CHAPTER-V
DISCUSSION

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Corrosion of a metal in an electrolyte is a dynamic and extremely complex chemical process. Even in the laboratory under known and carefully controlled conditions it is difficult to accurately describe what is taking place on a corroding surface. For many years, engineers studying the effect of different environments and operating conditions on metals had to rely on time consuming exposure tests and tedious examinations of corroded samples. In today's world, we are not permitted the luxury of time to carry out such evaluations. So more and more attention is given to the measurement and interpretation of electrochemical parameters of corroding surfaces.

corrosion. is classified, in the chemical sense, as an oxidation-reduction type of reaction. The oxidation reduction concept is essential in understanding the corrosion reaction.

Another important criterion that must be met for corrosion to occur is that any reaction considered must be thermodynamically possible. The change in energy must always be from a higher to a lower state for the reaction to be spontaneous. The equation relating the change of free energy for an oxidation-reduction system is written :

$$G = nFE \qquad (1)$$

where G is the free energy change in Joules;

n is the number of electrons taking part in the reaction;

F is the Faraday constant, 96,500 coulombs/ mole; and

E is the electromotive force of the reacting system in volts.

For a reaction to be possible there must be a decrease in energy i.e. G must be negative.

The potential, E, of the system under study can be expressed as the sum of the half cell potentials. Every oxidation-reduction type reaction has a half cell potential, the absolute value of which is not known. It is possible however, to measure the potential difference between two half cells using electrical instrumentation. By selecting one half cell reaction as a standard, all other half cells can be measured against it.

Figure - 1 gives polarity convention for oxidation-reduction cells.

The previous discussion of thermodynamics in a very brief and general form is a background material which must be appreciated for work with electrode kinetics and polarization. Thermodynamics will establish whether a corrosion reaction can occur but it says nothing about the rate of the reaction. It must be understood that when a metal is actively corroding, calculations based on reversible thermodynamics considerations do not hold.

Faraday's Law :

$$W = KIt \quad \text{or} \quad r = \frac{I}{nF} \qquad (2)$$

relates the quantity of material taking part in a reaction with electrical energy where W is the weight of material reacting;

K is the electrochemical equivalent of the material in weight units per coulomb;

I is current in ampere;

t is time in seconds;

r is rate of reaction in equivalents per second;

n is the number of equivalents (number of electrons) involved in the reaction; and

F is the Faraday constant 96,500 coulombs/ mole.

Let us consider an electrode consisting of a metal in a state of reversible equilibrium with a solution of its ions. Reversible equilibrium means that simultaneous oxidation and reduction is taking place with no net change in the weight of the electrode or the concentration of ions. The rate of oxidation and reduction taking place can be expressed in terms of Faraday's Law :

$$r_{ox} = r_{red} = \frac{i_o}{nF} \quad (3)$$

where i_0 is called the exchange current.

Since oxidation current and reduction current have opposite polarities, at equilibrium state there is no net current.

When the equilibrium of an electrode reaction is disturbed, there is a change in the potential of the electrode when measured against a stable reference. The difference between the equilibrium potential and the potential under the new condition is called polarization and is usually designated by the Greek letter Eta, η.

Mathematically :

$$\eta = E - E_{eq} \qquad (4)$$

where E_{eq} is the potential at equilibrium and E is the potential under the new conditions. Disturbance of the equilibrium condition alters the exchange current balance and results in a net current flow, either oxidation or reduction, which is representative of the net rate of reaction. One would therefore expect that polarization could result from any situation involving a net current flow to or from an electrode surface.

Resistance polarization :

Let us consider the flow of current from some point in an electrolyte to a metallic electrode. Unless the resistivity of the electrolyte is zero, there will be a voltage drop between the metal and any given point in the electrolyte, which results from the current density and resistivity. In addition, interface films may also have significant resistance effects. From a practical standpoint, resistance polarization resulting from IR drop may be a significant factor in making measurements of polarization potentials.

Activation polarization :

Resistance polarization has no electrochemical significance; whereas activation polarization and concentration polarization, discussed below, are electrochemical in nature.

If an electrochemical reaction takes place instantaneously there would be no activation polarization. This form of polarization results from some slow step in the reaction sequence and can be expressed as a chemical rate equation :

$$na = \pm B \log \frac{i}{i_0} \qquad (5)$$

where B is a constant for the particular system. The (+) sign is used when i is current flow from the electrode, (-) is used when i is current flow to the electrode.

Equation (5) is commonly referred to as the Tafel equation. Activation polarization is caused by energy barriers which control the reaction rate at the electrode surface.

Concentration polarization :

An electrochemical reaction which takes place at the surface of a metal electrode in contact with an electrolyte must have a supply of ions available if it is to proceed. Ions are charged atoms or molecules and as such have mass and occupy space. If ions are reacting at the electrode surface, their concentration is decreasing and additional ions must move in to take their place. If the reaction is proceeding slowly, diffusion of ions from the bulk electrolyte proceeds at a sufficient rate so as not to influence the rate of the reaction. If, however, the rate of reaction is rapid, the concentration of ions at the electrode surface becomes depleted. Finally a rate is reached when the instant an ion reaches the electrode it reacts and the reaction rate can not proceed faster than the diffusion of ions to the surface will permit.

Modern theory and the use of polarization effects :

The modern mixed-potential theory of electrochemical reactions involves two hypothesis :

1. Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions.

2. There can be no net accumulation of electrical charge during an electrochemical reaction.

The mixed potential theory and parameters, B, i_0 and i as defined in the preceeding discussion provide the tools in studying corrosion and its prevention.

The exchange current, io, for a given reversible electrode process may vary in magnitude depending on the particular electrode surface on which the reaction is taking place. The equilibrium potential of a reaction in all cases is 0.0 on the hydrogen scale. If an external current is applied to such an equilibrium reaction the potential, na will follow the behaviour predicted by the activation polarization potential equation :

$$na = + B \log \frac{i}{i_0} \qquad (6)$$

This is shown in figure - 2.

Moreover,

$$i_{app} \longrightarrow = i_a - i_c \text{ (anodic)} \qquad (7)$$

and

$$i_{app} \longrightarrow = i_c - i_a \text{ (cathodic)} \quad (8)$$

where

i_a = anodic current density;

i_c = cathodic current density;

i_{app} = externally applied current density.

By applying external current and observing the overvoltage, it is possible to determine the exchange current io and the Tafel slopes of the reaction.

A metal undergoing electrolytic corrosion must involve two or more such electrode reactions. Consider the corrosion of an active metal in a non oxidizing air free acid containing ions of the metal.

When the metal is immersed in the acid solution, its potential must lie at some point between the two reversible potentials. In this case, control of the corrosion rate rests primarily in the polarization of the cathode. I Corr is analogous to io of equilibrium reactions.

The equations for a corroding system under activation control with external current applied are :

$$E = E_{Corr} - E_I \quad (9)$$

$$E = B_a \log \frac{i_a}{I\ Corr} = - B_c \log \frac{i_c}{I\ Corr} \quad (10)$$

As the corrosion system becomes more complex, more partial reactions can occur. Equations (7) and (8) must never the less apply.

Figure - 3 is an idealized representation of a corrosion diagram showing the behaviour of a corrosion cell when an external current is applied both cathodically and anodically. As in previous cases, the local cathodes and anodes of the corrosion cell polarize toward a common potential, E Corr. The diagram shown represents a system which is under mixed control but with a slight tendency towards cathodic control. If an external current is applied to provide current flow either to or from the working electrode surface, the potential of the corrosion cell will be shifted. It must be remembered that under equilibrium conditions before the start of application of external currents, the corrosion current, I Corr is flowing between the local anode and local cathode with flow coming from the anodic surface and going to the cathodic surface. If current is applied externally in the anodic direction, the effect will be to increase the anode current density and simultaneously decrease the cathode current density of the corrosion cell. The path which the observed potential will follow is represented by the heavy line moving upward to the right. When all of the current at the local cathode has ceased to flow and has been in effect reversed at potential Ec, there will be a change in the characteristic slope of the potential current line at current iq. Similarly, if the externally applied current is made to flow into the corroding sample in a cathodic manner, the local cathodic current will be increased and the local anodic current decreased. When the potential Ea is reached there will be an inflection in the potential external current line as noted at point Ea, ip.

This represents cathodic protection, i.e. all local anode current has ceased to flow. Polarization data is one of the most useful methods of determining minimum current requirements for cathodic protection.

