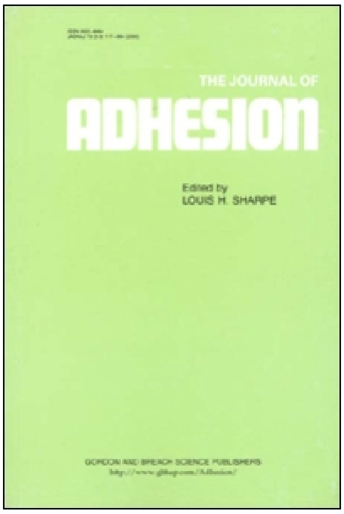

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# Disbondment Mechanisms for a Heat Shrink Polyethylene Coating on a Cathodically Protected Hot Pipeline

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# Disbondment Mechanisms for a Heat Shrink Polyethylene Coating on a Cathodically Protected Hot Pipeline

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Interfacial adhesive failure of a pipeline coating was found to be related to the operating temperature of the pipeline, the presence of moisture at the coating/steel interface and cathodic polarisation of the steel. The application of cathodic protection was found to be more detrimental to a pipeline coating than was the immersion of the coating specimens in alkaline environments without polarisation. It is suggested that in the system examined cathodic disbondment is initiated at a coating holiday by the electrochemical reduction of $Fe_3O_4$ in the interfacial oxide film and that propagation of the disbondment is associated with electrocapillary action which reduces the surface tension between the steel and the crevice solution. This process increases the thermodynamic disbonding force between the adhesive and the steel in the aqueous environment.

KEY WORDS Coating adhesion; interfacial failure; electrochemical reduction; steel pipeline; coating failure; electrocapillary effects.

## 1 INTRODUCTION

The environmental stability of adhesive tape systems presents specific problems which are not found in systems based upon rigid substrates. Even in the simplest tape system there are two interfaces, the adhesive/substrate interface and the adhesive/backing interface and the environment may at different times affect either of these interfaces. Tape systems are, in general, based upon pressure sensitive adhesives which have a lower modulus and strength than the backing or substrate which they join. As a result the locus of failure may be unequivocally cohesive in the adhesive or associated with one or both interfaces. Changes in the locus of failure will almost always be associated with environmental effects.

Whereas environmental breakdown of joint systems based upon rigid substrates is often associated with the diffusion of the aggressive species through the adhesive, in tape systems based upon a polymeric backing, diffusion through the polymeric backing may provide an easier route to the locus of failure.

Although tape systems have traditionally found greater usage in comparatively low stress applications such as the packaging, stationery or surgical fields, the oil and gas industry has long used tape wrapping as a means of providing corrosion protection to buried pipelines. In such applications, heavy duty backings are applied and the stresses involved both during pipe installation and subsequently as a result of soil stresses can be considerable. The environment in which such pipes may be installed is often very aggressive, both with regard to the breakdown of the adhesive joint formed between backing and steel substrate and also with regard to corrosive attack on the steel. To reduce the corrosive attack on the steel, cathodic protection is often applied to such a structure. Cathodic protection consists of applying a potential to the structure so that the reaction

$$\mathrm{Fe} \longrightarrow \mathrm{Fe}^{++} + 2\mathrm{e}^-$$

is suppressed. This potential is applied by passing an electric current through the ground to any coating defects ("holidays" in pipeline jargon) so that any exposed steel is made a cathode and either one or both of the following reactions occur.

$$\tfrac{1}{2}\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} + 2\mathrm{e}^- \longrightarrow 2\mathrm{OH}^-$$
$$2\mathrm{H}_2\mathrm{O} + 2\mathrm{e}^- \longrightarrow \mathrm{H}_2 + 2\mathrm{OH}^-$$

As a result of the liberation of hydroxyl ions by these reactions the local pH rises and the metal may be moved to a regime where its surface is covered by a protective (passive) oxide film. The application of cathodic protection to a tape wrapped system often gives rise to disbonding of the tape from the substrate and this paper is concerned with an examination of the mechanisms of cathodic disbonding of a crosslinked polyethylene tape from the steel substrate.

Although disbondment has often been ascribed to the alkalinity resulting from cathodic protection, the particular mechanism which may operate in a given system is often uncertain. Hammond *et al.*[1] suggested that hydroxyl ions take an active part either in disrupting the polymeric substrate or displacing it from the surface. Ritter[2] used ellipsometric techniques to show that dissolution of the oxide film in the high pH environment was the major mode of cathodic disbondment. Koehler[3] suggested that the prime mechanism was a displacement of the adhesive from the substrate by water facilitated by high pH conditions. Castle and Watts[4] suggested that hydrolysis of the interfacial bonds by the high pH was the predominant cause of disbonding when cathodic protection was applied to a polybutadiene coating on mild steel, but in a later study of epoxy coatings[5] on the same substrate showed that reduction of the interfacial oxide to metallic iron was the prime cause of the disbondment. Leidheiser proposed that the major mechanism for the delamination process is either reduction of the oxide film on the surface of the steel by cathodic polarisation[6] or the formation of the soluble ionic species, $\mathrm{HFeO}_2^-$, at high pH values.[7,8] However, as he pointed out, no delamination takes place when a coated metal is immersed in a strong NaOH solution and this may suggest that disbondment is primarily related to the cathodic polarisation.

