_{th} values the crack becomes sensitive to variation in the microstructure and stress field. In addition, it is possible in this more aggressive environment that some

crack tip blunting occurred due to the reaction of the metal with the sulphides. At -1150mV(SCE) the crack propagated to give a new K_{th} value of $10\text{MNm}^{-3/2}$ with no further crack growth at -1250mV(SCE) being observed. Reference to Figure 84 demonstrates that such low values of K_{th} would be intolerable in a structure.

Figure 86 shows the v:K diagram for SE500 in biologically active seawater. In this more aggressive environment the lower strength steel SE500 cracked at a potential of -850mV(SCE) to give a threshold value of $39\text{MNm}^{-3/2}$. This demonstrates that the presence of active SRB can cause HE in a steel which was resistant to this damage in sterile seawater, even when overprotected. Further crack propagation was achieved at a potential of -1050mV(SCE) to give a threshold value of $35\text{MNm}^{-3/2}$.

It was noticeable that compared to the sterile seawater, the calcareous deposits formed in the biologically active seawater were different. The volume of deposit formed was less, especially at the more negative test potentials. The kinetics of calcareous deposition can be affected by the level of aeration but it is believed that the difference was due to the organic content of the test solution. Table 3⁽¹⁶⁵⁾ demonstrates that a high organic content in seawater can have an affect on the scale composition. In addition, Dexter⁽¹⁸⁸⁾ has demonstrated that marine biofilms change the morphology of calcareous deposits and other work⁽¹⁹¹⁾ has shown that organic material can affect the structure of precipitated calcium carbonate.

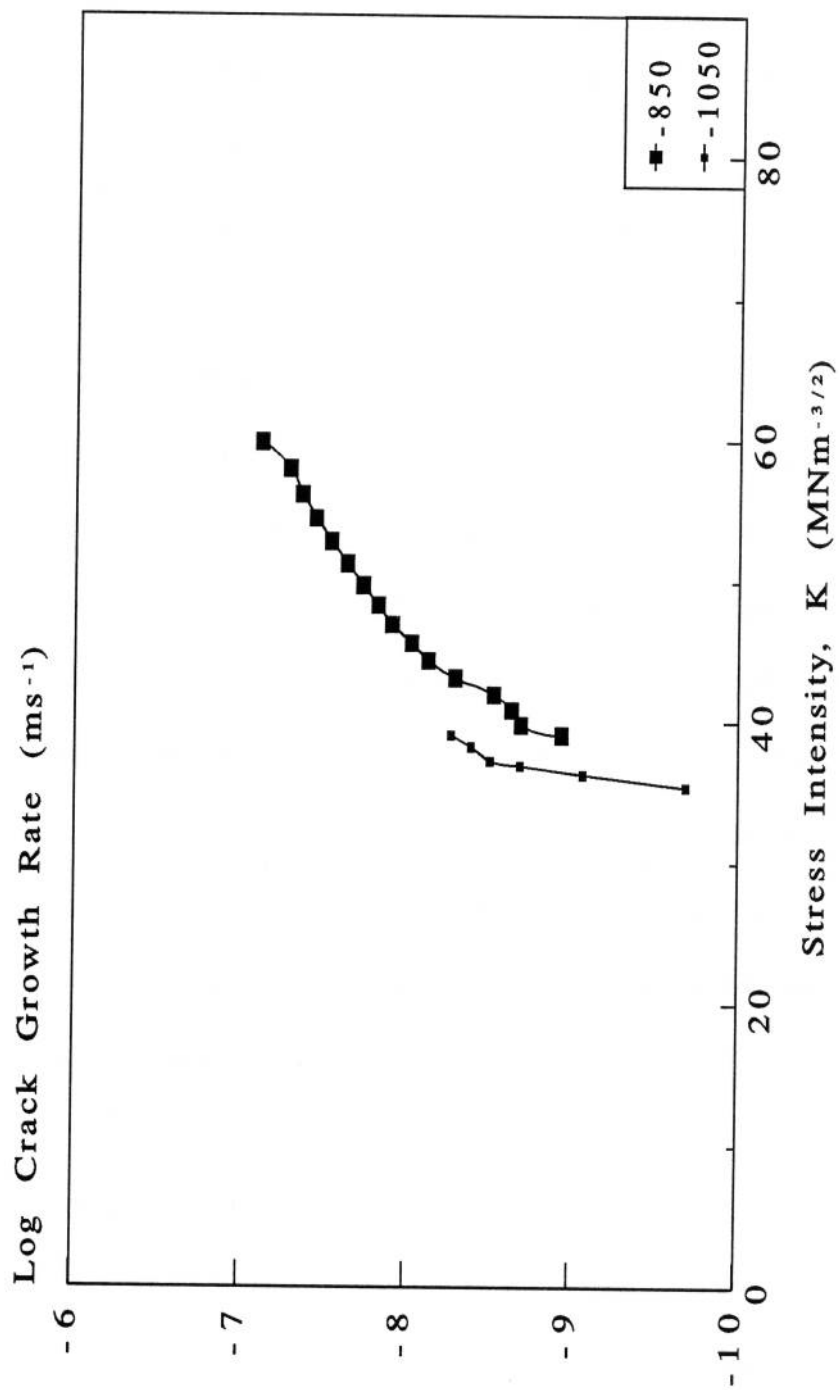


Figure 86. v:K Diagram For SE500 DCB at Cathodic Potential of -850 & -1050mV(SCE) in Active Seawater

5.3.4 HYDROGEN ABSORPTION INHIBITORS

The results obtained in the DCB testing demonstrate that steel strength, welding procedures, applied CP level and environment are important factors in HE and are linked in such a way that changes in one can affect the rest. These parameters in most cases will be fixed but it is possible to make changes to the local environment. The use of biocides may be useful in removing the SRB problem at source. Some substances when added to solution substantially reduce the entry of hydrogen^(193,202). These are mainly polar organic compounds containing nitrogen, sulphur or oxygen⁽²⁰²⁾. It has been suggested that the adsorption of certain organic molecules, such as valeronitrile, benzonitrile and naphthonitrile, restricts the access of hydrogen ions to the surface. Specific adsorption may change the structure and composition of the double layer^(193,277). Vertical adsorption of large organic molecules may hinder hydrogen approach by increasing the double layer thickness compared to the same molecule adsorbed horizontally⁽¹⁹³⁾. Energy would have to be expended on pushing the hydrogen through the adsorbed organic layer, resulting in an increase in hydrogen overvoltage⁽²⁷⁷⁾, which would cause a decrease in hydrogen coverage.

Additions of sodium nitrite and sodium silicate (both anodic inhibitors), at 1 molar concentrations, to artificial seawater has been shown to reduce the amount of hydrogen absorbed by freely corroding steel, and therefore reduce the risk of HE⁽⁷⁰⁾. The addition of sodium nitrite to the seawater caused the steels K_{th} value to increase to the K_{lc} value. It was proposed that the sodium nitrite provided a protective film on the steel surface

and shifted the corrosion potential of the steel from -670mV(SCE) to -113mV(SCE). The noble shift in potential is presumably due to anodic inhibition. At this potential the hydrogen evolution reaction would not occur.

Other work ⁽²⁷⁸⁻²⁸⁰⁾ has shown that a range of organic compounds can also reduce hydrogen absorption. The efficiency of the organic substance in preventing hydrogen adsorption is connected to the adsorption characteristics of the molecule. Once adsorbed, the resulting adsorption film isolates the cathode surface from ions being transported to it. The hydrogen discharge reaction has been suggested to occur on the surface of that film and thus makes it difficult for H atoms to appear on the metal itself. The chemisorption of these organic molecules has caused a change in the potential of the steel. The greatest reduction in hydrogenation was found with amines with the general formula R-N (C₂H₅)₂, in particular where R=p-BrC₆H₄, decreases in plasticity loss between 30 to 70% were found. These substances also were found to be the best inhibitor of corrosion and biocide which has led to the suggested use as a corrosion inhibitor, hydrogen absorption inhibitor and biocide at the same time⁽²⁸⁰⁾. The use of such chemicals would be limited to specific conditions.

It is difficult to describe a general hydrogen entry inhibition mechanism because the mechanism may change with experimental conditions. It is generally accepted that the primary step in the action of inhibitors is their adsorption on the metal surface⁽²⁰²⁾. The adsorbed inhibitor then acts to retard the process of hydrogen entry in the following ways.

Firstly, the adsorbed inhibitor may form a surface film which acts as a physical barrier to diffusion of hydronium ions (H_3O^+), or water molecules, to the metal surface and thus retard the HER. This mechanism occurs when the inhibitor molecules are large or when the inhibitor can form a multimolecular surface film. Surface films of this type give rise to resistance and concentration polarisation.

Secondly, inhibitors can act by partially blocking surface metal atoms (active sites) for the HER, and consequently for the HAR. The reduction of the reactions would be in proportion to the extent of inhibitor adsorption. When the mechanism of the HER is not affected, a displacement of the cathodic polarisation curve without a change in the Tafel slope is observed.

Lastly, inhibitors may change the HER mechanism. For instance, the recombination velocity of adsorbed hydrogen atoms. The adsorbed hydrogen atom coverage of the metal surface may decrease and thus the rate of the HAR might be decreased too. This case of inhibitor action should be indicated by increase in the Tafel slope of the cathodic polarisation curve. These different mechanisms for inhibitor action may occur simultaneously. The predominant mechanism may vary with such parameters as the inhibitor concentration, pH, nature of the anion of the solution, presence of other species in the solution, and nature of the metal.

5.3.5 THRESHOLD STRESS INTENSITIES VERSUS SURFACE HYDROGEN CONCENTRATIONS

The K_{th} values obtained for DSE690 in sterile and biologically active seawater are plotted against the corresponding C_o values in Figure 87. The results suggest that there is a linear relationship between C_o and $\log K_{th}$, the relationship being;

$$\log K_{th} = -0.65C_o + 1.6 \quad (84a)$$

which can be expressed in the form;

$$K_{th} = 43.1 e^{-1.49C_o} \quad (84b)$$

The linear plot given in Figure 87 indicates that the mechanism of HE did not change between the sterile and biologically active environments. This suggests that differences in surface reactions between the two environments which led to hydrogen charging was not a critical component of the HE observed. Thus, the method of hydrogen charging should not be important, as it is the value of C_o that controls cracking.

This would mean that if a $K_{th} : C_o$ correlation can be made in a environment for a given steel then further mechanical testing in other environments would not be necessary. C_o values would only have to be measured electrochemically for the required environments then these could be compared to the $K_{th} : C_o$ plot. It would be possible to avoid expensive and time consuming mechanical testing. In this work each K_{th} value required 2-3 months whereas the measurement of each C_o value required only 2 to 4 days. In addition, it should be easier to measure C_o values in real environments or close simulations than to carry out mechanical tests.

Figure 88 compares the $K_{th} : C_O$ obtained in this work with others obtained for steels in chloride containing environments. The variation in the relationships obtained demonstrate the range of responses of different steels to hydrogen charging. As a rule the susceptibility of steels to the effects of hydrogen increase as the strength level of the steel increases⁽²⁸¹⁾. For this reason, the most severe effects of hydrogen on the ductility of steel and their susceptibility to HAC under static load are observed in steels with yield strengths in excess of 800MPa. It is surprising then that the steel used in this work shows the greatest sensitivity to changes in hydrogen concentration even though it is of lower strength.