It is possible to determine corrosion rates by determining points iq and ip. These are related by the equation :

$$I\ Corr = \frac{i_q \times i_p}{i_q + i_p}$$

It has been shown that corrosion rates can be approximated by determining the rate of change of potential with externally applied current over the first 10 to 20 millivolts of polarization shift (E) from the equilibrium point. At this low externally applied current density there is negligible permanent effect on the corroding system. Thus, it is possible, by periodic measurement to determine instantaneous corrosion rates which can be plotted to obtain a corrosion history of the sample with time. The relationship is represented in the formula:

$$I\ Corr = \frac{1}{2.3} \times \frac{I}{E} \times \frac{Ba \times Bc}{Ba + Bc}$$

Derivation of this equation is based on the relationships contained in equations (7) through (10). For many practical systems, this equation can be reduced to :

$$I\ Corr = 0.026 \frac{I}{E}$$

The nature of anodic curve of current vs potential values depend closely on the metal or alloy under tests. In Iron and its alloys, the dissolution reaction of Fe to Fe^{++} is over come by another reaction i.e. oxidation of Fe^{++} to Fe^{+++} and in aqueous solutions, the reaction product is a compact oxide layer which reduces the further dissolution of the metal. This phenomenon, commonly known as passivation can also take place in presence of oxidising inhibitors, thereby almost eliminating the requirement of external current to retard the corrosion of the base metal. The current potential curve in such case has a general trend as in Figure - 2, p.33.

Many pertinent points can be derived considering current potential curves like passivation current (ip), corrosion current (I Corr) and Tafel parameters, especially anodic Tafel (Ba). Polarization resistance (Rp) and corrosion rates derived from these values also gives relevant information about the inhibitive properties.

Critical current density (icc) is also an important criterion for predicting the corrosive nature of the corrodent. As given in the introduction part of this chapter, it can be derived from these values whether the inhibitors studies are anodic or cathodic or both.

In the presence of vanadium pentoxide (V_2O_5), Ba increases with additions of ferric ions, but Bc at all concentrations of ferric ions remains almost constant. I Corr also increases marginally up to 0.02% ferric ion concentrations but at 0.03% ferric ion concentration there is a drop in Ba and corresponding drop in I Corr. This indicates the anodic control of the inhibitors. The I Corr values are also higher than the ip values indicating that the metal surface is not completely passivated.

With pot. dichromate ($K_2Cr_2O_7$) inhibitor in Syn. GVSL, the increase in I Corr is always preceeded by increase in Ba values, and Bc is almost a constant at increasing ferric ion concentrations, showing anodic control of the inhibitor. ip values at zero ferric ions are very much comparable or less than I Corr values, but with ferric ion additions ip is far higher and incomparable with I Corr, showing no passivation is ocurring.

With sodium nitrite and metavanadate both Ba and Bc are decreasing with decreasing I Corr, showing both anodic and cathodic control of this inhibitors synergistically. Except at zero ferric ions, where ip is less than I Corr, for all ferric ion additions ip is slightly higher or comparable with I Corr showing good passivation behavior.

Ammonium metavanadate and ammonium tartrate behaves in a similar way like V_2O_5, only exception being at 0.02% ferric ion concentration, where there is a decrease in Ba with a decrease in I Corr. Bc remains almost constant and hence it can be said that these inhibi tors control the current anodically. ip is also higher than I Corr, only exception being at 0.03% ferric ion concentration, where it is less, indicating incomplete passivation of CS.

With any concentrations of antimony oxide (0.075% to 0.15% Sb_2O_3) and in presence of ferric ions there is gradual decrease in Ba and I Corr values. Bc remains almost a constant, proving the anodic control of Sb_2O_3 and ferric ions. Any increase at any concentration of ferric ion is preceeded by an increase in I Corr in almost all cases.

When ip is compared with I Corr it is seen that both are having lower values when compared with other inhibitor systems, especially at more than 0.02% ferric ion concentration. But neverthless ip is not less than I Corr at any condition indicating that to be passive CS has to corrode to achieve that.

Critical current density (icc) values for CS in syn. GVSL solutions with Sb_2O_3 and in presence of ferric ions (at more than 0.02% ferric ions up to 0.14% Sb_2O_3 and at 0.01% or more than that for 0.15% Sb_2O_3)

are found to be decreasing with increasing concentrations of ferric ions. This behavior is not seen with any other inhibitors studied, where there is always either an icc increase or is a constant. Very low ip and I Corr values coupled with lower icc values and shifting of potentials towards more noble direction for Sb_2O_3 - ferric ions shows the passivating characteristics of this inhibitors which is achieved by synergistic action.

Corrosion rates calculated from Ba, Bc and I Corr values (Table-3, p. 168) shows that for all inhibitors ($K_2Cr_2O_7$, V_2O_5, $NaNO_2$, metavanadate) and its various combinations, there is an increase in corrosion rate giving negative effeciencies, except for metavanadate - nitrite combination with ferric ions, where it is positive. Thus it is seen that these inhibitor combinations do not act as good inhibitors for the system.

Sb_2O_3 additions to syn. GVSL solution shows aggressive action of ferric ions in lower concentrations (up to 0.02%), however, further addition of ferric ions play an important role in the synergistic action of ferric and antimony ions and thus at higher concentration of ferric ions the protective action of the inhibitors is observed. However, only at the Sb_2O_3 concentration of 0.15%, the protective properties of ferric-antimony combination is observed even at the lowest concentration (0.01%) of ferric ions and increases with an increase in its concentration up to 0.03%. Thus this combination of Sb_2O_3 and ferric ions is the ideal combination for the system. This is also observed in the zonal graphs where the OCP lies in passivation zone. Polarization resistance (Rp) calculated from the values obtained from polarization curves is found to be the highest for CS in syn. GVSL solution containing 0.15% Sb_2O_3 and 0.03% ferric ions.

In order to understand the inhibitive action of the synergistic effect of ferric ions and Sb_2O_3, Rp values are also derived from impedance data where lower perturbations of the double layer maintains the system at almost a steady state. The Rp values derived by this method show a slightly different trend. The addition of 0.01% ferric ions decreases the Rp initially, however, further additions of ferric ions increase Rp and only at 0.03% ferric ions and 0.15% Sb_2O_3 it is maximum, as is observed from polarization data.

It is also observed that Rp obtained from impedance measurements is higher than that obtained from polarization measurements. This may be due to the high scan rate used in the polarization studies and it is to be noted here that the scanning was started from highly cathodic side (-850 mV) for obtaining zonal characterisics for super imposition of OCP on it. This disturbs the double layer formed at the CS surface.

It is also noted here (ref. 103 - 104, p. 44), that when passivation occurs anodic and cathodic Tafel are never constant and corrosion current obtained is an approximation due to high polarization of CS.

On the other hand, in AC impedance studies, surface on the CS is maintained and not disturbed even when AC waves are imposed on it thereby giving exact details. Polarization resistance therefore calculated from these studies is nearer to the truth. Corrosion rates are not derived from these data since for this Ba and Bc values are to be taken from polarization data. This is the limitations of AC impedance studies.

Double layer capacitance (Cdl) values decreases with any passivation on the CS surface as is seen with the value for 0.15% Sb_2O_3 and 0.03% ferric ion concentration in syn. GVSL solution. At this concentration, Cdl of 222 microfarads is obtained, which is lowest when it is compared with the values obtained for other combinations of Sb_2O_3 and ferric ions.

High Rp and low Cdl values for 0.15% Sb_2O_3 and 0.03% ferric ion concentration in syn. GVSL solution amply establishes the passivation characteristics on CS as is the case with OCP and polarization studies (ref. 102, p.44).

Therefore, it can be seen that Sb_2O_3 - ferric ion inhibitor combination works as an anodic inhibitor synergistically to control corrosion by lowering corrosion current, thereby lowering anodic Tafel and giving low corrosion rate and high polarization resistance values. The lowering of critical current density and passive current values also takes place consequently. Thus it is shown that how current values associated with the polarization studies can be used to identify the utility of various inhibitors for controlling corrosion.

On the other hand, CS exposed to uninhibited GVSL solution showed high corrosion current confirming active dissolution of the metal. Microstructurally also,CS in uninhibited and aerated GVSL solution showed an increased loss of pearlitic phase as well as on set of localised attack at non-homogenous sights like inclusions, partially filled with corrosion products. This may be expected to contribute to change in chemistry of GV as far as concentration of ferrous/ ferric ions are concerned. Since OCP of -750 mV also lies in the free corrosion zone in the polarization plot, leaching of pearlitic phase may be attributed to the active surface at the potential of CS in GV solution. The visual observations of the solution (dark yellow colouration) also confirms the presence of ferric ions in the GV solution, which could be the leached and oxidized iron from the pearlitic phase of the CS.