Gledhill and Kinloch,[9] in related studies, examined butt joints formed with epoxy resin on mild steel substrates. These were immersed in water at different temperatures and for various exposure times prior to testing. They found that the joint strength decreased as the time of exposure to water increased and that the rate of decrease was greater at higher temperatures. They observed a mixed mode of failure in that, in general, the centre of the joint failed cohesively whereas the edges of the joint failed interfacially. The proportion of interfacial failure increased at the higher temperatures. These authors also demonstrated that the corrosion process which resulted in the formation of magnetite succeeded the disbonding process. Gledhill and Kinloch explained the significant reduction in adhesive bond strength at increased temperature and exposure time on the basis of the displacement of the adhesive from the metal oxide surface by water. Their X-ray diffraction investigations suggested that ferric oxide, $Fe_2O_3$, was originally present on the mild steel surfaces and that magnetitie, $Fe_3O_4$, was formed some time after the debonding had taken place. The work of adhesion for the epoxy/ferric oxide interface was calculated to be $291\,mJ/m^2$ in a dry environment but in the presence of an adsorbed layer of water at the interface, was $-255\,mJ/m^2$. These authors regarded the change from a positive value for the work of adhesion to a negative value as the driving force for the displacement of the adhesive from the metal oxide surface by water. Cherry and Thomson[10,11] examined the fracture mechanics of environmentally assisted joint breakdown and determined the relationship between the fracture surface energy for interfacial failure and the rate at which the failure front moved through the interface. They found that a minimum strain energy release rate of about $5\,J/m^2$ was necessary before the crack front could move at a discernable rate. They, therefore, suggested that a thermodynamic driving force of about 200 to $300\,mJ/m^2$ was, by itself, too small to bring about debonding within experimentally accessible times. They did, however, suggest that the application of mechanical forces (shrinkage stresses in the case of Cherry and Thomson's work) combined with the thermodynamic instability calculated by Gledhill and Kinloch brought about the disbonding. Although shrinkage stresses may play a major role in facilitating the rupture of joint systems based upon a rigid epoxy adhesive, it seems unlikely that in the rubbery systems with which this paper is concerned, that such stresses would be maintained in adhesives with a considerable capacity for creep. Such systems should, therefore, be more environmentally stable or if they are not, an alternative additional mechanism for disbondment must be sought.

In another study, a blister test was used by Stevenson and Andrews[12] to study the adhesive fracture surface energies of epoxy/titanium bonds in alkaline and acidic environments at different temperatures. They observed an increase in the maximum fracture surface energy as the pH of the solution increased from 7.8 to 13.0. This result, because it suggests that $H^+$ ions are more active than $OH^-$ ions in disrupting interfacial epoxy/titanium bonds, conflicts with the work that suggested that $OH^-$ ions take an active part in cathodic disbondment.

The work to be described in this programme formed part of an investigation of the corrosion which took place beneath disbonded coating on a hot, underground oil pipeline.[13] The primary objective of the work reported in this paper was a determination of the conditions which give rise to interfacial failure between either: (1) the backing and the adhesive; or (2) the adhesive and the pipeline steel.

## 2 EXPERIMENTAL

Experiments were carried out on a commercially applied coating which consisted of a 0.4 mm thick radiation crosslinked polythylene backing and a 0.8 mm thick semi-crystalline polyolefin adhesive. The fracture surface energy of the joint formed between the coating and the steel was determined under immersed conditions at a number of different values for the pH and applied potentials, using the 90° peel test rig shown in Figure 1. The test rig was mounted on the