This may be explained by the variation in composition and microstructure between the steels. A great many studies have been carried out on the effects of composition and microstructure on the HE of steels⁽²⁸²⁾. In all steels the dominant factor is the yield strength. At lower yield strengths around 1000MPa, composition and microstructure can be fairly important.

At yield strengths of 1000 to 1300MPa there is fairly general agreement that high levels of carbon and manganese have deleterious effects, but this can vary with heat treatment and other alloy additions. Variations in chromium, nickel, molybdenum and cobalt have either no effect or give conflicting results. However, a high total level of alloying additions could be beneficial because the diffusion rate of hydrogen would be reduced. Comparison of stage II crack growth rate data in stress corrosion show that at comparable yield strengths, maraging steels displayed an order of magnitude lower crack

velocity compared to quenched and tempered steels⁽²⁸³⁾. Impurity elements can also be very important. Sulphur and phosphorus often have been observed to be detrimental. It has been suggested that high levels of impurity result in inclusion particles which can act as crack nucleation sites.

The effect of microstructure on the resistance of steel to hydrogen degradation can be of more importance than that of chemical composition⁽²⁸⁴⁾, but the effects are not always clear cut⁽²⁸⁵⁾. It is agreed that twinned martensite is much more susceptible to cracking than lath martensite. Tempered martensite or bainite are considered the best microstructure and untempered martensite the worst.

Grain size is difficult to categorize, since different studies have found that finer grain size is beneficial, detrimental or has no effect. Gerberich and Wright⁽²⁸⁶⁾ have reviewed much of the earlier work and concluded that the effects of grain size depends upon the alloy purity. In high purity steel, increasing the grain size leads to greater impurity segregation in the grain boundaries and this is deleterious. In less pure steels the grain boundaries are saturated with impurities at all grain sizes. Coarse grain sizes then are beneficial because the microfracture zone size is larger and suitably orientated grains will be able to retard crack growth.

Trapping of hydrogen can also be important and is dependent on trap type and source of hydrogen charging for the crack process. A correlation exists between the susceptibility to HE and the ability of different microstructural features in the steel to

trap hydrogen⁽²⁸⁴⁾. The trapping efficiency seems to decrease in the following order; martensite>bainite>coarse pearlite>small second phase particles. The tendency to be embrittled by hydrogen is greater for martensite than for bainite and lamellar or spheroidized pearlite. The best overall microstructure would be to have no reversible traps and a high, uniform density of small, incoherent particles that act as irreversible traps⁽²⁸⁷⁾. By providing a large number of irreversible traps the hydrogen build up at any individual trap would be minimised. Such a microstructure also would be effective in homogenising slip, and thus reducing local stress concentrations at the particles.

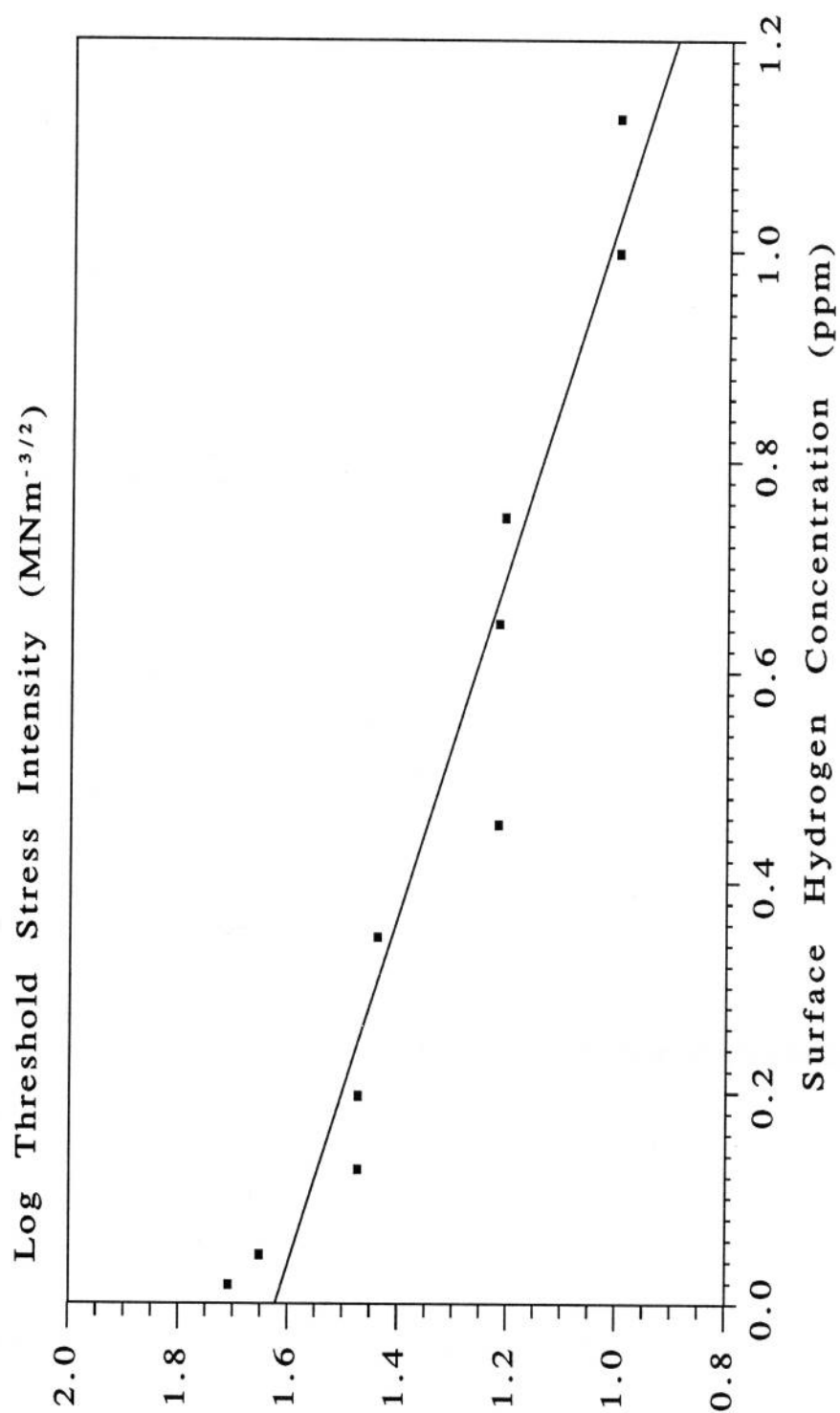


Figure 87. Surface Hydrogen Concentration Against Log Threshold Stress Intensity For DSE690.

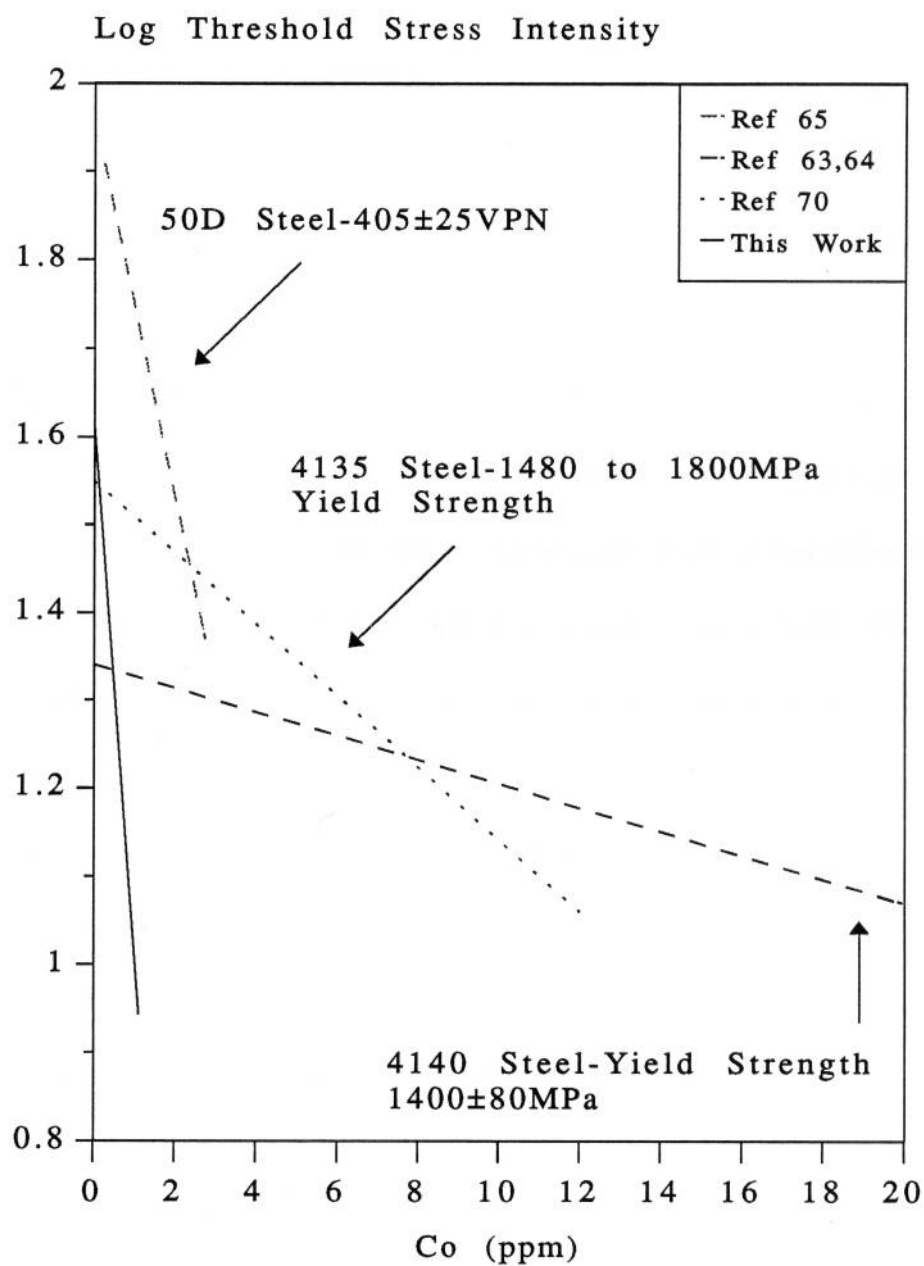


Figure 88. Comparison of Co Against Threshold Stress Intensity Data From Other Work in Aqueous Chloride Environments

5.4 HYDROGEN PERMEATION

5.4.1 SEDIMENT CELL

The C_o values measured at each test potential for both sediments were almost identical (Figure 89). Initial TS measurements (68ppm in the North Sea sediment and 109ppm in the Mersey sediment) were different for each sediment sample, and these values remained constant throughout testing. If no sulphides were produced during the tests, then this indicates that there was little or no SRB activity. In addition, the numbers of SRB present remained constant as shown in Table 24 ($>10^7$ bacteria per gram of wet sediment for the North Sea sediment and 10^3 bacteria per gram of wet sediment for the Mersey sediment). The high bacterial numbers measured in the North Sea sediment provides an excellent example of the pitfall of relying on bacterial numbers to indicate the effect SRB are having on their local environment. The high numbers of SRB measured indicated bacteria with low activity or in a dormant state and therefore having little or no effect on their local environment. If conditions in the environment changed to become more favourable for SRB growth then this community could become active and have dramatic effects on the local environment. Thus, it is the activity of the bacteria that is of more significance as it indicates the present state of the colony. Measurements of TS provide a better indication of possible SRB problems as a small number of SRB could produce large amounts of sulphide and conversely a large population could produce small amounts of sulphide.