The chemical analysis of the GV solution after the experimentation was not attempted since the ferrous ions which are leached out are oxidized by O_2 and is used in the passivation of the surface of CS and therefore the concentration of the ferrous/ ferric ions would not be quantitative in nature.

On the other hand, CS in GVSL solution with 0.1% Sb_2O_3 and 0.03% ferric ions at an OCP of -480 mV, shows only mildly etched pearlitic phase, but with initiation of localised attack at the inclusions. These localised pits were not showing any corrosion products, clearly indicating that general corrosion was under control. As the OCP of -480 mV falls on the borderline of free corrosion zone and SCC zone, shift in potential was enough only to push it to this borderline and hence general corrosion was arrested, but the initiation of localised attack may lead to SCC as the potential falls in this zone. Similar observation of the SCC occuring at the borderline is also noted by Turner (4). Visually also, the solution had retained its original yellow colouration.

CS in GVSL solution with 0.15% Sb_2O_3 and 0.03% ferric ions at an OCP of -305 mV, shows only very mildly etched pearlitic phase, but inclusions are non affected. The almost intact nature of the pearlitic phase and the absence of any localised features and corrosion products coupled with an OCP of -305 mV shows that the surface is well passivated. The minor leaching observed adjacent to elongated inclusions may be attributed to the formation of passive layer. Thus the shift in potential to the passivation zone not only had arrested general corrosion, but also had reduced susceptibility of CS to SCC. This confirms earlier observations from polarization and AC impedance results. Thus the influence of inhibitor combination on the pearlite leaching of CS in GV solutions is established and by addition of antimony oxide and ferric ions reduces, to a great extent, the leaching of pearlite from the CS surface, and almost completely arrests general corrosion.

Pourbaix diagram and current potential relationship :

The thermodynamic data pertinent to the corrosion of metals in aqueous solutions have been systematically assembled by Pourbaix in a form that has become known as pourbaix diagram. The data include the potential and pH dependence of metal, metal oxide and metal hydroxide reactions and in some cases complex ions. Along with the specific data for a given metal, the potential and pH dependence of the hydrogen and oxygen reaction are superimposed on the diagram. The Pourbaix diagram for the iron water system is shown in figure -4 The hydrogen reaction line is (a), the line representing the reduction reaction :

$$2H^+ + 2e^- —— H_2$$

and the oxygen line is (b), i.e., the line representing the oxidation reaction :

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

If the potential is moved below the dashed line (more negative) at a fixed pH, H_2 will be evolved. At a fixed pH, movement of the potential above the dashed line (b) will cause O_2 to be evolved. Thus the region between the dashed line indicates the region of thermodynamic stability of H_2O. Generally, the Pourbaix diagram represents well the basic thermodynamic stability of the metal water system and should be considered the starting point for any corrosion study.

pH is a very important factor in corrosion and its control. It can also have major effects on resistance to stress corrosion cracking (SCC) and pitting. A Pourbaix diagram relates the pH of the corrodent and the electrode potential showing possibility of corrosion at a steady state. It actually deals with thermodynamic equilibria and gives a picture of what might happen in a metal corrodent system and gives us clues as to how corrosion could be minimized.

In Figure - 5, theoretical conditions for corrosion of metallic iron in water is given. There are zones of corrosion, immunity from corrosion and passivity. This diagram is useful as a pictorial display of corrosion control measures. If we consider corrosion of iron in neutral water (pH=7) with a corrosion potential of -400 mV, it is seen that it falls in corrosion zone in the Pourbaix diagram. If, some how we shift the potential to -800 mV, iron would be immune to corrosion (cathodic protection) or if we shift it to 0 mV or higher, we can greatly reduce the corrosion rate since the potential shifts to passive zone (anodic protection). By raising the pH also we can reduce corrosion rate since it falls in the passive zone. These three conditions for corrosion control measures is given in Figure - 5. (1)

It is essential here to understand the dependency of corrosion potential and passivation of CS on pH and temperature studied by Parkins et. al. (2), (3), (4), Craig et. al. (5), Davies et. al. (6) and Thomas et. al. (7). Parkins have derived the diagram showing the potential - pH relationship and SCC suscesptible regions for CS in carbonate - bicarbonate solutions at 75 Deg. C. The dissolution related SCC appears to fall within a reasonably well defined domain, with the lowest test temperature being associated with pH values of greater than 9. The absence of visible films at potentials in the ductile region above the cracking domain and the presence of a black film (magnetite), within the latter, suggests that the upper boundary of the cracking domain corresponds to the change from Fe_3O_4 to Fe_2O_3.It was also shown that $FeCO_3$ is present within the films formed in the cracking domain.

Figure - 6 shows the principal phases observed by X-ray analysis and supplemented by microscopical observations for CS surfaces after exposure to solutions of various pH values at different potentials. In this diagram, α - Fe_2O_3 was shown as the outer phase at high potentials (-0.4 V) with underlying Fe_3O_4 film. $FeCO_3$ and Fe_3O_4 at intermediate potentials at lower pH solutions and Fe_3O_4 at intermediate potentials in high pH solutions and Fe (metallic) occupying the outer layers at low potentials.

The precise nature of the dissolution reaction for Fe in carbonate and bicarbonate solutions has been discussed in a number of papers, summarized by Davies and Burstein (6), who favour the formation of the stable soluble complex anion $Fe\ (CO_3)^{2-}$. The intermediates that enter into the dissolution reaction are of lesser importance than the equilibrium phases that eventually form, but the potential of the first oxidation peak is the lower limit of the potential range for SCC of CS in $CO_3\ ^{2-}$ - HCO_3^- solutions and it is established that the crack growth process occurs by the dissolution of Fe. However, the solubility of $FeCO_3$ is such that the soluated Fe will soon precipitate. The difference in the allowable Fe^{2+} concentrations and measured Fe^{2+} concentrations in bicarbonate solutions prompted Davies and Burstein to suggest that the Fe forms a soluble complex. Both solubilities are relatively low so that $FeCO_3$ may be expected to precipitate, especially since the solubility of Fe^{2+} in $CO_3\ ^{2-}$ - HCO_3^- solutions decreases by about an order of magnitude in increasing temperatures from 25 to 75 Deg. C., at which later temperature most of the work described was performed.

The $FeCO_3$ does not form a very protective film, although the protectiveness improves when Fe_3O_4 begins to form, and SCC then can occur, but the least negative potential limit for SCC occurs when the passivating Fe_2O_3 becomes the dominant phase. The peak anodic current and its subsequent decay in moving to less negative potentials is therefore likely to be due to a transition from Fe_3O_4 to Fe_2O_3 as the stable phase. A plot of the first oxidation and reduction peak is shown in Figure - 7, and together with the line calculated from the following equations :

$$2Fe_3O_4 + H_2O \longrightarrow 3Fe_2O_3 + 2H^+ + 2e^- \text{ ——— } (1)$$

$$FeCO_3 + 3H_2O \longrightarrow Fe\,(OH)_3 + HCO_3^- + 2H^+ + e^- \text{ —— } (2)$$

The similarities of the slopes of all three lines and their proximity suggests that it is reaction (1) rather than (2) that is controlling. An addition reason for preferring equation (1) to (2) is found in their temperature sensitivities,

for equation (1)

at 75°C. $Eo = -0.004 - 0.069\ pH$

at 90°C. $Eo = -0.006 - 0.072\ pH$

for equation (2)

at 75°C. $Eo = 0.757 - 0.138\ pH + 0.06 \log (HCO_3^-)$

at 90°C. $Eo = 0.767 - 0.144\ pH + 0.072 \log (HCO_3^-)$

Clearly, the experimental data have the temperature dependency of reaction (1) rather than (2) from which it is reasonable to conclude that the first oxidation and reduction peaks relate to the same reaction, which is concerned with transformations between Fe_3O_4 and Fe_2O_3. This is not to imply that reaction (2) does not occur; indeed it does and reasonably predicts the upper boundary of the domain for $FeCO_3$ formation, but the resistance potentials observed in constant current tests and the associated peaks in potentiodynamic tests do not reflect reaction (2).