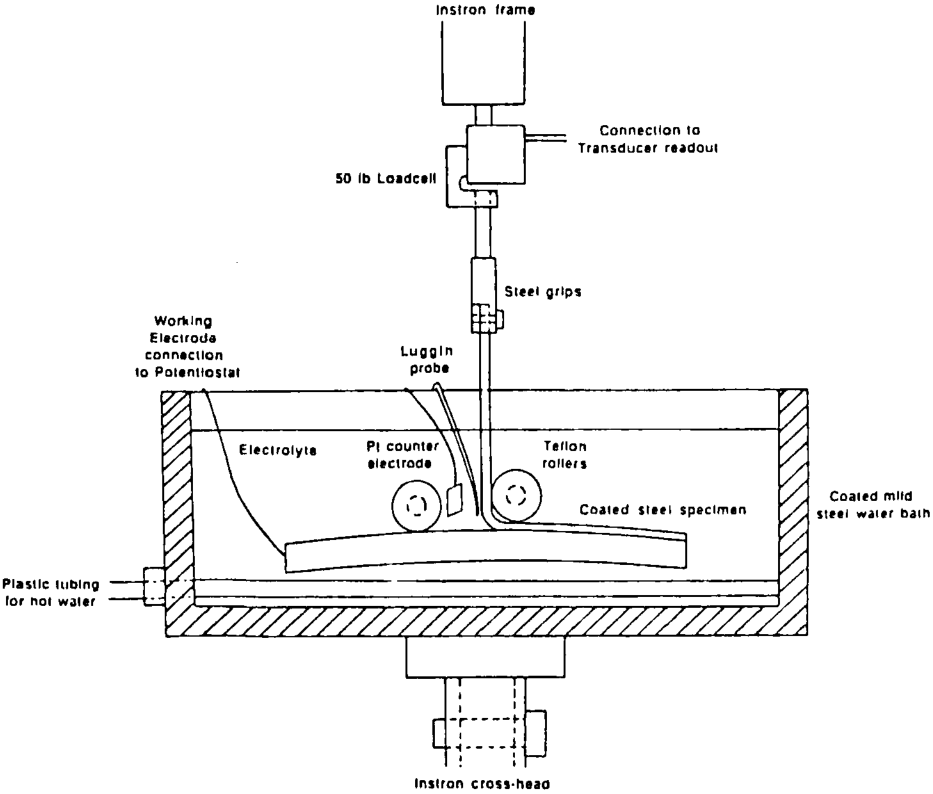

FIGURE 1 Schematic representation of the 90° peel test rig.

cross head of an Instron TT-D fitted with a 50 lb Interface SM50 Loadcell. The cross head speed was 0.02 inch $\min^{-1}$ (0.5 mm $\min^{-1}$) and the force required to peel the coating was determined.

The coating was cut away along half the length of a coated steel specimen. Experiments were carried out in solutions of 0.03 M NaCl to which various concentrations of $Na_2CO_3$ had been added to produce a range of alkaline environments. Concentrated sodium hydroxide was added when necessary to obtain pH values greater than about 11.5. The temperature of the solutions was set at either 25 ± 1°C or 60 ± 1°C and was maintained by a water-bath. For experiments carried out under cathodic polarisation, the potential was maintained constant with respect to a Luggin probe saturated calomel electrode (all potentials are reported with respect to the saturated calomel electrode) located at the tip of the crevice formed between the peeling coating and the substrate.

## 3.0 RESULTS

After the debonding process, the adhesive remained either on the steel substrate or on the tape backing. Failure in which the locus of failure was obviously within the bulk of the adhesive was not observed. In some tests the locus of failure remained the same throughout the peel and in some cases it moved from the substrate/adhesive interface to the adhesive/backing interface at different points along the joint. It will be assumed that the essential difference between the adhesive/substrate interface and the adhesive/backing interface is that in the former, polar interactions play a major role in determining the strength of the joint whereas in the latter dispersion forces predominate. It is on this basis that the four different types of failure observed are characterised in Table I.

The points shown in Figures 2 to 4 are marked with a number which corresponds to the type of failure. The peel force was taken as the plateau in the load *versus* displacement curve. In the case of type 2 or type 3 failure, the plateau in the curve varied by about 0.2 N to 1.0 N in some cases, corresponding to variations in the fracture surface energy values of up to about 20%. In these instances, the peel force was taken as the average value of the load. A problem associated with examining the plateau was the regular appearance of spikes or

TABLE I

| Type | Name | Form of failure |
|---|---|---|
| 1 | dispersion | A uniform interfacial failure in which the adhesive remained on the steel while the tape backing disbonded from the adhesive. |
| 2 | dispersion (polar) | A mixed mode failure in which most of the adhesive stuck to the surface of the steel. |
| 3 | polar (dispersion) | A mixed mode failure in which most of the adhesive, together with the backing disbonded from the steel. |
| 4 | polar | A uniform interfacial failure in which the adhesive disbonded from the steel and remained on the backing. |

sudden decreases in the readout. These correlated with slippage of the specimen under the rollers.

### 3.1 The effect of pH and exposure period on the adhesive bond strength

Initial experiments were carried out to examine the effect of the pH of the environment without an applied potential. The effect of exposure to solutions of different pH for different exposure times in the absence of an applied potential is shown in Figure 2. In this series of tests nearly all (80%) of the coating failures were of type 1, that is, dispersion type failures when the adhesive separated from the backing. The remaining 20% failed in the dispersion (polar), type 2 fashion. This suggests that the major effect of exposure to the aqueous environment is the breakdown of the bond between the backing and the adhesive.

The general trend of the effect of exposure time on the force required to bring about the disbondment was an increase in the fracture surface energies by about 20 to 40% as the period of exposure to solution was increased from 1 to 14 days. This appeared to be largely independent of the pH of the environment. Since failure predominantly involved the dispersion bonded interface it may be postulated that the increase in fracture surface energy is due to diffusion of water through the polyethylene based coating and plasticisation of the adhesive by the water which would toughen the joint. Since failure in such circumstances may not be due to $OH^-$ ions the independence of pH is understandable. Stevenson and