The initial amount of sulphide present in the sediments (68ppm in the North Sea

sediment and 109ppm in the Mersey sediment) would be expected to cause enhanced hydrogen absorption. There was a significant increase in the value compared to sterile seawater, but an increase may be expected due to the anaerobic conditions alone. Barth and Troiano⁽²⁸⁸⁾ proposed that hydrogen permeation was influenced by the amount of oxygen present in the solution. It was found that at an applied potential of -900mV(SCE) the permeability of hydrogen under aerated solution exposure was at least one order of magnitude less than when the same solution was deaerated. The oxygen caused a passive oxide film to be formed on the surface of the metal. This film could then act as a diffusion barrier to the hydrogen whilst also reducing active sites of cathodic hydrogen generation. It is also quite well recognised that strongly adsorbed molecules or ions may cause hydrogen ions to be discharged not at the metallic surface but at some distance on the adsorbed layer with negligible penetration of this layer⁽²⁸⁸⁾. In Figure 89 the C_o values for the sediment are compared to those obtained during DCB testing. It could be argued that the difference is caused by the greater sulphide concentration in the DCB tests. When compared to the increases measured in the double hydrogen cell with small sulphide additions the value is still less than would be predicted.

The explanation for this might be due to lower diffusion of species to and from the membrane in the sediment compared to the totally aqueous solutions. The formation of a biofilm at the metal surface could also reduce the amount of hydrogen being absorbed into the steel. The attachment of the bacteria involves the production of EPS which could block the surface and again hinder diffusion⁽¹⁰⁴⁾. It could be possible that the

molecular hydrogen formed at the metal surface was trapped and formed bubbles which shielded the surface.

The sulphides in the sediment may also be bound up in some form which reduces their effectiveness in enhancing hydrogen absorption. Such sulphides would be expected to be detected by the TS measurements. The effectiveness of the sulphides could also be linked to age, such that freshly produced sulphides are more effective than older ones. King et al⁽¹³⁵⁾ showed that the corrosivity of iron sulphide was a function of the sulphur stoichiometry, and also that the corrosion by iron sulphides decreased with time. It was suggested that the bacteria had the effect of regenerating a chemically active sulphide surface which would otherwise become less efficient with time. It is not thought that there was a chemical agent (such as a component of the oil in the North Sea sediment) in the sediment that was acting as a hydrogen absorption inhibitor due to similarity between the results obtained for the different sediments.

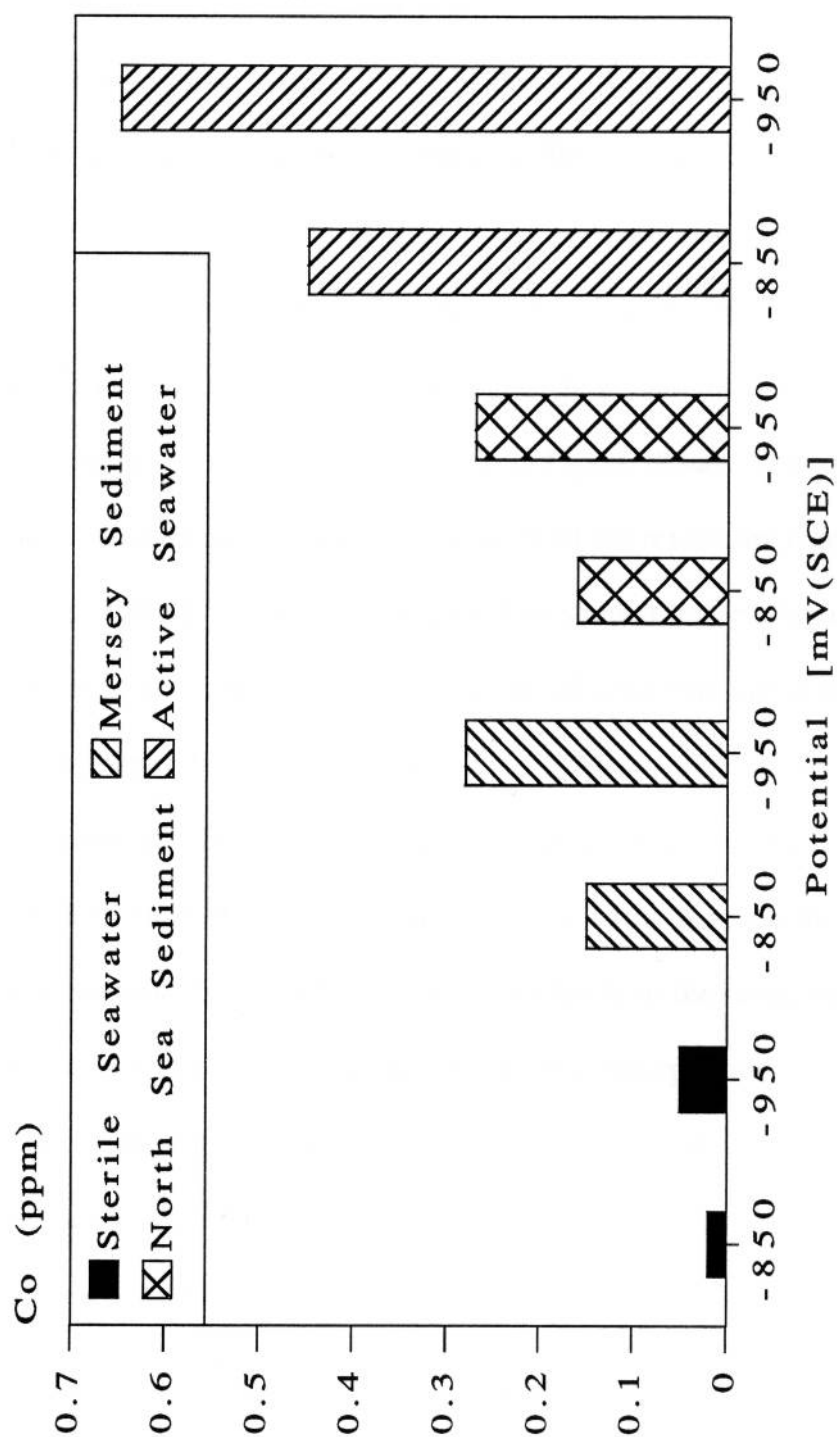


Figure 89. Comparison of Results Obtained With Sediments and Sterile and Biologically Active Seawater

5.4.2 DOUBLE HYDROGEN CELL - BIOLOGICALLY ACTIVE SEAWATER

The bar chart shown in Figure 74 (section 4.6.1) demonstrates that the biologically active solution causes considerably enhanced hydrogen absorption in the thin steel membrane compared to the sterile condition. This has been observed in other work⁽¹⁵⁹⁾ (Figure 90). The work with the double cell demonstrated this again but in addition indicated a relationship between C_o and bulk TS. Figures 75 to 78 (section 4.6.4) show that the C_o values appear to mimic the trends shown in bulk TS. The peak C_o values and corresponding peak TS values taken from Figure 78 have been plotted in Figure 91 and suggest a linear relationship. However, if all the results are compared (Figure 92), no such trend exists. Each test is expected to show a linear relationship as shown in Figure 91 but overall differences in experimental conditions mean that the trend is not apparent in Figure 90. The TS levels and C_o values were changing while the SRB numbers remained stable which indicates that SRB numbers were not directly important in the changes in hydrogen absorption occurring. It is believed that the nature of the sulphides produced by the SRB was the major factor in the enhanced absorption. This has been demonstrated in other work⁽²⁸⁹⁾ where hydrogen permeation measurements were made with SRB in contact with the and excluded from the metal. In both cases the biogenic sulphide produced by the SRB was present. It was concluded that hydrogen absorption was controlled by the biogenic sulphide.

The presence of hydrogen sulphide would change the cathodic reactions occurring compared to that expected in neutral anaerobic seawater (equation 32);



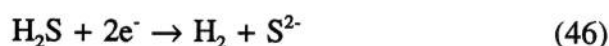
in the presence of H_2S another cathodic reaction has been suggested^(203,289);



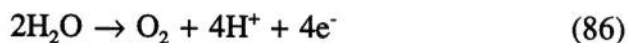
which is limited by diffusion of H_2S to the electrode surface. Equation 45 leads to another reaction that may occur;



or alternatively as Kaesche⁽²⁰⁴⁾ suggested, equation 45 and 85 can be combined;



Reference to Figure 16 shows that the dominant sulphide would be HS^- in a solution of pH 8.2. Furthermore, at the metal surface the application of CP causes the pH at the surface to rise to values above 10⁽¹⁶³⁾. At pH 10 and above, no H_2S would exist, so reaction 85 is the dominant cathodic reaction at the cathodically protected metal surface. As the platinum auxiliary electrode was external to the cell it was in aerated seawater so the main anodic reaction was expected to be;



In addition, some chlorine may be produced;



It is known for many metals including iron, in deaerated aqueous solutions, the rate determining process for the cathodic reaction is associated with the recombination of adsorbed atomic hydrogen to produce molecular hydrogen gas, as it requires the largest activation energy. The classical theory of SRB enhanced corrosion employed the fact that bacteria containing hydrogenase could utilize cathodic hydrogen as part of their metabolism. Removal of this hydrogen from the cathode would bypass the slow

recombination step, and therefore would depolarise the cathodic reaction and stimulate corrosion.

Gangloff⁽²³⁴⁾ has suggested that removal of atomic hydrogen from the cathode by SRB would lower the amount of hydrogen available to enter the metal. This may not be strictly correct for two reasons. Firstly, the number of sites for hydrogen production, and therefore, the hydrogen surface coverage should not be changed by the SRB as surface coverage is controlled by electrode potential. The rate of hydrogen entry into steel in acid has been shown to be determined by the absorbed hydrogen coverage on the steel surface, and the coverage is controlled by potential over a limited range⁽¹⁹⁵⁾. For neutral and slightly alkaline solutions, such as seawater, with low hydrogen ion concentrations, linearity over a much wider range would be expected⁽¹⁵⁷⁾. Depolarisation of the cathode is in effect an increase in the rate of the cathodic reaction, so the removal of hydrogen would be compensated by increased production. Work by Robinson et al⁽²⁸⁹⁾ suggests that this effect is small compared to the effect of the sulphides produced by the SRB.

Secondly, it is debatable whether SRB have any effect on atomic hydrogen in the first place. It is well established that SRB use molecular hydrogen via hydrogenases^(290,291). Stott⁽²⁹⁰⁾ argues that the original proposed catalysis of two reversible reactions;



has been shown by radiotracer work to definitely not occur. It would therefore be impossible for hydrogenase to depolarise a cathode by removal of atomic hydrogen, as

hydrogenase cannot work on atomic hydrogen at all. It has also been questioned whether the bacterial uptake of hydrogen could accelerate the HER because the desorption of molecular hydrogen does not control the reaction rate⁽¹¹⁹⁾. One way that SRB could affect the cathodic reaction is by removing molecular hydrogen and thereby allowing easier diffusion of H_2S and HS^- to the site of the cathodic reaction.