When Giammarco-Vetrocoke solution (pH ~ 10) is considered, CS acquires a corrosion potential of around -700 to -750 mV and it falls on the borderline of corrosion, immunity and passive zone in the Pourbaix diagram. Any shift in potential without disturbing the pH which is very high, would drive it to the passivation state. This condition of shifting the potential to more positive values is achieved by the addition of 0.1% vanadium pentoxide (-330 mV), 0.7% pot. dichromate (-400 mV), 0.6% sodium silicate - 0.02% pot. di-chromate (-398 mV), 1% ammonium metavanadate - 0.25% sodium nitrite (-329 mV) and 0.1% amm. metavanadate - 0.1% pot. antimonyl tartrate - 0.01% tartaric acid (-402 mV). The above mentioned potential obtained with the inhibitor additions falls in passive zone of the pourbaix diagram and it is also noted that antimony oxide additions from 0.075% to 0.15% to the GVSL solution does not shift the potential and therefore stays in the corrosion/ immunity/ passive borderline. But the fact that the ferric ion presence in the GV solution which is an unavoidable consequence of the CO_2 removal system changes the line of this argument altogether. It is seen from chapter IV, Table - 1 of OCP values, that any presence of ferric ions in the GVSL solution either shifts the potential towards more negative values (like in pot. dichromate and sod. silicate - pot. dichromate and vanadium pentoxide) or the potential stays there as it is as in other two inhibitor systems.

But with antimony oxide (at 0.075 to 0.14% conc.) and ferric ions above 0.02% conc, it is seen that there is tremendous shift in potentials, all falling in the passive zone in the pourbaix diagram. With 0.15% antimony oxide and 0.03% ferric ions addition the potential of -305 mv is achieved and it seen that it falls deeper into the passive zone. In fact, with 0.15% antimony oxide, the shift of potential starts from 0.01% ferric ions which is not observed with other Sb_2O_3 - ferric ion combination.

It was established from the polarization curves that the shift in potential actually does not necessarily drive it towards passivity zone. In fact it hovers around flade potential and passivity zone. Flade potential zone is the zone where maximum susceptibility towards SCC is possible.

Figure - 8 depicts the relationship between pH/ potential conditions for severe cracking susceptibility of CS in various environments. (8) It is seen from the figure that carbonate/ bicarbonate solution, which is of our interest, falls in the 7-10 pH range at a potential of -150 mV to -570 mV respectively. For a crack to advance in aqueous environments by a dissolution based mechanism it is necessary for not only dissolution to be thermodynamically possible but that a protective film (oxide, mixed oxide etc) also be thermodynamically stable to prevent the degradation of the crack into a pit due to undue corrosion of the crack sides. (8), (9), (10). This view provides a predictive capability for identifying the potential/ pH combinations where danger situation may exist in practice. From Figure - 8 again, cracking of CS in aqueous environments is confined to potential/ pH regions where a soluble species (Fe^{2+}, $HFeO_2^-$) can form when a protective magnetite, mixed oxide or salt film in OH^-, NO_3^-, CO_3^{2-} or PO_4^{3-} containing solutions is ruptured. The action of inhibitors, other than antimony oxide, in presence of ferric ions does not shift the potential out of this danger level. With antimony oxide, especially at 0.15% and in presence of ferric ions the shifting of potential keeps the potential away from this danger level and stays in the passivity zone (Fe_2O_3 in the graph). It is to be noted here that the passivity has to be maintained, since any breakdown in it can initiate a crack growth due to the formation of ferrous ions in the solution.

The importance of passivation kinetics on cracking is studied by many scientists including Staehle (11), Beck (8), Scully (12), Ambrose and Kruger (13), (14), Leidheiser and Kellerman (15), Theus and Staehle (17). They found that slow passivation rates at the crack tip will promote cracking due to excessive dissolution on the crack sides. Whereas very fast rates will minimize the amount crack tip penetration per oxide rupture event. Maximum susceptibility to cracking will occur at intermediate passivation rates. The effect of potential and anions and cations on cracking susceptibility may be quantitatively understood by this concept. Figure - 9 shows electrode potential/ current density relationships for poorly passivating and strongly passivating systems for CS in aqueous environments. It is seen that, cracking susceptibility in poorly passivating systems will be increased by actions which promote passivation. Thus in these systems cracking susceptibility will be greatest in potential ranges adjacent to active/ passive transitions on a polarization curve (Figures - 9a, 9b) shows the effect for strongly passivating systems, where alloys will crack most severely under potential conditions where passivity breakdown occurs.

Whenever the potential is shifted through this active passive area, it has to be obtained with considerable speed and antimony oxide (0.15%) and ferric ions (0.03%) does exactly this, not allowing any time for CS material to stay in this region where cracking susceptibility is maximum. Within minutes of immersing CS in GVSL solution when these inhibitors are present, the potential is found to be shifting towards more positive value and a steady state is obtained at a reasonably faster rate. With other inhibitor systems and especially with the presence of ferric ions the system was established to be poorly passivating in nature. Even with antimony oxide concentrations of 0.075%, 0.1%, 0.13% and 0.14% with more than 0.02% ferric ions the potentials are shifted faster but it falls in active passive borderline where the susceptibility to cracking is maximum. With the presence of ferric ions alone in the GVSL solution, the potential of CS was found to be shifting at a very slow rate (around 24-48 hrs was required to obtain a constant potential). Thus antimony oxide in combination with ferric ions passivates CS in GVSL solution at a faster rate and therefore prevents not only general corrosion but also avoids cracking susceptibility. This is achieved by 0.15% antimony oxide and 0.03% ferric ion concentrations.

The cracking susceptibility/ electrode potential relationship has to be used with utmost caution since these relationships are due to the potential dependence of the rate determining step, not the crack advancement reaction itself (16). But in cases where the rate determining reaction is common to both, it is apparent that cracking susceptibility can be minimized by control of the rate determining reaction. Thus any change in operating condition which alters the corrosion potential so that it enters the range of passivation, thus maintaining the crack rate but allowing appreciable crack tip penetration during each oxide rupture event, will increase the cracking susceptibility (17), (18), (19).

The argument holds good for both strongly passivating as well as poorly passivating systems. For eg., alteration of potential in the positive direction due to the presence of oxidizing species is deleterious for strongly passivating systems (Figure - 3a) to and additions of oxides like PbO (lead oxide) in poorly passivating systems of mild steel/ NaOH or KOH solution.

The effect of addition of Sb and V, to GV solution has been studied by many scientists.

Fyfe David (20) found that SCC of CS in CO_2 absorption is prevented by raising the redox potential of the solution by adding Fe^{3+}, Sb or V ions. Thus, without any additions, and using an alkaline solution containing potassium carbonate 30% and arsenic oxide 10% (As^{3+} : As^{5+} = 9:1), the least negative corrosion potential at a carbonation index of 0.9 at which SCC occurs is -790 mV and with a CI of 1.7 is -660 mV and a solution with a corrosion potential of -800 mV will have it changed to -590 mV by the addition of Fe^{3+} 100 ppm and Sb_2O_3 0.10%.

Plummer (21) points out the importance of corrosion potential measurements in such systems. He found that corrosion potential was maintained at values where SCC is prevented by the combined effect of two inhibitors, one of them (proprietary, hence not revealed), presumably Sb_2O_3 at 0.1% and the other ferric ions. Ferric ions are controlled by injection of air into the system. Direct addition of ferric salts is not recommended since reduction to ferrous state can take place and this would also lead to unacceptably high levels of iron and thereby to solids formation.

Alemanno (22) found that for normal passivation condition in GV solution, it should contain with increasing antimony concentrations at least 150 - 160 ppm of ferric ions.

Atkins et. al. (23) also found that SCC only took place when the electrochemical potential of the steel in contact with the solution lay within a well defined range of values. They reveald that cracking in vetrocoke liquor is not a form of carbonate SCC but is hydrogen embrittlement due to the arsenite. Two inhibitors were identified which synergistically combine to prevent cracking. Ferric ions, according to them, is one of the two components which is produced by air injection into the system. Electrochemical potential thus was proved to be the boundary between cracking and non cracking condition.

Sutcliffe et. al. (24) investigating the SCC of low carbon steels in carbonate solutions have shown cracking to occur in a range of electrode potential anodic to that corresponding to maximum anodic current density, measured potentiodynamically. Similar observations where correlation between electrochemical parameters and SCC was established by Fessler et. al. (25) and Armstrong and Coates (26).

