THE BEHAVIOUR OF ZINC ALLOY ANODES AT
ABOVE AMBIENT TEMPERATURE IN SEA WATER.

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## Abstract

During the present programme of oil and gas exporation and production
in the North Sea and other continental shelf areas, corrosive circumstances
have been encountered that have not been experienced previously by the oil
industry.  For example, apart from fiercer wave action, the platforms are sited
in deeper, often fully aerated, waters and the flow lines handle hotter crudes.
There is little evidence that the depth of the water *per se* creates a corrosion
problem; by contrast, the hotter crude introduces problems associated with heat
transfer and exacerbated by mass transfer.  One specific instance of the latter
has been the premature failure of a zinc alloy bracelet sacrificial anode
installed on a riser carrying hot crude (ca $90^{\circ}C$) and immersed in sea bed mud.
The failure took the form of intense intergranular dissolution, loss of grain
boundary cohesion with catastrophic loss of anode current capacity.

This paper presents the results of a laboratory investigation into this
problem with a view to identifying its causes, highlighting other possible
conditions where this form of failure might occur and suggesting methods whereby
it might be avoided.

## Introduction

The application of cathodic protection to control the corrosion of marine based structures is now well established. Cathodic protection has even been employed in the North Sea oil and gas fields despite the fierce operating conditions. The latter include the ambient temperature and wave action, the depth of water commonly experienced and the fact that hot crudes (90$^{o}$C at the well head) are handled. Until comparatively recently, the cathodic protection schemes installed in the North Sea have been based almost exclusively on the use of sacrificial anodes rather than the impressed current technique. This preference for sacrificial anodes was, it appears, based upon the accepted reliability of zinc -, and latterly aluminium -, based anodes in seawater and concern about the less robust and more vulnerable design of the impressed current systems. Since operating evidence gathered over more than a decade has proved the efficacy of cathodic protection in controlling corrosion in the North Sea, it was all the more surprising when the failure of a zinc alloy anode was reported in 1977[1]. The report referred specifically to the premature failure of a bracelet-type zinc alloy anode which was attached directly to, and therefore was transferring heat from, a hot riser operating at well above ambient temperature. The anode in question had suffered intense intergranular dissolution leading to a loss of grain boundary cohesion, and the anticipation was that a major reduction in current efficiency would occur. The matter was of concern for two reasons. Firstly, there was reason to believe that in other fields similar anodes had been, or were likely to be, installed under similar circumstances. Secondly, within the gas fields, conditions could be envisaged where at some stage in the operating lifetime an anode would be exposed to seawater at temperatures above ambient.

This paper reports a successful attempt to simulate the intergranular dissolution phenomenon on a zinc alloy anode and describes experiments designed to

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show the mechanism of the failure. Deriving from this, a method of overcoming the problem is suggested. The experimental programme was based on a limited electrochemical study, and the use of electronoptical techniques and simple metallography.

At the time the problem was reported a school of thought developed that it could be explained in terms of the well known potential reversal that occurs between steel and zinc in certain environments as the temperature is raised. Briefly at room temperature (ca 25°C) and in most corrosive environments, steel has a more positive electrode potential than zinc. Thus in a galvanic cell between the two, zinc becomes a sacrificial anode and protects the steel. However, Schikorr[2] reported that in Berlin tap water above 60°C the potential of zinc rose, ultimately becoming more noble than steel and, at that stage, failing to protect it i.e. a potential reversal had occurred. To relate this phenomenon to the failure of the zinc anode in the North Sea is a mistake for a number of reasons. In the first place, a polarity reversal if it occurred, would lead to cathodic protection of the zinc and not, in the absence of some other controlling factor, to a marked change in dissolution morphology. Secondly, Ashworth et al[3] have shown that polarity reversal is due to the build up of a dense, continuous corrosion product on the zinc above 60°C. Although this build up occurs in solutions containing significant amounts of chloride ion, local breakdown of the film prevents the potential reversal from occurring.

In the present paper it is suggested that the intergranular attack may be associated with the developing presence of an aluminium rich phase in the grain boundaries of the zinc anode when operating at elevated temperatures.