The premise that SRB could reduce the amount of hydrogen being absorbed could be tested experimentally by carrying out work similar to that of Booth^(127,128). By working in a sulphate free environment the effects of the produced sulphides would be avoided, so hydrogen permeation measurements could be carried out to determine the effect that the SRB and produced biofilm have on hydrogen entry. If the bacteria were then killed the effects of the biofilm on hydrogen permeation could be measured. Scotto⁽¹¹²⁾ added sodium azide to kill lifeforms present without causing detachment of the biofilm.

The production of sulphide or other metabolite by SRB would be expected to increase the uptake efficiency of the hydrogen produced on the occluded crack tip or boldly exposed metal surface by the application of CP or by corrosion processes. Walch^(249,250) has shown that hydrogen uptake into steel is enhanced in near neutral solutions containing SRB. Sulphides produced by the SRB could react with the membrane to form iron sulphide. If the iron sulphide was the cathodic site for hydrogen reduction the activation energy for hydrogen recombination may be reduced. A simple increase in the effective area of the sulphide could also lead to an increase in the cathodic reaction rate since the total exchange current is the product of the exchange current density and

cathode surface area.

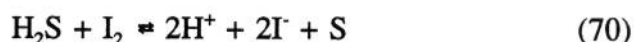
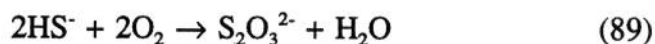
Although the results have demonstrated that C_o is related to the bulk TS, enhanced hydrogen absorption was sustained in tests even after the bulk TS was allowed to fall to zero (Figure 77). This would suggest that the surface sulphide film was responsible for the enhanced hydrogen absorption, and that the initial bulk TS had some effect on this films efficiency. It would be predicted that the initial iron sulphide formed would be mackinawite⁽²¹⁰⁾. The decline in C_o could be due to transformations in the nature of the initial sulphide film with time, as shown in Figure 17. In addition, bacterial EPS could be incorporated into the sulphide film during its growth and also be deposited on the outer surface. This organic material could affect the films ability to enhance hydrogen entry. The effect of adding fresh sulphide on an existing aged sulphide film could be in some way to regenerate it, possibly producing mackinawite. The scatter between the results obtained from the all tests (Figure 92) demonstrates the importance of the sulphide film formed on the steel surface.

The results also show that low concentrations of bulk TS can lead to higher hydrogen concentrations in the steel compared to much larger bulk TS levels. It is believed that the thickness of the sulphide film was of importance in determining the extent of hydrogen entry. Sulphide films are known to be efficient cathode surfaces at which hydrogen production can occur as a result of both microbial corrosion and CP. Low concentrations of bulk TS would be expected to produce a thin sulphide film on the steel surface. On this thin sulphide film the hydrogen is produced close to the metal surface

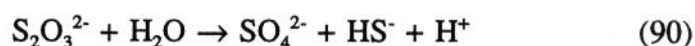
and absorption could occur at film defects. In higher concentrations of bulk TS the surface sulphide film would be thicker, and hydrogen production would take place further away from the metal surface, resulting in a lower concentration of absorbed hydrogen.

During the tests the bulk TS levels dropped. It is possible that the volatile H_2S in the cell was lost by leakage. The feeding solution put into the fermenter was corrected to a pH 7.5. The distribution of H_2S and HS^- in the solution can be calculated from the ionization constant for H_2S and solution pH for a given solution conductivity and temperature from tables⁽²⁹²⁾. At 20°C, pH 7.5 and a solution conductivity of 50000 $\mu\text{mhos/cm}$ (corresponding to seawater) the distribution is 24% H_2S with the balance made up of HS^- . The concentration of S^{2-} would be negligible (<0.05% at pH 11). The high level of the volatile sulphide in the aqueous phase would give a high concentration in the gas phase above the solution and could be reduced by leakage from the cell.

In addition, the cell had the platinum auxiliary electrode external to the cell and was linked by a plugged tube which allowed ionic conduction between the platinum electrode and the working electrode (membrane). This link could allow sulphide to diffuse out of the cell and also allow oxygen to diffuse in. This oxygen would react with the sulphide present to give thiosulphate (equation 89);



The thiosulphate produced will also react with the iodine in the iodometric titration, effectively being measured as sulphide, but only at a quarter of the concentration of the sulphide required to produce it. Most if not all SRB are able to utilise thiosulphate instead of sulphate⁽²⁹³⁾,



It would also be possible for reaction between the steel membrane and the sulphides to produce an iron sulphide film on the surface. This will remove sulphides from the bulk solution. This film is known to have formed due the characteristic blackening of the surface of the membrane. It is not thought that this could account for the all the sulphide that was lost during the tests. For continued removal of the sulphide from bulk solution by creating a sulphide film would require the film to become thicker with time. This would be expected to result in the maximum C_o values reducing with time. Reference to Figures 75,76 and 78 demonstrate that this was not observed. It is probable that the TS levels dropped through a combination of the effects described above with the major cause being due to the ionic link to the external auxiliary electrode.

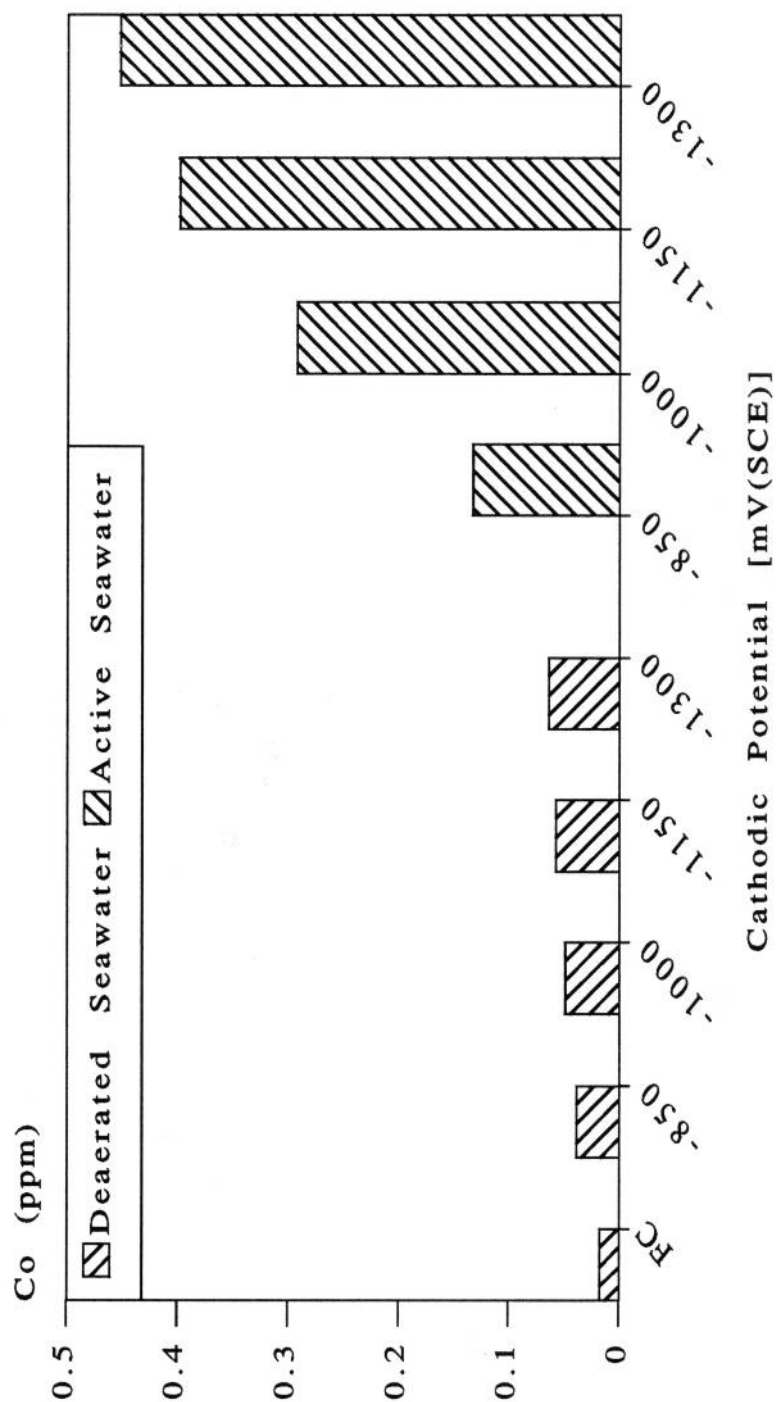


Figure 90. Co Values Obtained in Deaerated Artificial seawater and Biologically Active Seawater (159)

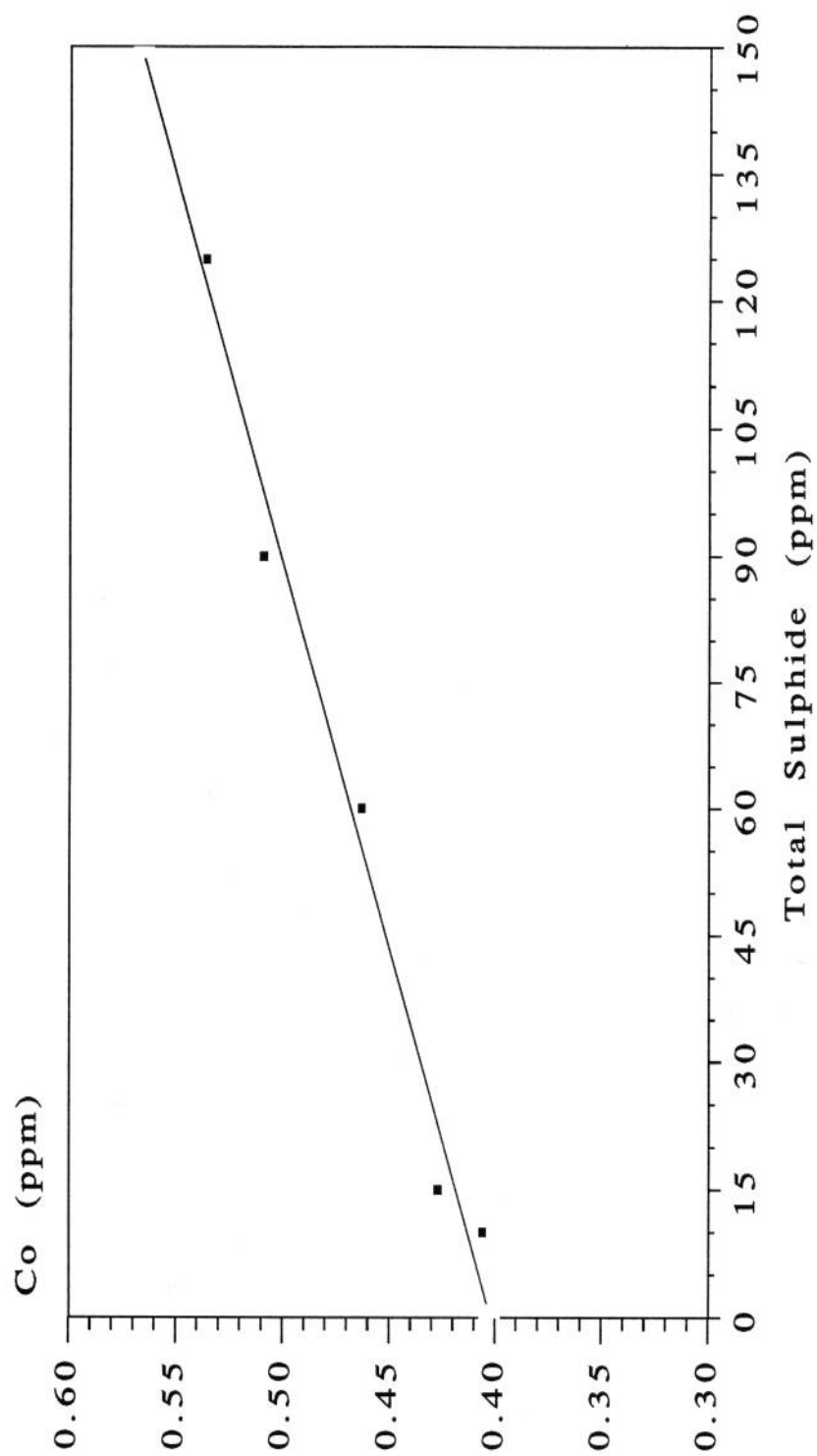


Figure 91. Peak Co Against Peak Total Sulphide in Fermenter Solution at -950mV(SCE)