Parkins (27) points the use of inhibitor 'X' (proprietory) at a concentration below 0.1% and ferric ions at 50 - 300 ppm with air injection, effectively changes and controls the corrosion potential and thereby cracking in vetrocoke systems using arsenic oxide. The minimum concentrations of the two inhibitors was found to be interdependent for effective control.

Turner (28) in his patent points out the importance of increasing the redox potential to reduce intergranular corrosion of CS in vetrocoke solution containing arsenic oxide (0.1 - 14%). he found from microscopic investigation, that ferric ions at 100 - 300 ppm and antimony ions at 0.05 - 0.20% increases this redox potential to safe levels and thereby reduces intergranular corrosion.

The above paragraphs though establishes the protective properties of Sb & Fe, there seems to be a controversey over the concentration and passivation potentials.

In the present study, oxygen (introduced as air) and ferric ions act as oxidizing species and presence of antimony oxide shifts the potential to completely passivated condition, but as the potential becomes steady, the cracking susceptibility is considered minimum because of poorly passivating property of the solution.

By performing potentiodynamic scan, prediction of cracking susceptibility is achieved for CS in GVSL solution. It is to be kept in mind that this method of prediction is of use in preliminary failure analysis or risk assessments only.

Plant GVSL solution collected on various intervals of time after additions of Sb_2O_3 in the CO_2 removal system was subjected to electrochemical characterization experiments w.r.t. its passivity characteristics. It is seen that there is a gradual shift in potential (OCP) towards positive direction for CS in GVSL collected on 7.4.90 through 13.6.90, without or with aeration.

If we consider without aerated condition of GVSL solution, it is seen that the OCP had shifted from -748 mV (7.4.90) to -291 mV (13.6.90), but this OCP's fall in the corrosion zone of the polarization curve. Only at -291 mV it is near flade potential zone.

With aerated condition the OCP is again shifted to more positive values reaching -185 mV (31.5.90) and -195 mV (13.6.90).

For GVSL dated 7.4.90 after aeration the OCP of -570 mV falls again in the FC zone, for GVSL dated 23.5.90 OCP is shifted through FC and FP zone and falls in the borderline of FP and passivation zone.

For both GVSL dated (31.5.90) and (13.6.90) the shift in OCP is tremendous, but it is seen from the polarization curve that it is still in the borderline of FP and passivation zone. As argued earlier with the help of pourbaix diagram and electrode potential/ current density relationship diagram, it is clear that these conditions may lead to localised attack like SCC, since crack rate is maintained, but appreciable crack tip penetration occurs at each oxide rupture. This is due to the incomplete passivation of the CS, even if the potentials obtained are very positive when compared with results of CS in Syn. GVSL with Sb_2O_3 and ferric ions. This condition will increase cracking suscesptibility. It is also seen from the chemical analysis (Chapter IV,Table -6) that carbonation index of GVSL (plant) solutions is on the higher side (1.2 to 1.25). This may be due to the higher operating load of the plant and lower As_2O_3 content. Therefore it becomes mandatory that potential should be constantly monitored in the system, so that such a condition does not prevail.

This condition may not be compatible to prevent further localised attack on the CS surface.

In the following paragraphs, the effect of oxidizing anions studied in Syn. GVSL solution w.r.t. its effect on SCC with the help of potential/ current relationship diagrams and zonal characteristics graphs, is discussed.

Taking first, the condition of CS in Syn. GVSL without any inhibitor additions, but containing arsenic trioxide in abundance, it is observed that CS shows an OCP of -745 mV. ASO_3^- or ASO_2^- both are present in the solution. The OCP falls in the free corrosion zone in the zonal characteristics graph. Poorly passivating property of the solution coupled with the presence of oxidising species like ferric ions may prove to be passivating in nature in the long run, but this may lead to not only general corrosion but also to localised corrosion or SCC, since the potential is not shifting towards passive region thus allowing retention time at SCC zone in the polarization curve. The cracking suscesptibility thus increases with AsO_2^- or AsO_3^- and this was amply proved by the real life corrosion problems in our CO_2 removal system. This condition have lead to localised corrosion effects as shown in plates 1 to 5, Chapter II.

Vanadates (VO_2) in the syn. GVSL solution shifts the OCP of CS to -330 mV, but falls in near FP zone where cracking susceptibility is maximum. Any presence of ferric ions shifts this OCP towards more negative values. This condition may retard the cracking susceptibility criteria, but general corrosion will fully occur adding to the sludge formation in the CO_2 removal system. Also, any reduction in the concentration of ferric ions will drive the potential towards more positive values, and therefore will stay in the cracking zone as is seen from the zonal characteristics graph.

Again, we can argue that poorly passivating property of GVSL solution in conjunction with oxidizing species like VO_3 coupled with ferric ions will definitely lead to more general corrosion problems and also will increase cracking suscesptibility due to reduction in ferric ion concentration. It is also known that VO_3 ions are strongly oxidizing in character and therefore it is possible that it oxidizes readily arsenite to arsenate and hence losses its inhibition property. This may be the reason why there is a shift in potential towards more negative values when ferric ions are present. As the VO_3 ions are used up in the oxidation of arsenite and ferrous ions are slowly oxidized by aeration.

Chromate (CrO_4) anions in Syn. GVSL solution shifts the OCP right in to the cracking zone as shown in the zonal characteristics graph. Any presence of ferric ions shifts this OCP again to far inside the corrosion zone. This is again the same situation as encountered with VO_3 ions, the only difference being CrO_4 ions addition without any ferric ions imparts higher cracking susceptibility than VO_3 ions. Again, general corrosion will be of high order in presence of ferric ions. Poorly passivating property of GVSL solution coupled with CrO_4 and ferric ions may lead to highest cracking suscesptibility for CS in such systems. CrO_4 ions are also strongly oxidizing in character and the argument given for VO_3 holds good here also.

Nitrite (NO_2^-) addition to syn. GVSL solution with and without the presence of ferric ions shows almost a constant OCP, but falling well in the cracking zone (FP) in the zonal graph. Actually the susceptibility of cracking can not be overcome because nitrite will be oxidized by air and becomes non effective. Thus poor passivation property of GVSL solution and the non effect of ferric ions presence with NO_2^- ions may lead to higher cracking susceptibility.

Antimony oxide (SbO_2 anions) on the other hand without the presence of ferric ions does not shift the OCP at all and in the zonal graph it stays in free corrosion zone. but the presence of ferric ions, especially more than 0.02% shift the potential to more noble values and passing through the cracking zone enters into the passivation zone. At 0.15% Sb_2O_3 this behavior is not altered even when aeration is discontinued for some time. But it has to be kept in mind that any concentration of Sb_2O_3 less than 0.15% may drive the OCP towards cracking zone. Ferric ion level has to be more than 0.02% to achieve this condition. Once achieving this condition it was seen that the shifting towards cracking zone was not faster even if this level was slightly reduced and reducing aeration of the system also does not shift the potential rapidly towards cracking zone. Poorly passivating characteristics of GVSL solution in presence of Sb_2O_3 and ferric ions shift the OCP to passivation zone and there fore reduces cracking susceptibility substantially, if both concentrations are kept at a concentration known as critical concentrations. The passive layer formed in the most ideal combination of Sb_2O_3 and Fe thus seems to have more stability and compactness not allowing the disturbance in the continuity of the layer and thus preventing any chances of initiation of a crack.

It requires to consider the above situation and to compare with uninhibited GVSL solution in detail, thermodyanamically.

If we compare the ionization energies of antimony and arsenic, for oxidizing their trivalent ions to pentavalent and consequently reducing from pentavalent to trivalent ions, an interesting postulation is derived.

Following are the ionization energies when the metals are oxidized to trivalent ions and then are oxidized to pentavalent ions (29, 30)

$$\mathrm{As} \xrightarrow[\text{KJ/mole}]{2734} \mathrm{As}^{3+} \xrightarrow[\text{KJ/mole}]{3306} \mathrm{As}^{5+}$$

$$\mathrm{Sb} \xrightarrow[\text{KJ/mole}]{2450} \mathrm{Sb}^{3+} \xrightarrow[\text{KJ/mole}]{2950} \mathrm{Sb}^{5+}$$

Considering the GVSL system, this oxidation is done by oxygen molecules introduced in the form of air.