### Experimental.

Three materials were examined in this work. The majority of the experiments were made with a commercial 0.27% Al, 0.03% Cd, zinc alloy (Fe 0.0019%, Cu 0.001%,

Pb <0.003%, Si 0.01%); this analysis falls within the US Military Specification
MIL-18001H, and the material is referred to below as the zinc alloy.   Limited
experiments were made using pure zinc[3] and an aluminium-zinc alloy (1.01% Zn,
0.05% Si, 0.004% Pb, <0.01% Fe).  These two materials represent compositions
corresponding to the terminal solid solutions in the zinc-aluminium system and are
referred to as pure zinc and the aluminium alloy below.

Electrodes of $1cm^3$ were machined from each of these materials.  After
fixing electrical connections to one face, the electrodes were mounted in an
epoxy  resin.  A second face of the electrode thus formed was revealed by grinding,
and prepared by polishing to a $1\mu m$ finish using diamond paste.  Before use the
electrodes were rinsed in distilled water, then methanol and air dried.

All electrochemical experiments were made in a closed reaction vessel
containing $0.8\ell$ of synthetic sea water[4] and maintained at either 25 or
70 $\pm 1^o$C using a thermostatically controlled water bath.  Since precise
experimental conditions are given elsewhere[5] only a brief description is given
here.  The free corrosion potential of the zinc alloy was monitored in air
saturated and deaerated solutions.  The same materials was anodically polarized
in deaerated solution both by galvanic coupling and impressed current methods.
In the former case the galvanic cells were formed by coupling the zinc alloy ($1cm^2$)
to mild steel ($10cm^2$) through a $400\Omega$ measuring resistor; in the impressed current
experiments a current density of $10A/m^2$ was used.   Finally, all three materials
were anodically polarized using a potentiodynamic technique (sweep rate 0.5 mV/s)
from a potential slightly more negative than the corrosion potential to a
potential where an anodic current in excess of $100A/m^2$ was delivered by the
potentiostat; typically this was in the range  -0.5 to -0.75V (SHE).

### Results and Discussion.

The corrosion potential of the zinc alloy in synthetic sea water was monitored

over a period of 15 days at $70^\circ$C. In the first few hours of exposure there was a relatively rapid rise in potential and thereafter relatively steady values (-0.79V and -0.77V in deaerated and air saturated solutions respectively) were adopted. In either solution, although the samples suffered general corrosion revealing a crystallographically etched appearance, some minor pitting was apparent. However, there was no evidence of the reported intergranular attack.

By contrast, the zinc alloy specimen subjected to anodic polarization by galvanic coupling at $70^\circ$C did suffer intergranular dissolution. At the conclusion of the 14 day experiment the specimen was covered with corrosion product which was nodular in places. Removal of the nodules revealed shallow pits, and within each pit grain boundary dissolution was clearly visible (Plate 1). The importance of anodic polarization in promoting the effect was confirmed in the impressed current experiments where, once again, the specimen exposed at $70^\circ$C suffered intergranular attack (Plate 2). The extent of preferential grain boundary dissolution was sufficiently severe in these latter experiments that in a 90 - day test it was found that whole grains were undermined and some completely removed mechanically. However, in an otherwise identical experiment conducted at $25^\circ$C the dissolution pattern was not grain boundary directed but corresponded to that observed in the unpolarized experiment at $70^\circ$C (Plate 3). It appears that temperature and anodic polarization are both important parameters in controlling the morphology of dissolution.

An electron probe microanalysis of a metallographically prepared sample from the zinc alloy anode that had failed in service in the North Sea showed very considerable aluminium enrichment in the grain boundary region. A similar analysis of an as-received sample of the zinc alloy used in this work failed to reveal any segregation of the alloying additions. Nevertheless, after heating the specimen at $100^\circ$C for four days a line scan microanalysis did reveal aluminium

enrichment in the grain boundaries and showed concentration levels correponding

to those of the failed anode. These electron probe microanalysis results suggest

solid state diffusion of aluminium in zinc at temperatures in the region 70-100°C.

This possibility was tested by two subsidiary experiments. Figure 1 shows changes

in hardness ($H_v$) of the as-received zinc alloy on ageing at 70 and 95°C for various

time periods up to 30 days. The data quoted represent the mean and standard

deviation of twenty determinations per specimen. The results provide curves

typical of age hardenable aluminium alloys [6]. These have been explained by

postulating movement of the solute atoms in super saturated solid solution to form

second phase particles with subsequent interaction between these particles and

mobile dislocations and a similar mechanism may be envisaged in the zinc alloy.