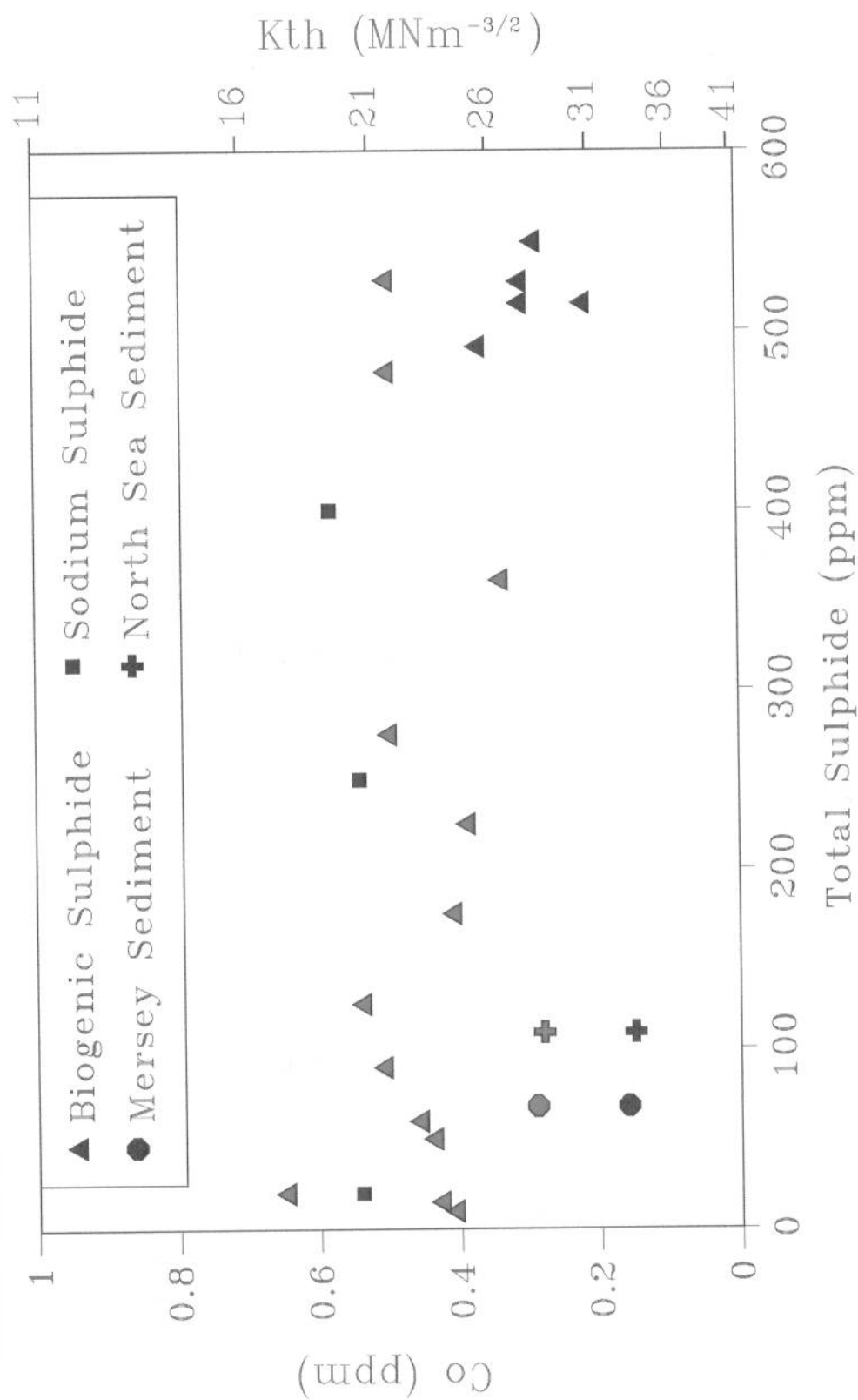
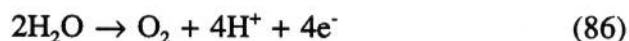


Figure 92. Scatterchart of Co, Kth & Total Sulphide
 Blue -850mV(SCE) Red -950mV(SCE)

5.4.3 DOUBLE HYDROGEN CELL - PREPARED SULPHIDE SOLUTION

Hydrogen permeation measurements using the prepared sulphide solution gave C_o values that were higher than in the biologically active solution at corresponding TS values, as shown in Figure 92. In addition, changes in the bulk TS levels did not appear to affect C_o which remained stable. Similar cathodic reactions would be expected in this solution as in the biologically active solution as described in the previous section. The anodic reaction would not be the same as the platinum electrode was situated in the cell and therefore was in a deaerated solution;



At -850 and -950mV(SCE) it was not expected that significant amounts of chlorine would be produced;



The prepared sulphide solution was made up in deaerated seawater with a pH of 8.2. If the analysis of the proportions of the sulphides is carried out as in the previous section, the amount of H_2S is calculated to be 6%. It is surprising that such a small variation in pH has such a large effect on the concentrations of the sulphides. The biologically active solution was predicted to have four times the concentration of the volatile hydrogen sulphide and thus greater losses from leakage would be predicted for the biologically active solution. In addition, there was no ionic link used with the prepared sulphide solution as the anode was situated within the cell. The fact that the TS level again reduced with time suggests that the anodic reaction may have produced

significant amounts of oxygen (equation 84). The produced oxygen would be available to react with the sulphides as shown in equation 89. It also indicates that the reaction between bulk sulphides and the steel membrane may be of importance in explaining where the bulk TS went.

The higher C_o values obtained in the prepared sulphide solution compared to the biologically active seawater could be due to some form of hydrogen absorption inhibition being missing which is present in the other solution. The prepared sulphide solution contains no organic material whereas the biologically active solution contained a complex mixture of organic material. This organic material comes from the original Postgates solution and is further complicated by the break down products of bacterial activity. It has been suggested⁽²³⁴⁾ that this organic material in the Postgates solution could have an effect on hydrogen absorption. In particular, it has been found that yeast extract causes a reduction in the amount of hydrogen absorbed into steel ⁽¹³⁷⁾. The prepared sulphide solution is a more severe environment compared to the biologically active seawater and suggests that the bacteria are protective.

The iron sulphide film formed in this solution would again be predicted to be initially mackinawite⁽²¹⁰⁾. The presence of organic material in the biologically active seawater could affect the formation of the sulphide film and its efficiency to enhance hydrogen absorption. Mara and Williams⁽²¹⁰⁾ found that chemically prepared sulphides gave greater depolarisation of iron electrodes than biogenically produced sulphides.

SRB and other bacteria could reduce hydrogen absorption by blocking the surface physically with their cells and/or indirectly by biofilm material formation. Both could act as barriers to diffusion of species to and from the surface.

5.5 FATIGUE

Results for the fatigue tests carried out on each steel are compared in Figures 93 (SE500) and 94 (DSE690). The fatigue behaviour of specimens tested in air and freely corroding in sterile seawater is similar, both steels displayed enhanced crack growth rates when CP was applied. Increasing the level of protection caused increased growth rates due to the increased hydrogen production and entry into the steel.

The crack growth rate of SE500 in sterile seawater under CP was slightly higher than that found in DSE690. When tested in the biologically active solution the DSE690 was found to have the higher crack growth rate. This is demonstrated by comparing the relative increase in growth rate for the two steels in the differing environments. At $\Delta K = 14 \text{ MNm}^{-3/2}$ the crack growth rate in SE500 was increased by a factor of two when the SRB were present for each potential. A similar comparison for DSE690 gives a fourfold increase in crack growth rates.

The results obtained at a potential of -1100 mV(SCE) displayed typical fatigue behaviour for HSLA steels, with a positive gradient in region II. In contrast, at a potential of -950 mV(SCE) both steels showed an anomalous response, with the crack growth rates remaining almost constant over a wide range of ΔK values. Other workers^(172,175,230,240,244,245) testing CMn steels in seawater at similar CP potentials have reported a similar plateau in growth rate in region II. There is sufficient evidence to suggest that the lowering of da/dN at potentials close to -950 mV(SCE) is a real effect