Now, the presence of ferrous ions in the system, either added to the system as done in the laboratory, or is already there in the system due to corrosion of CS as in the real life condition, is oxidized by either As^{5+} or Sb^{5+}, the reaction being :

$$As^{5+} + Fe^{2+} \xrightarrow{E1} Fe^{3+} + As^{3+}$$

$$Sb^{5+} + Fe^{2+} \xrightarrow{E2} Fe^{3+} + Sb^{3+}$$

It is seen that free energy required for the oxidation of Sb^{3+} to Sb^{5+} and reduction of Sb^{5+} to Sb^{3+} is less than what is needed for the same with arsenic ions, i.e. $E2 < E1$. Therefore introduction of air into the GVSL system oxidizes Sb^{3+} ions at a faster rate and consequently Sb^{5+} ions oxidizes Fe^{2+} ions and itself gets reduced to Sb^{3+} ions. If introduction of air is controlled properly, then only Sb^{3+} ions will be oxidized and therefore the problem of sludge formation due to As_2O_5 formation will be reduced. A pertinent point to note here is that As_2O_3 which is added to the GVSL solution increases by almost ten times the absorption capacity of GV solution, but it is found that As_2O_5 has not got this property (31). Therefore undue oxidation of As_2O_3 to As_2O_5 will not only reduce the absorption capacity but also would increase the cracking susceptibility of CS in such systems. It is a common practice with such plants to aerate the system for oxidizing ferrous ions to ferric ions (32). It would be pertinent here to understand the situation arising out of excessive aeration in the CO_2 removal system. The introduction of air which is done primarily to oxidize ferrous ions to ferric ions, mixes with the synthesis gas and if it enters into the methanator section, where carbon monoxide and remaining CO_2 is converted into methane, it increases the methanator temperature. Coupled with the temperature and presence of oxygen and hydrogen creates an alarming situation. The iron removal system by side stream plant which is a part of the CO_2 removal system also faces choking problems due to ferrous/ ferric ions in the GV solution. The heat exchanger tubes and other cold zones also faces sludge formation problems due to the precipitation of iron complexes with arsenic.

By addition of Sb_2O_3, we not only achieve passivation of CS in such system, but also the aeration is controlled and therefore any undue conversion of As_2O_3 to As_2O_5 is also avoided. Excessive aeration which leads to the presence of oxygen in the methanator section is also controlled well. The load on the iron removal system is also greatly reduced by controlled aeration. It is necessary to point here that after passivation of the CS in GVSL solution, the concen tration of iron in the solution will become steady.

Standard electrode potentials of Sb^{5+} and As^{5+} when it is reduced to their trivalent state is also noteworthy (33),

$$Sb^{5+} + 2e \longrightarrow Sb^{3+} \quad -0.428 \text{ mV}$$

$$As^{5+} + 2e \longrightarrow As^{3+} \quad -0.670 \text{ mV}$$

The more noble potential of Sb^{5+} when compared with the potential of As^{5+} also greatly helps in the oxidation of ferrous ions to ferric ions at the surface of the CS material.

Coupled with the lower ionization energy required and more noble potential of Sb^{5+} to Sb^{3+} ions, when compared with these values for arsenic ions, Sb_2O_3 is capable of passivating the CS material in GVSL solution and therefore general corrosion and localised attack like SCC is greatly reduced.

In the above paragraphs the corrosion of CS in synthetic and plant GVSL solutions studied by polarization, AC impedance, pearlite leaching and measurement of corrosion potential have been discussed. The theories discussed above and the references cited shows the inhibitive action of antimony trioxide in conjunction with ferric ions and air. Of all the inhibitors studied chromates and vanadates seem to have negative effect of iron on their inhibitive action. Nitrite alongwith vanadate and tartrate with vanadate are unaffected by presence ferric ions in the solution.

However, the presence of ferric ions above a certain level and aeration in the solution containing antimony trioxide renders the metal surface passive, thereby reducing corrosion current, double layer capacitance, corrosion rate, leaching of pearlitic phase and increasing polarization resistance, corrosion potential and inhibitor effeciency, substantiated by electrochemical theory of corrosion and its inhibition, potential - pH relationship, thermodynamics of oxidation - reduction of antimonite ions and phase characterisation leading to following conclusions.