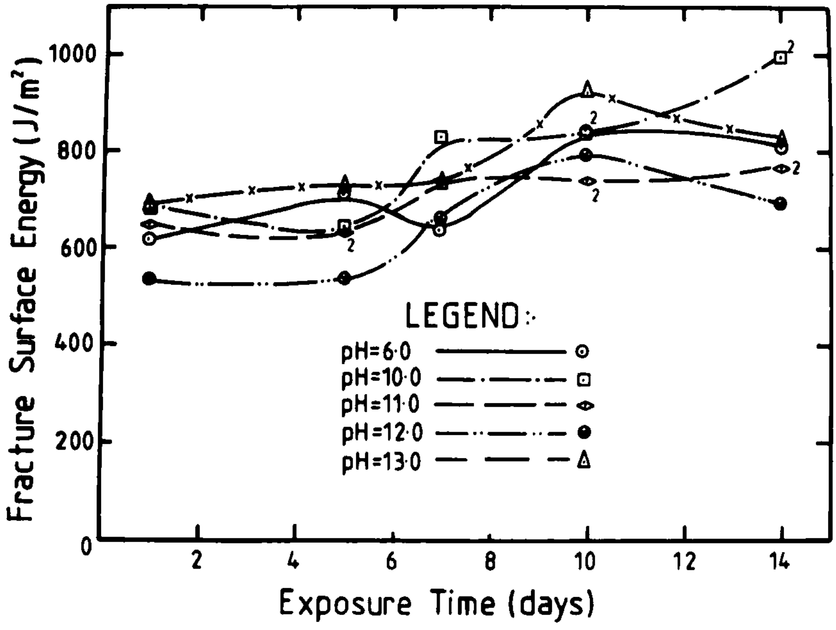

FIGURE 2 Effect of exposure time on fracture surface energy.

Andrews[12] suggested a similar explanation for the results which they observed in their work.

### 3.2 The effects of temperature and short term polarisation on the joint strength

Tests were then carried out to examine the effects of temperature and short term polarisation on the joint strength. The electrolyte used was 0.03 M NaCl at pH values of 6.0 and 13.0. The samples were maintained at temperatures of 25°C and 60°C for 14 days. Thirty minutes before the peel test, the steel exposed under the coating near the adhesive joint was cathodically polarised at one of a range of potentials between −0.78 and −1.50 V (SCE).

It was found that the joint strength decreased to about one-sixth of its 25°C value when the temperature of the solution was increased from 25°C to 60°C and the decrease was independent of pH. At both temperatures the fracture surface energy was largely independent of the applied potential. The failures which occurred at 25°C were predominantly dispersion failures but, in contrast to this, two incidences of apparently complete polar failure (type 4) were recorded at the higher temperature. A similar six-fold decrease in the fracture surface energy was observed by Stevenson and Andrews[12] when the temperature of the solution in their experiments was increased from 20°C to 80°C. A similar trend towards interfacial adhesive/substrate failure at higher temperatures was also observed by Gledhill and Kinloch[7] in their study of epoxy/mild steel adhesive joints. In order to ensure that temperature effects did not mask the effect of other variables, all the remaining tests were performed at 25°C.

### 3.3 The effect of cathodic polarisation on the adhesive bond strength

The effect of prolonged periods of cathodic polarisation on adhesive bond strength is shown in Figure 3. At all levels of pH there was an initial increase in the values of the fracture surface energy as time passed. This may result from the same plasticisation effect which was postulated as the cause of the results shown in Figure 2.

After longer periods of polarisation, there was a decrease in the fracture surface energy associated with an increasing amount of polar disbonding from the steel. It may be postulated that the transition from a dispersion (adhesive/backing) failure to a polar (adhesive/metal substrate) failure could be associated with the combined effects of increasing strength of the adhesive/backing interface and decreasing strength of the adhesive/metal substrate interface as the time under cathodic polarisation increased.

Under the conditions which promoted adhesive/metal interface failure the joint strength between the adhesive and the steel decreased as the polarisation potential became more negative. The rate of decrease with respect to change in potential was greatest in the neutral solutions; however, the absolute value of the fracture surface energy was lowest in the high pH, more negative potential region

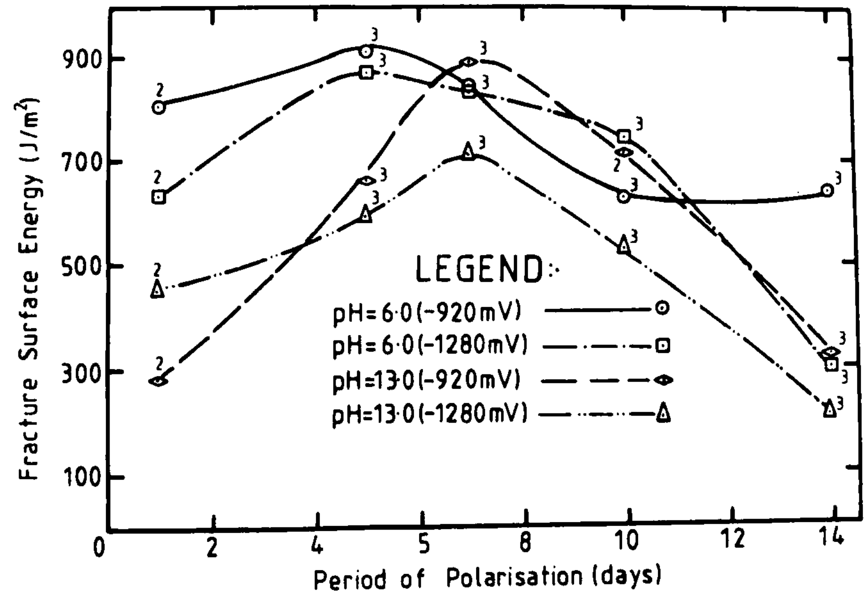

FIGURE 3 Effect of a prolonged period of exposure to cathodic polarisation on fracture surface energy.

as shown by the replotted results in Figure 4. Figure 4 illustrates the fact that throughout the pH range studied the adhesive bond strength is reduced during cathodic polarisation. However, the fracture surface energy is generally lower at high pH values. This result reflects the general trend for the other periods of polarisation shown in Figure 3.