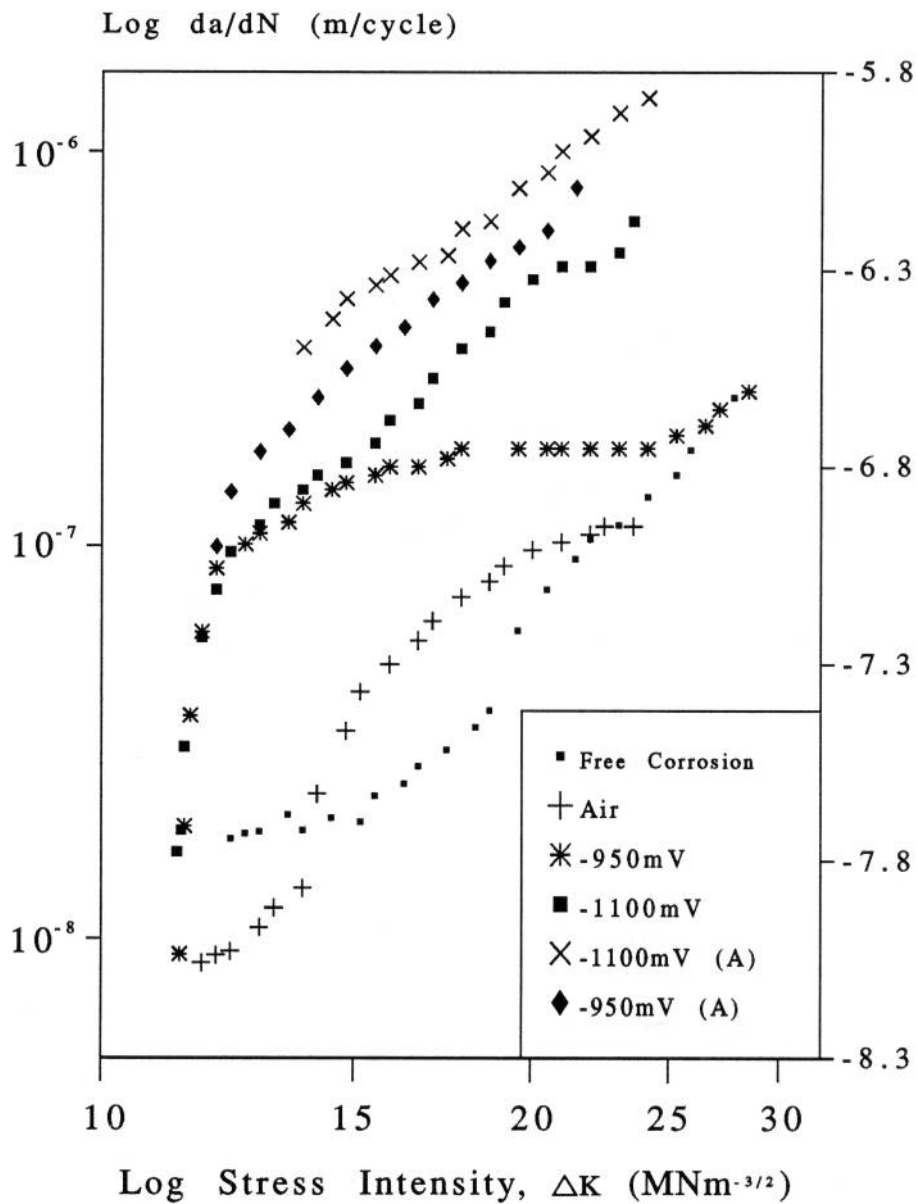


Figure 93. Corrosion Fatigue Data For SE500 in Sterile & Active (A) Seawater, 0.5Hz & R=0.6

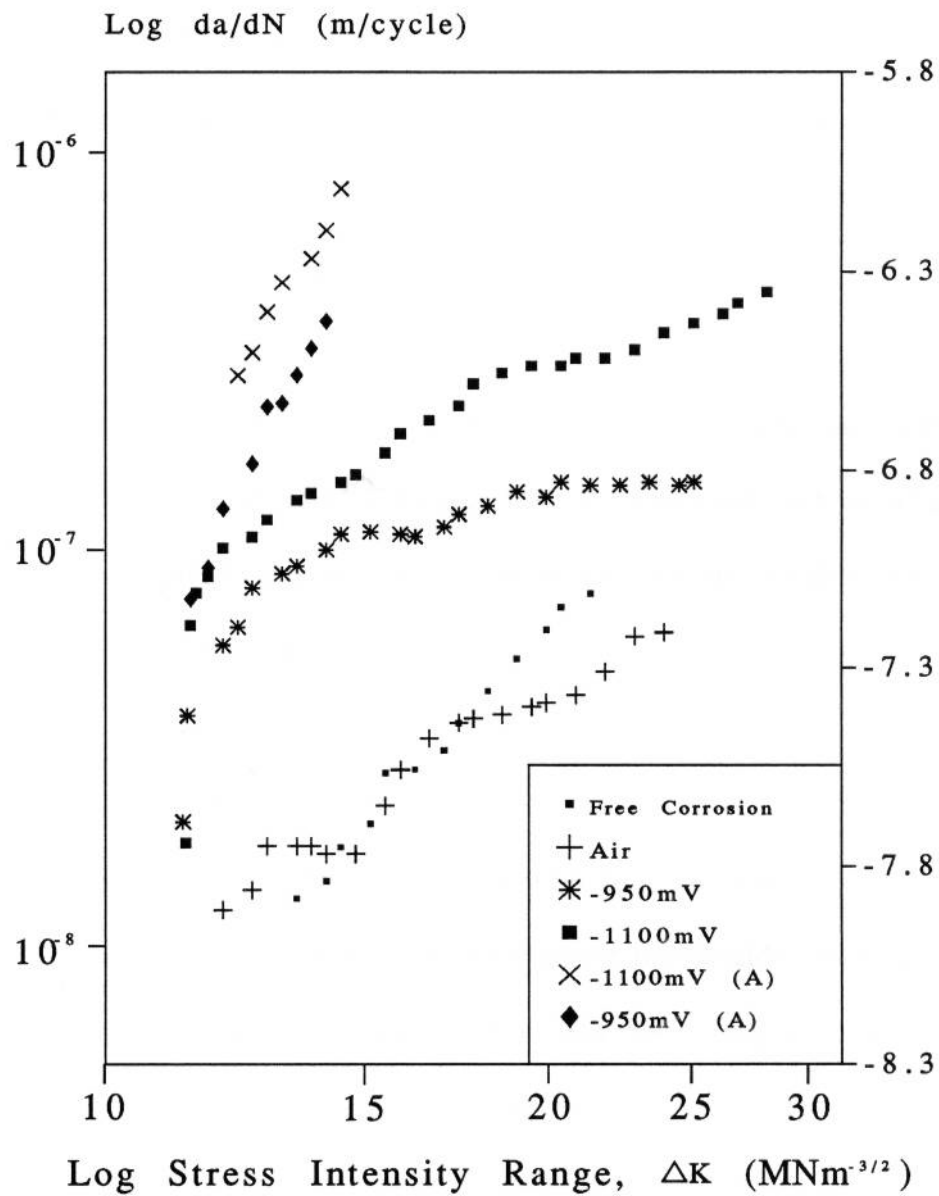


Figure 94. Corrosion Fatigue Data For DSE690 in Sterile & Active (A) Seawater, 0.5Hz & R=0.6

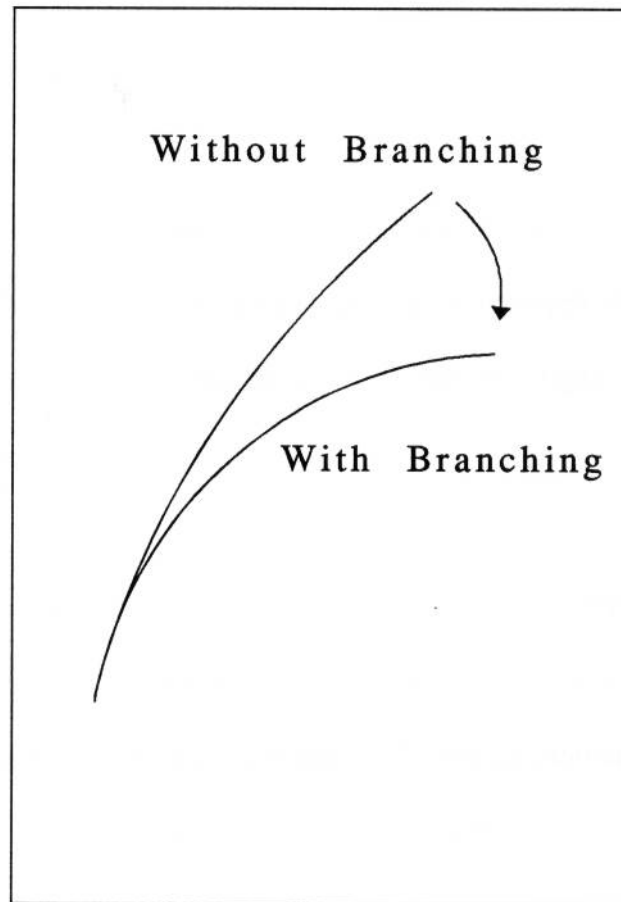
and three possible reasons for this behaviour are now discussed.

Firstly, crack branching has been discussed in detail in section 2.1.3. The occurrence of microbranching during the propagation of a fatigue crack was expected. The crack will follow preferred paths as it progresses through the microstructure and this is particularly the case in welded test pieces, in which there are significant differences in structure between the weld metal, parent plate and HAZ.

During fatigue crack growth microbranching does not develop into macrobranching. If one branch were to extend ahead of another, the more advanced crack would experience a higher stress intensity range and, as the growth rate is proportional to this ΔK value, it would continue to grow ahead.

When macrobranching does occur, in some types of stress corrosion cracking for example⁽⁵⁶⁾, it can be argued that branching lowers the stress intensity at each crack tip by a factor of $1/\sqrt{2}$ and a reduction in the crack growth rate would be expected to follow. The implication of this analysis is that any branching that takes place during the fatigue test would lower the da/dN v ΔK plot as shown schematically in Figure 95. To explain the reduced crack growth rates observed at a potential of -950mV(SCE) however, it would be necessary for the extent of crack branching to increase progressively as the applied ΔK increased during the test. While some macrobranching was detected in sections taken through the fracture surface, there did not appear to be any significant difference between specimens tested at -950 and -1100mV(SCE). Crack branching is

da/dN



ΔK

Figure 95. Schematic Diagram of Lowering of Fatigue Crack Growth Plot Due to Crack Branching

not thought to be a major factor in the observed plateau behaviour.

Secondly, another explanation for the observed shape of the da/dN v ΔK plots at -950mV(SCE) involves the formation of calcareous deposits formed on the crack sides due to the pH increase at the metal surface. Such deposits could prevent the crack from closing normally during the fatigue cycle, resulting in a lower effective stress intensity range. Calcareous deposit induced crack closure has been used to explain plateau regions obtained in fatigue tests in other work^(172,175,230,244,245). While the formation of calcareous scales would be expected to assume greater importance at the more protective potential of -1100mV(SCE), it is known that increased hydrogen absorption also takes place at this potential and this would seem to explain the higher crack growth rates observed in this case.

In addition, it is known that at the more protective potentials the deposit formed is more porous and less adherent⁽¹⁷⁰⁾ and it may be more easily flushed from the crack. It is unclear whether at the higher crack growth rates sufficient calcareous deposit could form in the short duration of the fatigue test to have an effect.

The third explanation proposes that crack growth at this potential is limited by the absorption and diffusion of hydrogen to the crack tip region. At more negative potentials or in the presence of SRB, the process is no longer diffusion limited as a larger hydrogen concentration gradient would exist at the metal surface resulting in increased mass transfer⁽²⁴⁰⁾. In addition, it has been suggested that the dominant site of

hydrogen charging can change with applied potential⁽²³⁷⁾.

In this work the fatigue specimens were allowed a two week cathodic precharge at the test potential before fatigue testing. This precharge would give a hydrogen concentration profile similar to that of the 0.4 line given in Figure 81. A steel structure which was cathodically protected would be expected to have a uniform hydrogen concentration throughout the material after a fraction of its exposure time. It would therefore be a more representative test if the fatigue tests were carried out on specimens with a uniform hydrogen profile as well.

By using the same calculation carried out for the DCB specimens (equation 76) the time required for precharging to give a uniform concentration of hydrogen throughout the fatigue specimen can be found. For a fatigue specimen of width 18mm, a time of approximately eight weeks is required (using the previous value of D). The results obtained from these tests are conservative for this reason. In addition, the fatigue specimens tested in biologically active seawater were precharged in sterile seawater at the test potential. Figure 74 demonstrates that the C_0 values in sterile seawater are much lower than those obtained with the active solution. If the fatigue specimens were precharged to give a hydrogen concentration in the specimen equal to that produced in the active solution, then increased fatigue crack growth rates would have been observed.