Such behaviour would not be entirely unexpected in the 0.27% aluminium – zinc alloy,

for on examining the equilibrium phase diagram for Al-Zn, the solid solubility of

aluminium at 382°C is in excess of 1%, whereas at room temperature it is only

0.05% [7]. Further, during the process of chill casting, the technique that would

have been adopted in fabricating the zinc alloy, it has been shown [8] that the

equilibrium solubility at room temperature may be exceeded and values of 0.30%

are not uncommon. The electron probe microanalysis results on the as-received

alloy are in accordance with these observations and are indicative of a super-

saturated solid solution. Further, during heat treatment at 70 or 95°C, or

operation at 70°C, the supersaturated solid solution of aluminium in zinc would

be expected to decompose to give precipitation of an aluminium rich phase, the

possibility of grain boundary enrichment by aluminium and the observed hardening

effects.

The second experiment has been reported elsewhere [5]. Briefly, the zinc

alloy was heat treated and quenched to ensure that all the aluminium was in solid

solution. The treated sample was then fractured in liquid nitrogen and the

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fracture surface examined in an Auger electron spectrometer. Initially, using a

0.5mm diameter, 4 keV beam, a small aluminium peak was observed. However, on

heating the specimen in the spectrometer the height of the aluminium peak increased

by a factor of six. Thus it is shown that at above ambient temperatures aluminium

diffuses to a free surface, and therefore presumably to a grain boundary, in the

zinc alloy.

It has been shown above that the susceptibility of the zinc alloy to inter-

granular dissolution depends on both temperature and anodic polarization. It

might therefore be assumed that the temperature sensitivity is due to purely

metallurgical factors. That is, once grain boundary enrichment has occurred

as the result of decomposition of the supersaturated solid solution, the driving

force for galvanic corrosion leading to preferential dissolution of the aluminium-

rich phase exists. This, of course, presumes that the aluminium-rich phase is

anodic to the aluminium-depleted bulk grain and follows a similar mechanism to the

intergranular dissolution of die cast materials proposed by Devillers and

Niessen [9]. To test this general hypothesis two samples of the alloy were

heated for several days, one at $70^{\circ}$C, the other at $100^{\circ}$C. The samples were

polarized subsequently for ten days in artificial seawater at $25^{\circ}$C at a constant

impressed current density of $10A/m^2$. It might be anticipated that grain boundary

enrichment would occur during the heat treatment and that, for the first time,

intergranular dissolution at $25^{\circ}$C would be observed. In practice, the dissolution

morphology of the zinc surface (Plate 4) was similar to that of the unaged sample

with the dissolution proceeding along specific crystallographic planes. Thus the

mere presence of the aluminium in the grain boundaries does not necessarily lead

to intergranular attack.

These results suggest that the increased temperature exerts both a

metallurgical and an electrochemical effect. As the presence of the grain boundary

aluminium - rich phase does not cause intergranular attack at $25^{\circ}$C its dissolution
rate, both polarised and unpolarised, must be comparable with that of the zinc -
rich matrix.  For intergranular attack to occur at $70^{\circ}$C under anodic polarization,
however, its anodic dissolution rate must become significantly greater than that
of the matrix.  That is, the temperature coefficient of anodic dissolution of
the aluminium - rich phase is greater than that of the zinc - rich phase.

To test this hypothesis the dissolution characertistics of two materials
chosen to represent these two phases; namely an aluminium - 1% zinc alloy and pure
zinc were examined by potentiodynamic anodic polarization at both $25^{\circ}$C and $70^{\circ}$C.
Before discussing the results however, it is useful to consider the reported
behaviour [10] of the zinc alloy, for which a typical anodic polarization
curve determined at $70^{\circ}$C, is shown in figure 2.  The figure also shows two
cathodic polarization curves for mild steel with their abscissae adjusted to
represent anode to cathode area ratios of 1/100 and 1/10.  The intersection of the
anodic curve with each cathodic curve (at potentials (a) and (b)) indicates the
coupled potential of each system and hence the working potential range, (b)-(a),
of the zinc alloy in most protected structures.

It must be understood that this superimposition of anodic and cathodic
potentiodynamic polarization curves is an inexact representation of the service
condition of the anode.  It takes no account of the ohmic potential drop within the
cell resulting from the resistance of the environment, nor does it reflect the
natural negative drift of the potential of the galvanic couple as a function of
time in the early stage of coupling.  More representative data are obtained from
constant impressed current or, preferably, galvanic coupling tests.  Nevertheless,
the instantaneous value of the anode working potential range inferred from
figure 2 is useful in that it may be compared quite properly with the same parameter
for the pure zinc and the aluminium - 1% zinc alloy obtained from identical

experiments.  Further, any general effect of increased temperature on the anodic

behaviour of either material would be apparent from this test.