The dominant type of failure after longer periods of polarisation was polar (dispersion) in contrast to the dispersion failure observed after shorter periods of

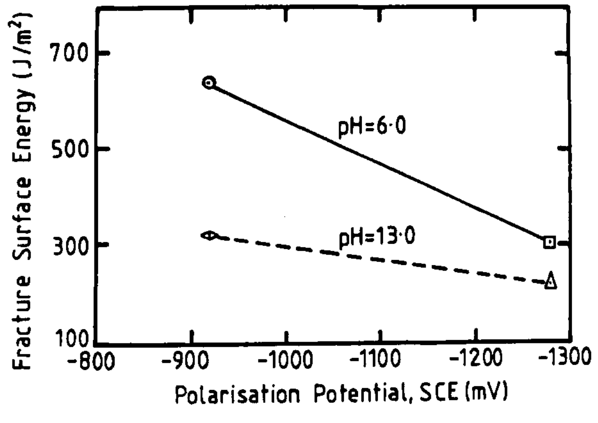

FIGURE 4 Effect of pH and potential on fracture surface energy.

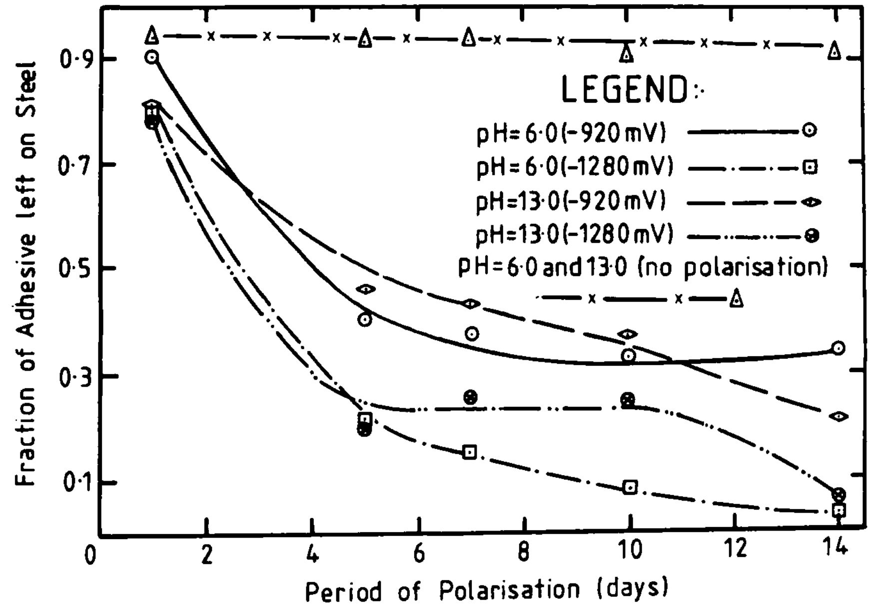

FIGURE 5 Effect of pH on the amount of adhesive left on the steel substrate.

exposure. The fraction of adhesive remaining on the steel was plotted as a function of the period of polarisation in Figure 5 from which it can be seen that polarisation promotes failure of the adhesive/steel interface.

The application of cathodic potentials was thus found to have two effects on the coating/steel bond. Cathodic polarisation changed the mode of failure and the longer the period of polarisation or the more negative the potential the greater was the proportion of adhesive failure. The application of cathodic polarisation reduced the adhesive bond strength and it was noted that in a solution of high pH value the reduction in adhesive bond strength was lower than in a solution of lower pH value.

## 4 DISCUSSION OF RESULTS

### 4.1 The effect of temperature and the presence of water

Gledhill and Kinloch[7] and Stevenson and Andrews[12] described an Arrhenius relationship between the fraction of interfacial failure and temperature. On the basis of the similarity of the activation energy for disbondment and that for the diffusion of water through the polymer, they proposed that the fraction of interfacial failure was controlled by the amount of water present at the interface and that this, in turn, was controlled by the diffusion of water through the polymeric phase. A similar explanation may account for the interfacial failure between the pipeline coating and steel at 60°C. The surface of the steel was grit blasted before the tape was applied and it is probable that it had a surface layer of an oxide such as $Fe_2O_3$. The values of $W_A$, the work of adhesion when the new surfaces are exposed to air or vacuum and $W_{AL}$, the work of adhesion when the new surfaces are exposed to an aqueous environment may therefore be calculated using surface free energies of $\gamma^D = 22.0\,mJ/m^2$, $\gamma^P = 50.2\,mJ/m^2$ for water; $\gamma^D = 107\,mJ/m^2$, $\gamma^P = 1250\,mJ/m^2$ for ferric oxide;[7] and $\gamma^D = 32.0\,mJ/m^2$, $\gamma^P = 1.1\,mJ/m^2$ for low density polyethylene.[14] The work of adhesion at the polyethylene/ferric oxide interface in the absence of moisture was calculated to be $191\,mJ/m^2$ and in the presence of moisture to be $-330\,mJ/m^2$. The change from a positive to a negative value for the thermodynamic work of adhesion is indicative of a driving force for the displacement of the polyethylene adhesive from the metal oxide by water. A higher temperature may facilitate failure at the steel/adhesive interface by increasing the diffusion rate of water through the coating.