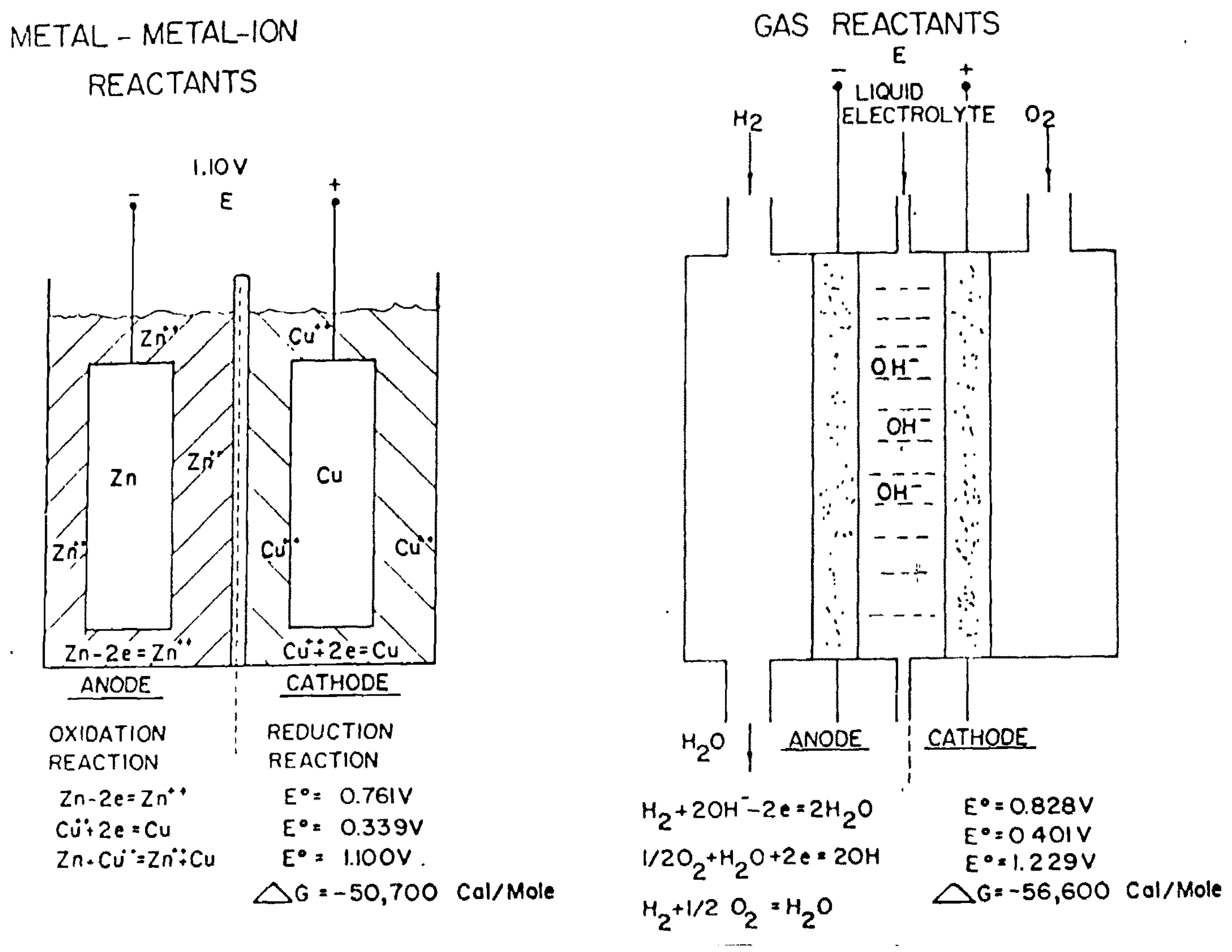


FIG.1 : POLARITY CONVENTION FOR OXIDATION - REDUCTION CELLS

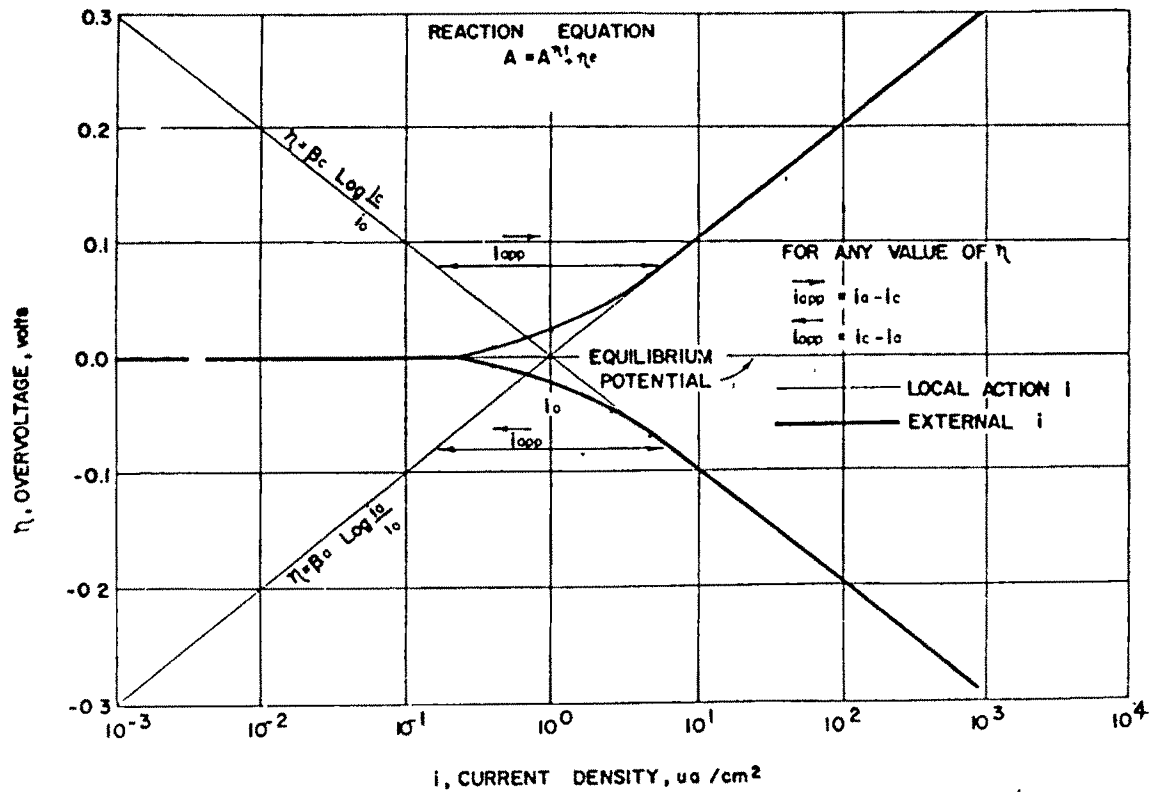


FIG.2 : ACTIVATION POLARIZATION OF A REVERSIBLE ELECTRODE

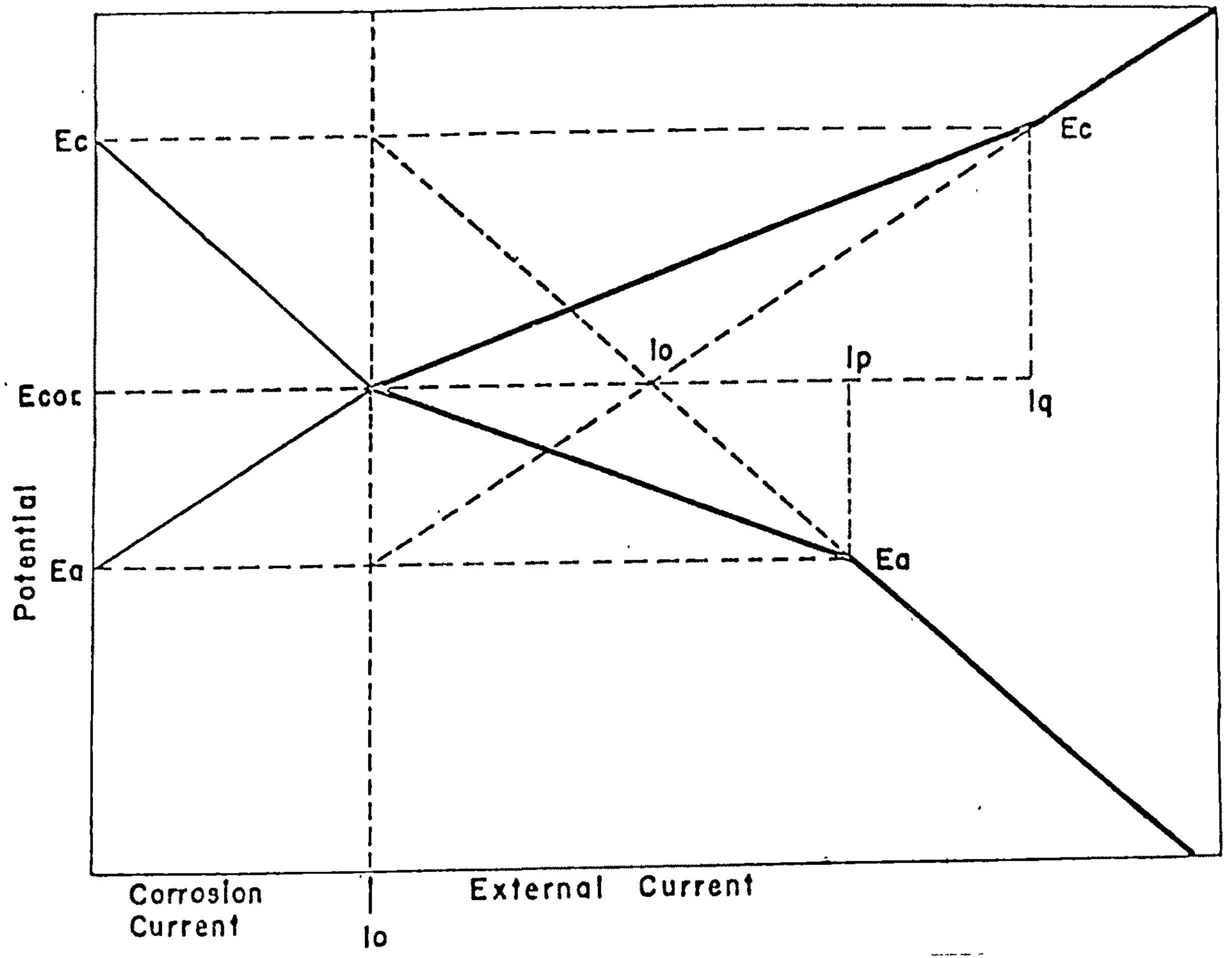


FIG.3 : IDEALISED REPRESENTATION OF THE EFFECT OF EXTERNAL CURRENT ON A MIXED CONTROL CORROSION CELL

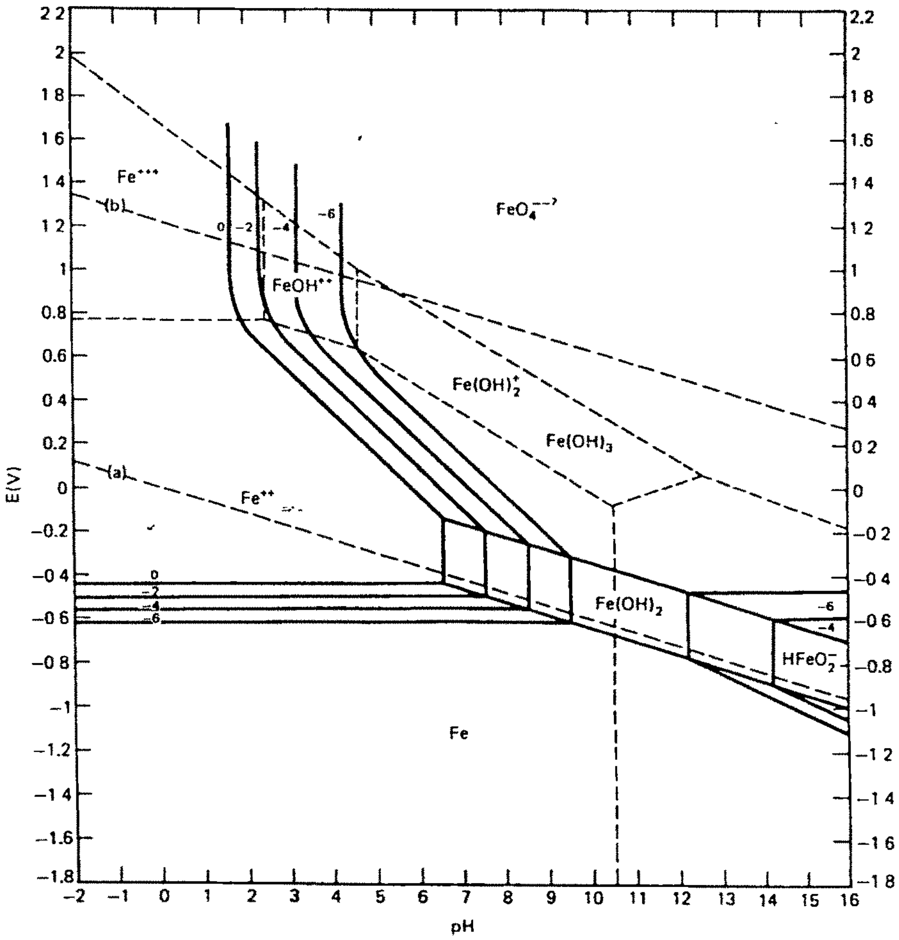


FIG.4 : POTENTIAL - PH EQUILIBRIUM DIAGRAM FOR SYSTEM IRON - WATER, AT 25 DEG.C

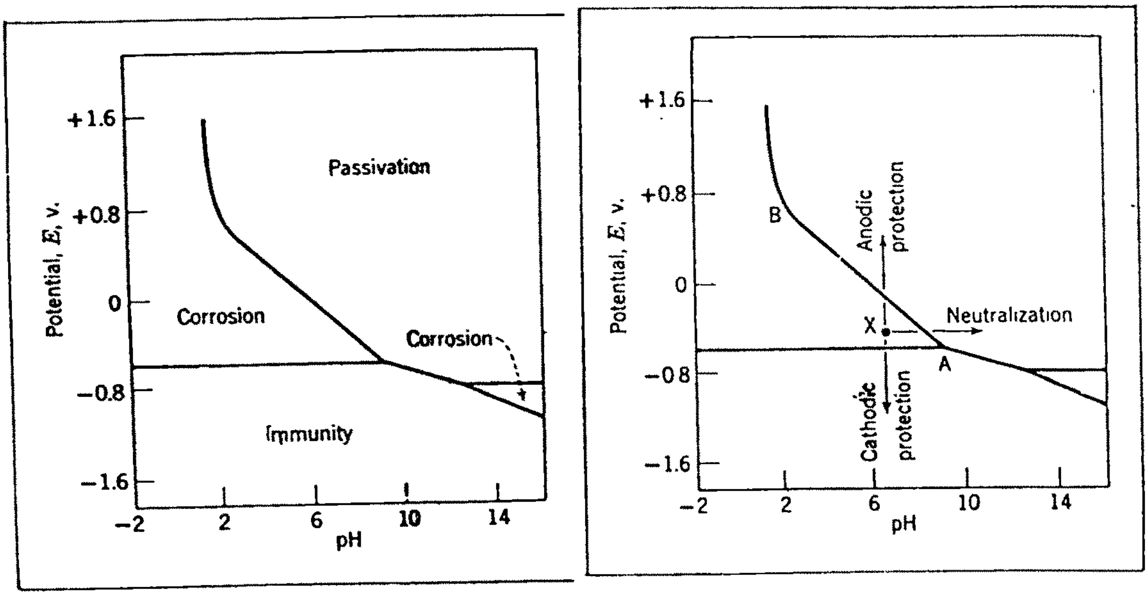


FIG.5 : POURBAIX DIAGRAMS SHOWING PASSIVITY, IMMUNITY AND CORROSION ZONES AND EFFECT OF CHANGE IN ENVIRONMENT

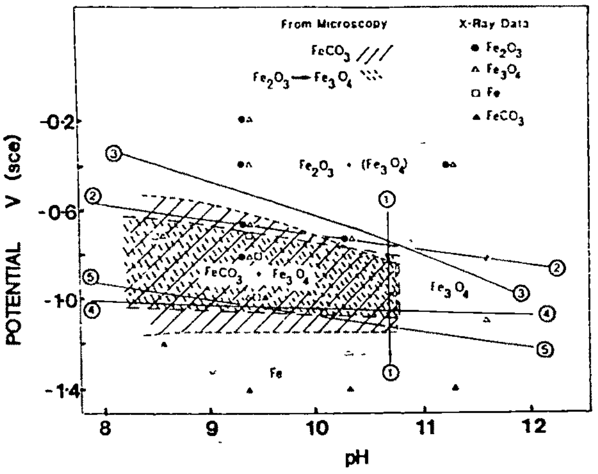