The above argument, as with the DCB specimens, assumes that the dominant charging site is the external surfaces. Crack tip charging would be expected to become less

important as C_o increases. It is believed that at the applied potentials used in the tests, the dominant charging site was not the crack tip and so the diffusible hydrogen concentration was not greater than C_o .

Non-biogenic sulphide has been used in fatigue tests to simulate SRB containing environments⁽²⁴⁰⁾. Mixtures of H_2S and N_2 were bubbled through seawater to produce the required levels of sulphide in the solution. The results were similar to those obtained in fatigue tests carried out in seawater containing various levels of H_2S produced by the bacterial decomposition of algal material (biogenic sulphide)⁽⁸⁶⁾. It was suggested that the environments were closely comparable, and that the use of non-biogenic sulphide was an effective way of simulating a biogenic sulphide environment. The results obtained with the double hydrogen cell indicate that this may be an incorrect conclusion as the biogenic and non-biogenic solutions were different. In fatigue tests without complete precharging the crack growth rate may be limited by factors other than the exact solution composition and source. Precharging of the specimens to give uniform hydrogen concentrations would be expected to give higher concentrations in the non-biogenic case. Subsequent testing may then show a difference in the crack growth rates in the different solutions.

5.6 EFFECTS OF BIOFILMS ON HYDROGEN ENTRY

When considering offshore structures it must be remembered that structures are designed with lifetimes of 20 to 30 years. After a short period of this time the structure would have a fully developed microfouling and macrofouling community on the submerged structure. In addition, hydrogen concentrations would be expected to have reached a uniform value throughout the submerged structure due mainly to the application of CP and promoter action in biofilms. Hydrogen can be produced by corrosion of the structure, but very low corrosion rates would be expected as the structure is cathodically protected, thus the amounts of hydrogen produced would be insignificant. Another possible source of hydrogen could be due to the action of hydrogen producing bacteria.

There are a wide range of anaerobic bacteria that produce hydrogen gas as an endproduct of the fermentation of carbohydrates⁽²⁴⁹⁾. These would be expected to be present as part of a community of bacteria and higher life forms which are part of the microfouling and macrofouling community. Such hydrogen produced by the bacteria would be available to be absorbed into the metal, provided dissociation into atomic hydrogen occurred initially.

Hydrogen would be expected to be consumed very quickly in the biofilm as microbial consumption of hydrogen is rapid in natural systems⁽²⁴⁹⁾. Indeed, it has been suggested that SRB growth is encouraged by supplying cathodic hydrogen as an energy source⁽¹⁸⁷⁾. It would be expected that SRB would have to compete for the cathodic hydrogen with

the other bacteria present in the biofilm. Their success in this competition could be dependent on the relative position of the bacteria within the biofilm. Conversely, CP has been suggested to inhibit SRB by producing a less suitable environment compared to freely corroding steel⁽¹⁸⁶⁾. The fact that sulphide deposits have been found under marine biofouling on offshore structures protected at -950mV(SCE) suggests that whilst corrosion may be reduced the activity of the bacteria is still significant⁽¹⁸⁶⁾.

Microfouling films can act as a physical barrier to the diffusion of species to and from the metal surface⁽¹⁰⁴⁾. Initially by limiting the diffusion of oxygen the biofilm may produce conditions which are anaerobic and able to support SRB activity. Once SRB activity has been established the biofilm may inhibit the SRB colony growth by limiting the supply of species. The results of this work suggest that biofilm formation had the beneficial effect of reducing hydrogen entry. Indeed, other workers⁽²⁹⁴⁾ have argued that macrofouling under certain circumstances may act as a partial barrier to hydrogen.

It is not believed that in this work the SRB were depolarising the cathode by removal of cathodic hydrogen as required by the classical mechanism⁽¹¹⁸⁾. The sulphides produced as a by-product of SRB activity were responsible for the enhanced absorption of hydrogen into the steel. If this is related back to a fully developed biofilm it can be seen that the location of the sulphides within the film is very important. To be effective in enhancing hydrogen entry the sulphides would have to be near to the metal surface.

Thicker fouling would be more likely to have the SRB activity and therefore, sulphide

production, occurring further away from the metal surface. Thus, it might be expected that thicker fouling does not produce as much hydrogen entry as thinner biofilms. The fact that thin biofilms are capable of producing sufficient sulphide at the metal surface to enhance hydrogen entry has been demonstrated⁽²⁹⁵⁾. An implication of this is that where thinner biofilms are produced, possibly in the mud zone for example, greater hydrogen entry may occur.

5.7 RECOMMENDATIONS FOR CP

Various recommendations have been made for the level of CP that can be applied to a structure in a marine environment which is effective against corrosion but avoids HE. Recently a level approaching -830mV(SCE) has been recommended. It is proposed that this level of protection will give satisfactory corrosion protection without causing severe HE⁽²⁹⁶⁾. When steels used in construction of offshore structures are of higher strength and are therefore more hydrogen sensitive, then the levels of CP must be applied correctly over the entire submerged structure. The application of CP in marine environments is made difficult by the flowing nature of the aggressive electrolyte and the variety of complex shapes being protected. Thus structures tend to have a non-uniform distribution of potential resulting in areas of under and overprotection. The use of dissimilar materials and changes in the operational conditions that structures encounter further creates problems in deciding on correct protection levels. In addition, the structures CP profile can change significantly with time, both in the short and long term⁽²⁹⁷⁾.

Once a level of CP has been decided on, it is important that the potential can be applied accurately and be adjustable when required. This is only possible if the correct CP system has been installed. The choice of system is initially between sacrificial anode or impressed current. With sacrificial anode systems the current is applied to the structure to be protected by the dissolution of attached anodes. Normally aluminium, magnesium or zinc alloys are employed for this purpose. There are a number of

advantages of this type of system but it is the disadvantage of the applied voltage being fixed that is of concern in this work. The voltage is fixed close to the free corrosion potential of the alloy (-1050mV(SCE)). The number and weight of these anodes is calculated from assumptions of cathodic current density requirements which means that the system is set at the start and is very inflexible⁽²⁹⁷⁾.

Impressed current employs DC power supplies to provide the current to a structure, in conjunction with inert anodes, normally made of lead/silver or platinised titanium. The system can be divided into different zones, each with its own power supply to dedicated anodes. There are two choices of applying the current, galvanostatic control (fixed current) or potentiostatic control (fixed potential). Both offer the ability to vary the current provided by the system. Galvanostatic controlled CP is altered by the operator based on assumptions of current density requirements. Potentiostatic control is based on reference electrodes positioned around the structure which determine the required level of current density for the zone covered by that electrode.

Therefore, from the above argument it is clear that if the level of CP being applied to a structure has to be applied accurately and be able to respond to changes, then a potentiostatic impressed current system is the only choice. Use of a zonal system would allow the protection to be tailored to the requirements of the different areas of the structure (assuming there is the correct distribution of anodes). It would also allow for changes in the recommendations for CP levels.

The results from this work can be used to give an indication of the level of CP that can be safely applied to the two welded steel employed in the research. The lower strength steel (SE500) did not crack in the sterile seawater in the DCB tests but did crack in the biologically active seawater. If the analysis of critical flaw size (section 5.3.2) is carried out using the K_{th} value ($35\text{MNm}^{-3/2}$) obtained for this steel at a potential of $-1050\text{mV}(\text{SCE})$ in the more aggressive environment then some comments can be made on the level of protection. The steel's yield strength is 500MPa , but in the hardest region of the HAZ it is calculated to be 746MPa . If this value is used to calculate the critical cracklength, a_c , at an applied stress equal to the yield stress in the parent plate then a value of 3mm is obtained. If a more realistic applied stress value of $2/3$ yield stress is used then a_c is equal to nearly 7mm . In this steel, fatigue crack initiation resulting from corrosion can be considered, and the risk reduced by recommending a potential which protects against corrosion in this aggressive environment. Therefore, a potential of $-900\text{mV}(\text{SCE})$ is recommended from this work.

As there was more data obtained for the higher strength steel (DSE690) a slightly different approach has been used to discuss safe levels of CP. Equations 79 and 80 were combined to give an equation in terms of the applied tensile stress, σ ;

$$\sigma = \sqrt{[K_I^2 \pi^2 \sigma_{ys}^2 / (5 \pi a \sigma_{ys}^2 + 0.848 K_I^2)]} \quad (89)$$

So for a cracklength (a) of 2mm the value of σ that corresponds to K_I values that equal K_{th} for each applied potential can be calculated. The values of σ calculated are critical values above which failure is predicted. The values of K_{th} were calculated by using the values of C_o measured at each potential and calculating the corresponding K_{th} value for

DSE690 from Figure 87. The results from this analysis are shown in Figure 96. At a potential of -850mV(SCE) it can be seen from Figure 96 that in the sterile seawater failure would not be predicted by a HE mechanism even at an applied stress equal to the yield stress. In contrast, in the biologically active solution the application of -850mV(SCE) would be predicted to cause a failure at applied stresses above half the yield stress. Thus, in this more aggressive environment it would be recommended to keep potentials more positive than -850mV(SCE) .

This work has demonstrated that any recommendation concerning CP levels should be based on operating environments and steel type. But it is also clear that the level of protection should be kept at a minimum whilst maintaining the benefits of CP.