### 4.2 The effect of applying cathodic potentials

When samples were cathodically polarised there was a considerable increase in the proportion of the joint for which failure was associated with disruption of the polar bonds. In both neutral and alkaline solutions, in the absence of an applied potential, the locus of failure remained at the adhesive/backing (dispersion bond) interface for 95% of the joint and the fracture surface energy increased with time. On application of a polarising potential there was (after the initial seven days during which failure was predominantly at the adhesive/backing interface) a decrease in the fracture surface energy which increased with the magnitude of the polarising potential. This fall in the fracture surface energy could be associated with an increasing proportion of the joint for which failure was associated with the polar interface. It is, therefore, suggested that the cause of the shift of the locus of failure was the application of a cathodic potential and not the existence of an alkaline environment at a coating/substrate interface.

It is of interest to examine the mechanism by which the application of cathodic polarisation of the metal polymer interface brings about a decrease in the work of adhesion for that interface. The concept that reduction or solubilisation of the interfacial oxide may result in cathodic disbondment has been proposed by Leidheiser's school.[6,7,8,15] The exact nature of the interfacial oxide between the adhesive and the steel prior to cathodic disbondment is not known. It may, however, be composed principally of $Fe_2O_3$ and $Fe_3O_4$ before disbondment and in the presence of an aqueous environment, $Fe(OH)_2$, $Fe(OH)_3$, FeOOH and $FeCO_3$ may also be present. These iron compounds will be referred to in the following discussion as the "interfacial oxide film." A possible mechanism to explain the "solubilisation" of the interfacial oxide may involve electrochemical reduction of $Fe_3O_4$ in the interfacial oxide film. Figure 6 shows a portion of the potential-pH diagram which indicates the regions of thermodynamic stability of the various oxides of iron under differing conditions of pH and potential at 25°C.[16] Superimposed on Figure 6 is a region which represents a summary of the

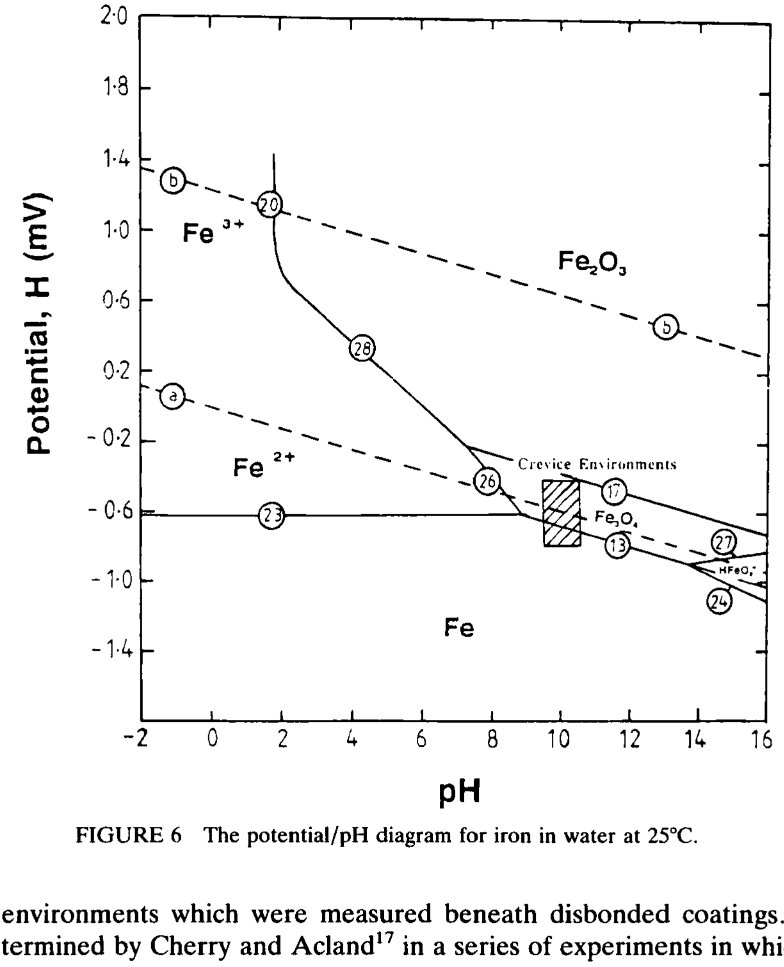

FIGURE 6 The potential/pH diagram for iron in water at 25°C.

crevice environments which were measured beneath disbonded coatings. These were determined by Cherry and Acland[17] in a series of experiments in which they attempted to determine the conditions which obtain at the tip of the crevice between a disbonding coating and the metal substrate. Cherry and Acland measured the potential by inserting probe electrodes through the organic coating and the chemical environment by analysing solution removed from the crevice tip region. The most negative potential indicated for the crevice environment region is −1.02 V (SCE) which is typically measured in potential studies on cathodically protected lines. The most positive potential, −0.640 V (SCE) in the region shown in Figure 6, was the most positive crevice potential value measured beneath a disbonded coating. The potential range −0.640 V to −1.060 V (SCE), therefore, represents the range of crevice potentials which may be found beneath a disbonded coating on a pipeline. The pH of the crevice solution beneath the coating was found to be in the range, 10.3 to 9.6.