FIG.6 : PRINCIPAL PHASES OBSERVED ON STEEL SURFACES AFTER EXPOSURE TO VARIOUS SOLUTIONS AT DIFFERENT POTENTIALS

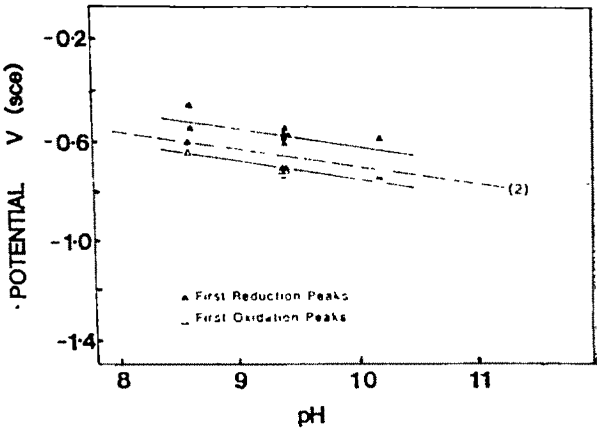


FIG.7 : EFFECTS OF SOLUTION PH ON THE POTENTIALS OF THE FIRST OXIDATION AND REDUCTION PEAKS OBSERVED ON STEEL SURFACES IN POTENTIODYNAMIC TESTS AT 75 DEG. C

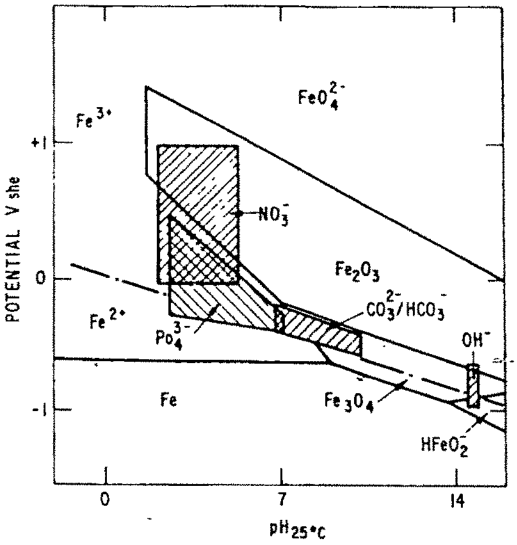
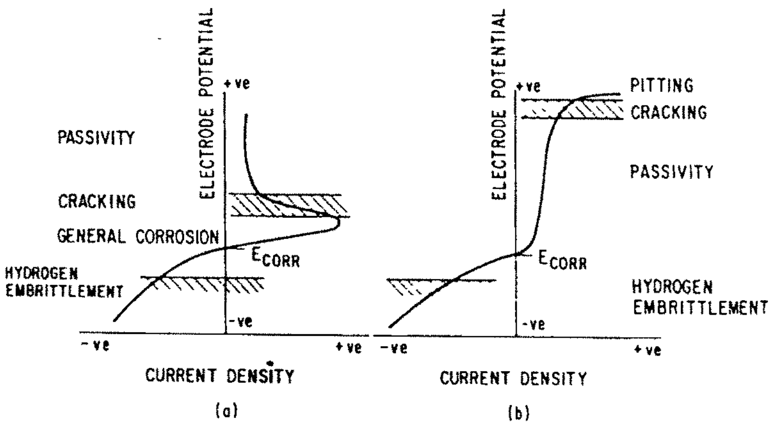


FIG.8 : RELATIONSHIP BETWEEN PH/POTENTIAL CONDITIONS FOR SEVERE CRACKING SUSCEPTIBILITY OF STEEL IN VARIOUS ENVIRONMENTS AND THE STABILITY REGIONS FOR DIFFERENT SPECIES



(a) (b)

FIG.9 : SCHEMATIC ELECTRODE POTENTIAL / CURRENT DENSITY RELATIONSHIPS FOR (a)'POORLY' PASSIVATING AND (b) 'STRONGLY' PASSIVATING SYSTEMS

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