The potentiodynamic anodic polarization curves for pure zinc and the

aluminium - 1% zinc alloy at 25°C and 70°C are shown in figures 3 and 4.  It is

seen that, on anodically polarizing pure zinc from its rest potential, at both

temperatures, there is an ill-defined passive region (-0.9 to -0.8V) followed

by rapid dissolution above -0.8V.  In this case the effect of increasing the

temperature is to cause a slight (50-100mV) positive shift of the potential range

over which the zinc is difficult to polarize (i.e. it includes the natural working

range of an anode).  The passive region of the aluminium- 1% zinc alloy is much

more extensive but in this case the effect of increasing the temperature is to

shift the working range in the active (negative) direction by approximately 200mV.Thus

the effect of increased temperature is to stimulate the dissolution of the

aluminium alloy and to inhibit that of the pure zinc.

If these anodic polarization curves are examined within the working potential

range of the zinc alloy, as defined by the lines (a) and (b), it is observed that

the effect of increased temperature is particularly significant.  At 25°C pure

zinc dissolves much faster than the aluminium alloy which remains passive.

However, at 70°C the aluminium alloy dissolution reaction is so depolarised that

it is now faster than that of the pure zinc.   Thus intergranular dissolution is

to be expected in a sensitized zinc alloy under anodic polarization at 70°C, but

not at 25°C.  This is clearly consistent with the above hypothesis.

### Conclusions.

1.  On heating a Zn-0.27 Al-0.03Cd alloy to 70°C an aluminium - rich phase forms

    in the grain boundaries.

2.  On anodic polarization in artificial seawater at 70°C the alloy undergoes

    intergranular dissolution by selective removal of the more readily dissolved

aluminium rich phase ; an unpolarized specimen is not subject to this attack.

3.   At $25^{\circ}$C neither precipitation, nor intergranular dissolution on anodic

polarization, occur.

4.   In an anode where the aluminium-rich phase  is already present, intergranular

dissolution does not occur at $25^{\circ}$C because in contrast to the behaviour at

$70^{\circ}$C the dissolution rate of the zinc matrix corresponds to that of the

aluminium - rich phase at this temperature.

5.   The temperature dependence of anodic dissolution of the aluminium-rich

phase is greater than that of the zinc - rich phase.

6.   It is probable that any Zn-Al alloy in which the aluminium content is above

the limit of equilibrium solid solubility of aluminium in zinc at $25^{\circ}$C will

be subject to intergranular dissolution in seawater at higher temperatures.

7.   Zn-Al sacrificial anodes must not, therefore, be operated in situations

where precipitation of an aluminium - rich phase is anticipated; in the

current case a threshold of approximately $50^{\circ}$C seems probable.

8.   It would appear that if the aluminium content of the alloy can be reduced

to below its equilibrium solid solubility level, zinc alloy anodes would be

immune to intergranular dissolution and would not suffer a major adverse

effect on performance providing the iron level was kept in strict control.

### References.

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### List of Plates.

1.    Zinc alloy after galvanic coupling for 14 days at $70^{\circ}$C (x 35).

2.    Zinc alloy after anodic polarization at 10 A/m$^2$ for 12 days at $70^{\circ}$C (x 100).

3.    Zinc alloy after anodic polarization at 10 A/m$^2$ for 10 days at $25^{\circ}$C.  Sample

      as-received (x 35).

4.    Zinc alloy after anodic polarization at 10 A/m$^2$ for 10 days at $25^{\circ}$C.  Sample

      pre-aged at $100^{\circ}$C for four days (x 35).

Plate 1.



Plate 2.