In Figure 6 the region which defines the crevice environments partially overlaps the stable regions of Fe and $Fe_3O_4$. The overlap into the region of iron stability suggests that polarisation into this region may bring about a reduction of the oxide by the reaction

$$Fe_3O_4 + 8H^+ + 8e^- \rightarrow 3Fe + 4H_2O.$$

This disrupts the film and permits a crevice to form beneath the coating. This mechanism for the initiation of cathodic disbondment is supported by the lower peel strengths which were measured when the adhesive joints were polarised to the negative potentials at which oxide reduction might be expected. The greater effect of the cathodic polarisation in the lower pH solution is also explained by the smaller degree of cathodic polarisation necessary to bring about reduction of the $Fe_3O_4$ at the lower pH.

The proposed mechanism is unable to explain, however, the generally lower value of peel strengths (associated with a larger degree of polar disbonding) in the higher pH environments and the great decrease in peel strength associated with an increase in temperature. In particular, it is not able to explain the continued growth of a crevice beneath a coating. Gould and Cherry[13] and Ackland and Cherry[17] have shown that at the tip of the crevice beneath a disbonded coating, the potential rises to regions in which the $Fe_3O_4$ is stable in the environments to which it is likely to be exposed.

A second possible mechanism is, therefore, proposed to explain the propagation of cathodic disbondment in the more positive potential regions. It was shown earlier that the presence of water at the polyethylene/ferric oxide interface led to a negative value for the thermodynamic work of adhesion, $W_{AL}$. This change explained the increased interfacial adhesive failure of the pipeline coating and steel at 60°C. The mechanism for the propagation of cathodic disbondment away from the holiday may involve a decrease in $W_{AL}$ brought about by cathodic polarisation of the steel. Electrocapillary curves, which describe the relationship between $\gamma_{sl}$ and the applied potential, reach a maximum value at the so-called "potential of zero charge" ($E_{pzc}$). Hence, $W_{AL}$ decreases at potentials more positive than the potential of zero charge. Lazarova[18] has examined the dependence of the $E_{pzc}$ value for iron on the pH in 0.01 N $Na_2SO_4$ solution. The $E_{pzc}$ for iron in the pH range 11.5 to 13.0 was about $-0.99$ V to $-1.04$ V (SCE). If the $E_{pcz}$ value for iron compounds in the interfacial oxide film is similar to the $E_{pcz}$ values for iron in the alkaline conditions examined by Lazarova then at potentials more positive than the $E_{pzc}$, $\gamma_{sl}$ would decrease. Crevice potentials which were measured beneath disbonded coating[17] with a holiday potential of $-1.06$ V (SCE) were more positive than the range of $E_{pzc}$ values mentioned above. Since a decrease in $\gamma_{sl}$ causes a subsequent decrease in $W_{AL}$, the effect of applying cathodic potentials along a crevice would, therefore, be to increase the thermodynamic driving force for the disbondment of the adhesive from the interfacial oxide film.

The mechanism for disbondment involving an electrocapillary action is supported by the results of the peel tests. An increased amount of adhesive/steel interfacial failure was observed when the coated steel specimens were immersed in 0.03 M NaCl at pH 6.0 or 13.0 while the steel was cathodically polarised to $-0.92$ V (SCE) compared with the situation when there was no polarisation.

It is also important to note that overprotection (the application of excessive cathodic protection in an attempt to ensure that the cathodic protection is adequate) provides a further mechanism for the cathodic disruption of the coating/metal bond. Holiday potentials more negative than −1.07 V (SCE) would be more negative than the $E_{pzc}$ values for iron which were measured by Lazarova. The application of potentials more negative than the $E_{pcz}$ at holidays would also result in a decrease in the value of $\gamma_{sl}$, causing a subsequent decrease in $W_{AL}$. Experimental results support this idea. The adhesive bond strength was reduced when the more negative potential −1.280 V (SCE) was applied to the steel exposed at the adhesive joint in solutions with pH values of 6.0 and 13.0.

It should be noted that the disruption of the polar bond which is observed at high temperatures under the conjoint action of a high pH and a negative potential may be explained by a third mechanism. The potential-pH equilibrium diagram for the system Fe–$CO_2$–$H_2O$ at 60°C shown in Figure 7 was constructed using