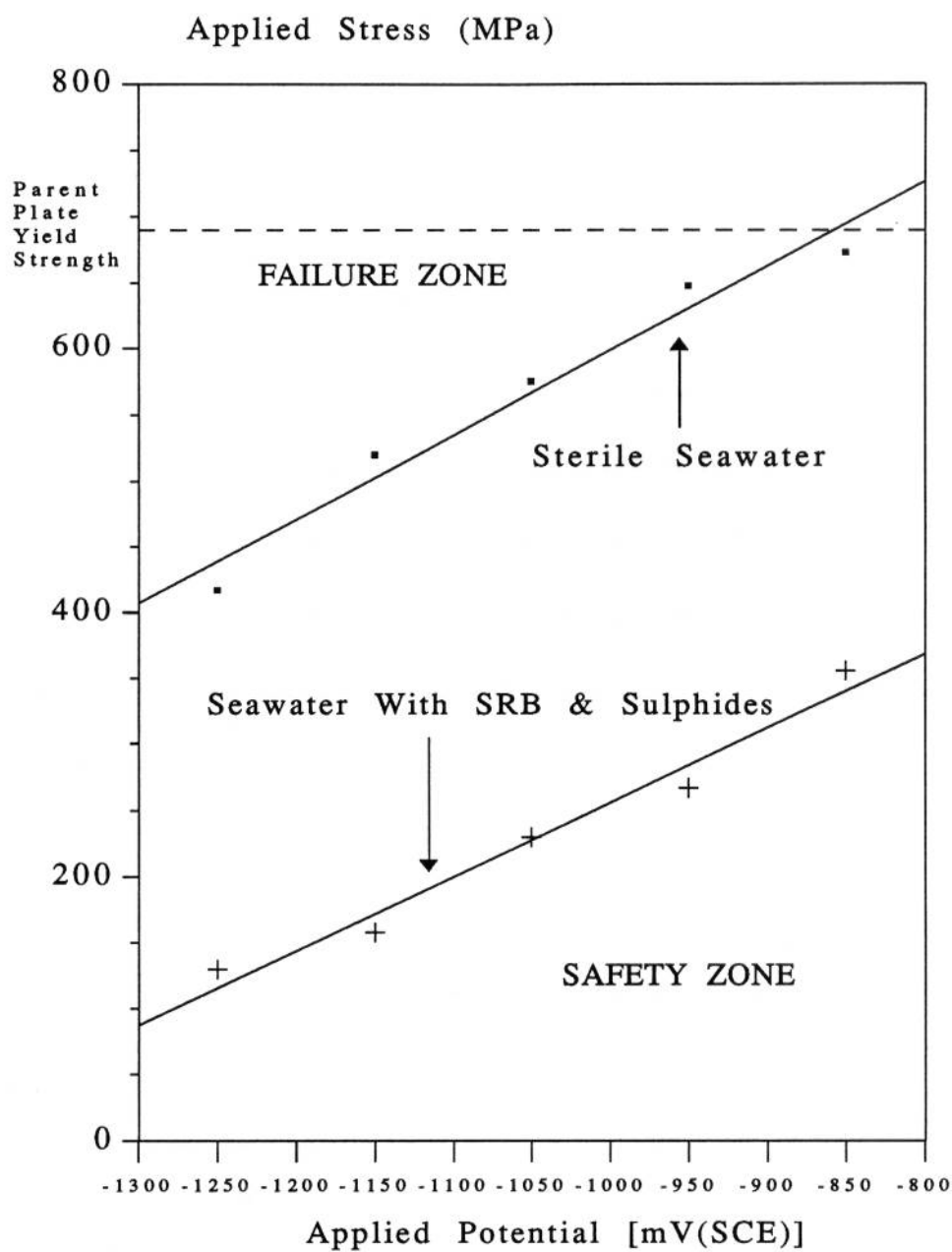


Figure 96. Failure-Safety Diagram Comparing Applied Stress and CP Potential For HE in DSE690 Containing 2mm Flaw.

6.0 CONCLUSIONS

The conclusions which are of greatest interest to industry are detailed first in conclusions one to five. The remaining conclusions (6-15) are important from a research view point.

1. The absorption of damaging atomic hydrogen by cathodically protected steel in seawater increased with more protective applied potentials. The absorption was considerably enhanced by the presence of a marine biofilm containing sulphate reducing bacteria (SRB). The work has demonstrated the quantitative effects of cathodic protection (CP) on the hydrogen embrittlement and corrosion fatigue of two welded quenched and tempered HSLA steels with yield strengths of 500 and 690MPa
2. The higher strength steel was appreciably more susceptible to hydrogen embrittlement due to the greater hardness of the microstructure in the heat affected zone (HAZ) of the welds. Hardness may control the maximum crack tip stresses and therefore influence the fracture processes.
3. Corrosion fatigue crack growth rates were dramatically increased when active SRB were present. The corrosion fatigue behaviour of the two steels were similar.
4. The results indicate that in the case of the more susceptible DSE690 steel exposed to anaerobic conditions containing high numbers of SRB it is necessary to employ a low level of protection to limit hydrogen absorption. For the lower

strength and less susceptible SE500 steel, the threshold stress intensity results obtained would permit more protective potentials to be applied to avoid the possibility of corrosion.

5. The threshold stress intensity for crack growth was shown to be inversely related to the concentration of hydrogen absorbed by the cathodically protected steel. The results enable the embrittlement of steel exposed to any particular environment to be predicted from relatively simple and indirect measurements of the hydrogen concentration.
6. There is an important synergism between the effects of CP and the bacteria. The presence of the bacteria did not introduce a new failure mechanism. The increased crack growth rates were attributable solely to the increased hydrogen content of the steel.
7. The risks associated with hydrogen absorption in the HAZ of welds can be minimised by selecting the optimum CP potentials for each type of steel.
8. The hydrogen concentration in the steel was shown to be controlled by the total sulphide (TS) concentration in the bulk environment. There appeared to be a linear relationship between the absorbed hydrogen concentration, C_o , and the bulk TS concentration.
9. The TS concentration in the bulk solution or sediment was an effective measure of microbial activity and gave a clearer indication of the risk of hydrogen embrittlement than microbial numbers.
10. Iron sulphide films promoted hydrogen entry even when the bulk TS had effectively fallen to zero.

11. The C_o values for cathodically protected steel in North Sea sediment and Mersey sediment were comparable, but lower than values obtained in other sulphide containing environments at the same potential.
12. Chemically prepared sulphides also gave enhanced hydrogen absorption, but the enhancement was greater than that produced by similar bulk concentrations of biogenic sulphide.
13. Whereas the chemically produced sulphides gave sustained levels of absorbed hydrogen, those generated biogenically decayed rapidly unless the sulphides concentration was maintained in the bulk solution. It is suggested that the organic components of the biofilm may provide some beneficial inhibition of surface reactions.
14. Low levels of bulk TS paradoxically caused higher hydrogen concentrations in the steel. It is believed that the thin iron sulphide film produced in these conditions stimulates hydrogen production near the metal surface yet gives little protection against hydrogen absorption.
15. Compared to thin sulphide films the thicker sulphide films resulted in lower C_o values as the hydrogen was formed further from the metal surface.

6.1 RECOMMENDATIONS FOR FURTHER WORK

1. The two steels used in this work have demonstrated the problems that can arise from a combination of CP and an environment containing SRB. To confirm that the results obtained in this work explain the failures that have occurred in actual jack-up rigs it would be useful to repeat the hydrogen embrittlement tests with DCB specimens made from jack-up steels. In particular, looking again at the hard region in the weld HAZ.
2. The proposed use of higher strength steels, up to 900MPa, for jack-up rigs will increase the risk of hydrogen related failures. Thus it is essential that these steels are tested before use. In this case it would be interesting to look at the plate material as well as the weld HAZ.
3. The work raised the question regarding the effects of organic material on hydrogen permeation. It is necessary to investigate the effects of the organic material in the Postgate solution and bacterial EPS on hydrogen entry to allow accurate predictions of an environments severity regarding hydrogen entry. In addition, more work is required studying the effects of sulphides films (thickness, composition etc.) on hydrogen permeation.
4. Further hydrogen permeation measurements need to be made in real sediment samples to further characterize these environments.

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APPENDIX A - Glossary of Microbiological Terms

Aerobic: A condition in which bacteria will grow in or on the surface of a simple solid medium exposed to air.

Anaerobic: A condition in which organisms will not grow in or on the surface of a simple solid medium freely exposed to air.

Autotrophic: (1)Any organism whose major or sole source of carbon is environmental CO₂, thus including microorganisms which can/must use trace amounts of organics (such as vitamins). (2)In a more strict sense it is any organism whose growth and reproduction are independent of external organic material.

Bacteria: Unicellular microscopic organisms. Bacteria reproduce by binary fission. According to shape they are either *coccoid* (round), *bacilli* (rods), *vibrio* (comma shaped) or *spirillum* (like screws).

Barophilic: Marine forms able to grow at relatively high pressures.

Coccoid: Refers to an organism whose length is not more than twice its width or whose longest diameter is not more than twice its shortest diameter. See bacteria.

Cytoplasm: That part of the protoplasm of a cell excluding the nucleus.

Faculative: Bacteria that have the optional ability to adopt an alternative lifestyle or mode of nutrition.

Fission, Binary: A form of asexual reproduction in which a single nuclear division is followed by a division of the cytoplasm in order to form two daughter cells of equal size. This method of reproduction is used by bacteria and usually protozoa.

Halophilic: Organisms that grow better in media of high sodium chloride concentration than in media with low salt concentration.

Heterotrophic: Organisms that depend upon organic substances for their nutritional needs.

Hydrogenase: An enzyme (organic substance) that catalyses the oxidation of hydrogen.

Mesophilic: Organisms whose best growth is achieved at moderate temperatures of about 25 to 45°C.

Methanobacteriaceae: All species of the methane producing bacteria are strict anaerobes. Some strains believed to be facultative autotrophs.

Nucleus: The dense inner mass of protoplasm of a cell containing the chromosomes.

Obligate: A term used to describe a metabolism restricted to a similar type, as in the expression obligate anaerobe.

Periplasm: The space between the plasma membrane and outer membrane of *gram negative* bacteria. It contains proteins secreted by the cell and a rigid peptide-oligosaccharide complex, the *peptidoglycan*.

Protoplasm: The viscid granular material, often referred to as the physical basis for life, common to all living cells.

Psychrophilic: Organisms that grow best at temperatures below 20°C.

Sessile: Fixed or attached to the substrate by its base.

Substrate: The specific substance on which an enzyme acts.

Thermophilic: Organisms that grow best at temperatures above 45°C.

APPENDIX B - Approximate Equivalence of VPN, R_c & Tensile Strength

VICKERS HARDNESS NUMBER	ROCKWELL NUMBER C SCALE 150Kg Load Brale Indenter	TENSILE STRENGTH (MPa)
508	49.6	1737
495	48.8	1682
491	48.5	1669
474	47.2	1593
472	47.1	1579
455	45.7	1517
440	44.5	1462
425	43.1	1393
410	41.8	1331
396	40.4	1269
383	39.1	1220
372	37.9	1186
360	36.6	1131
350	35.5	1096
339	34.3	1062
328	33.1	1027
319	32.1	1007
309	30.9	979
301	29.9	952
292	28.8	924
284	27.6	903
276	26.6	876
269	25.4	848
261	24.2	827
253	22.8	800
247	21.7	786
241	20.5	765

APPENDIX C - Anaerobic Jars

Modern anaerobic jars use a room temperature catalyst which consists of pellets of alumina coated with finely divided palladium. This catalyst removes oxygen in the presence of excess hydrogen producing water. This moisture reversibly inactivates the catalyst, therefore after use the catalyst requires to be dried in an oven. Failure of the catalyst can occur between consecutive uses due to moisture or poisoning and has to be replaced. Catalyst activity is monitored during its operation by the success or failure of producing anaerobic conditions within the sealed jar. Anaerobic conditions are indicated by resazurin soaked paper or solution. This can be purchased ready made or produced as below.

Table 27 Preparation of Resazurin Solution for

Use in Anaerobic Chambers⁽²⁵⁷⁾

<i>Tris(hydroxymethyl)aminoethane</i>	<i>4g</i>
<i>Glucose</i>	<i>0.2g</i>
<i>0.1%(w/v) Resazurin</i>	<i>1ml</i>

The above were dissolved in 19ml of distilled water and boiled (in a water bath) in a universal bottle until the solution was decolorized. After removal from the water bath it was transferred to the anaerobic jar. The clear solution turns pink when the oxygen concentration is about 300ppm. The intensity of the coloration is roughly proportional to oxygen concentration. Resazurin is also a pH indicator so when the solution begins to turn yellow (due to CO₂) it should be replaced.

The catalyst is stored in a gauze container when in use in the jar. This acts as a heat sink and protects against explosion which otherwise could occur during exothermic catalysis. Care must be taken to avoid allowing damaged catalyst pellets or powder from entering the body of the jar as this could again cause an explosion.

The hydrogen may be provided either from an external source, or as in our case, may be generated within the jar. Internal production of hydrogen was initiated by adding water to sodium borohydride in the presence of a cobalt catalyst. Another reaction produces carbon dioxide simultaneously with the hydrogen. Carbon dioxide is essential or stimulatory to the growth of many bacteria and is usually at a concentration of 5-10%.