HARDNESS VS. TIME
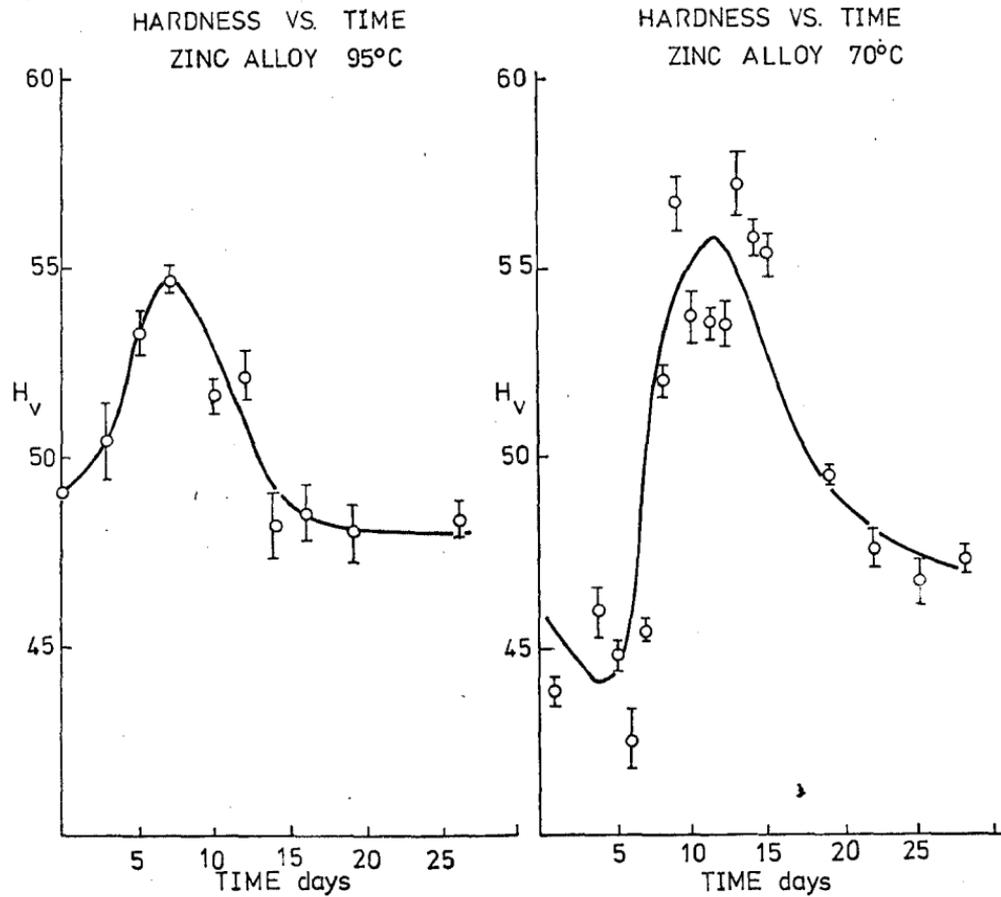ZINC ALLOY 95°C

HARDNESS VS. TIME
ZINC ALLOY 70°C

Figure 1.

255.

Figure 2.

Superimposition of polarization data: the predicted behaviour
of mild steel / zinc alloy galvanic couples in deaerated sea
water at 70°C.

steel / zinc alloy area ratios :-

(a)  100 / 1  ,  (b)  10 / 1



$E_{SHE}$
(V)

- 0·6

$E_{couple}$ (a)

$E_{couple}$ (b)

- 0·8

(b)          (a)

-1·0

O    Anodic kinetics of the zinc alloy
●    Cathodic kinetics on mild steel  (b)
△    Cathodic kinetics on mild steel  (a)