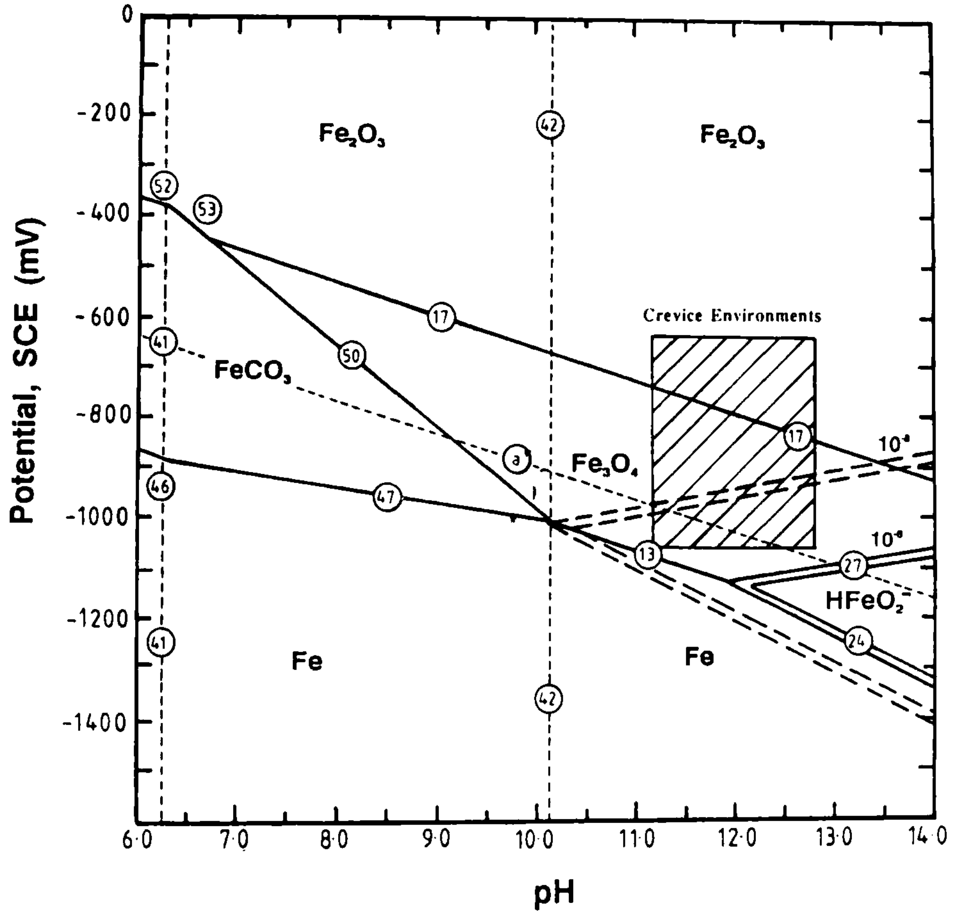

FIGURE 7 The potential/pH diagram for iron/carbon dioxide/water at 60°C.

thermodynamic data from Townsend[19] and Parkins *et al.*[20] who based their calculation of standard Gibbs free energy changes for reactions in aqueous environments at elevated temperatures on the work of Criss and Cobble.[21,22,23] The most noticeable difference between Figure 7 and potential-pH equilibrium diagrams at 25°C is that at elevated temperatures the stable domain for the dihypoferrite ion is increased significantly in the alkaline region. This effect has been described by Ashworth and Boden[24] and Townsend.[19] The double lines which define the region of dihypoferrite ion stability correspond to the uncertainty of the chemical potential for this anion which was used to calculate the equilibrium potentials for these reactions.

Superimposed on Figure 7 is a region which represents a summary of the crevice environments examined at 60°C from Gould and Cherry.[13] The region which defines the crevice environments partially overlaps the stable regions of $Fe_2O_3$, $Fe_3O_4$ and $HFeO_2^-$. In the latter case the overlap occurs when the dihypoferrite ion concentration is less than $10^{-6}\,\mathrm{mol\,l^{-1}}$. The overlap into the region of dihypoferrite ion stability occurs at the more negative potentials. The existence of part of the region which defines the crevice environments in the stable region of the dihypoferrite ion also depends on the alkaline environment of the holiday. It seems likely, therefore, that at elevated temperatures cathodic disbondment occurs by the reduction of $Fe_3O_4$ by

$$Fe_3O_4 + 2H_2O + 2e^- \longrightarrow 3HFeO_2^- + H^+$$

## 6 CONCLUSIONS

The investigation of the pipeline coating failures using peel tests revealed that, for the system examined, even in the absence of an applied potential, high pH conditions would be likely to cause a loss of adhesion between the pipeline coating and steel by disruption of the coating/adhesive interface. Disruption of the adhesive/metal interface required the application of a polarising potential and three separate mechanisms are postulated for this effect. The first mechanism involves failure at the adhesive/oxide interface in the presence of water due to the displacement of the adhesive by the water. This has been proposed previously. What has not been proposed previously is the suggestion that this would be facilitated by electrocapillary effects. The operating temperature of the pipeline may exacerbate the failure by increasing the diffusion rate of water through the coating.

Two mechanisms which are postulated to explain the loss of adhesion between the pipeline coating and steel involve cathodic polarisation. The first of these suggests that the iron compound, $Fe_3O_4$, in the interfacial oxide film may be electrochemically reduced when potentials which approach about $-1.07$ V[25] are applied at the holiday. This process will break adhesive/oxide bonds and is believed to be the initial stage of cathodic disbondment. The second mechanism involves electrocapillary action which reduces the surface tension between the steel and the crevice solution during the application of cathodic protection at a later stage of disbondment along the crevice. This process has not previously been proposed, but if it does take place then it may increase the thermodynamic disbonding force between the adhesive and the steel in the presence of an aqueous environment, and it is believed that this may explain the propagation of the disbondment front away from a holiday.

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