Current  A·m⁻²

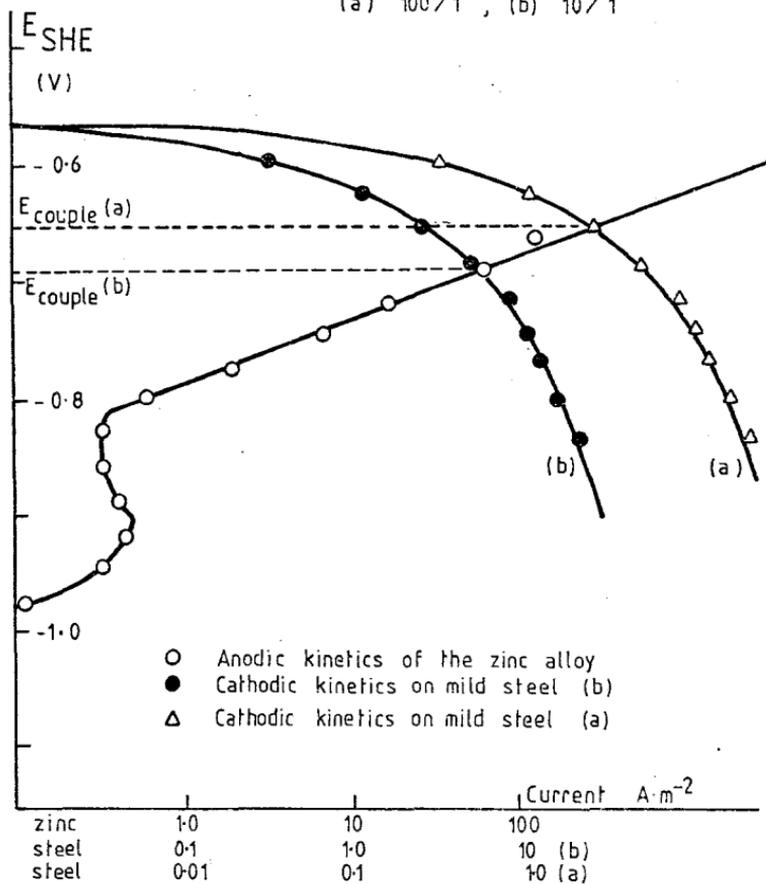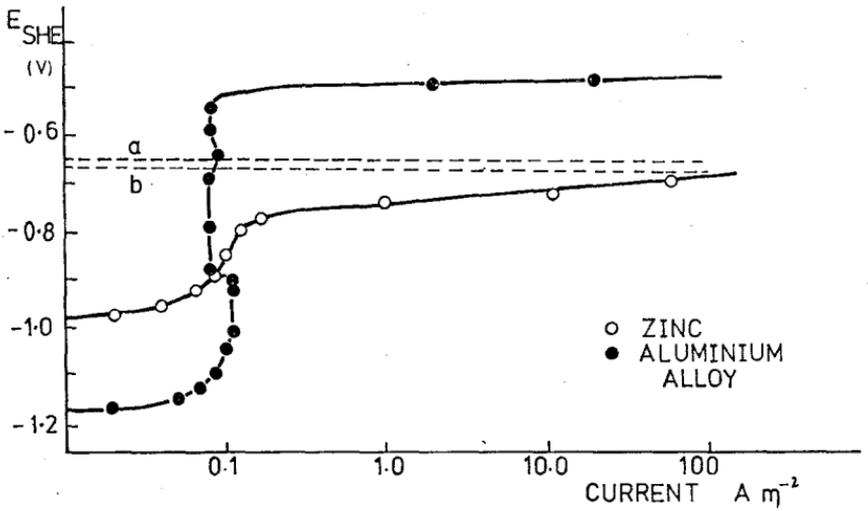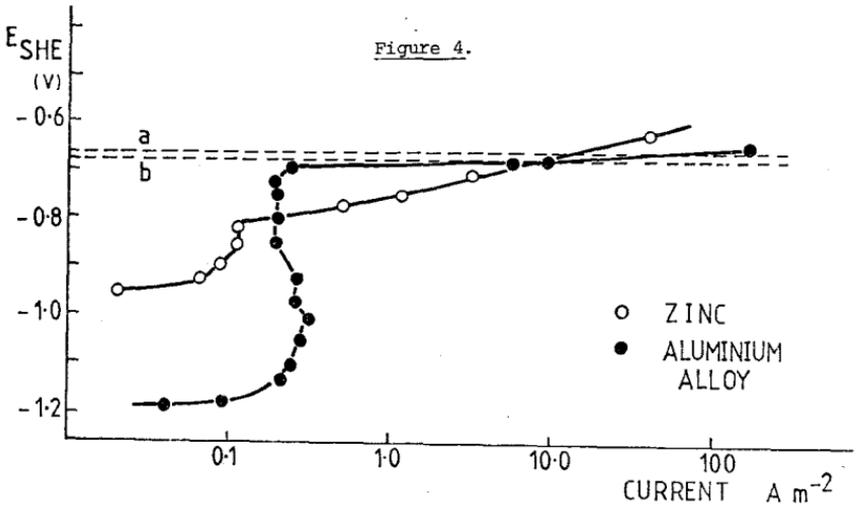| zinc | 1·0 | 10 | 100 | |
| steel | 0·1 | 1·0 | 10 | (b) |
| steel | 0·01 | 0·1 | 1·0 | (a) |

Figure 3.

ANODIC KINETICS ZINC and ALUMINIUM ALLOY 25°C



Figure 4.

ANODIC KINETICS ZINC and ALUMINIUM ALLOY 70°C