Chapter (4-C)

Corrosion Kinetics- Part (C):

Mixed Potential Theory, Passivity, Environment & Material Effects

Oct., 11th , 2017

Mixed Potentials Theory

- Net current density on freely-corroding electrode must be zero.

- Therefore potential (E_{corr}) will be that at which anodic and cathodic current densities are equal *(lines intersect)* and opposite.

- Sometimes called a *mixed equilibrium* Potential because the system is *not at true electro-chemical equilibrium.*

Combined Electrodes

Zinc corrodes in an acid solution. Anodic and cathodic reactions take place simultaneously on the surface:

$$Zn = Zn^{2+} + 2e^{-}$$ Anodic

$$2H^{+} + 2e^{-} = H_2$$ Cathodic

The two half-cell potentials:

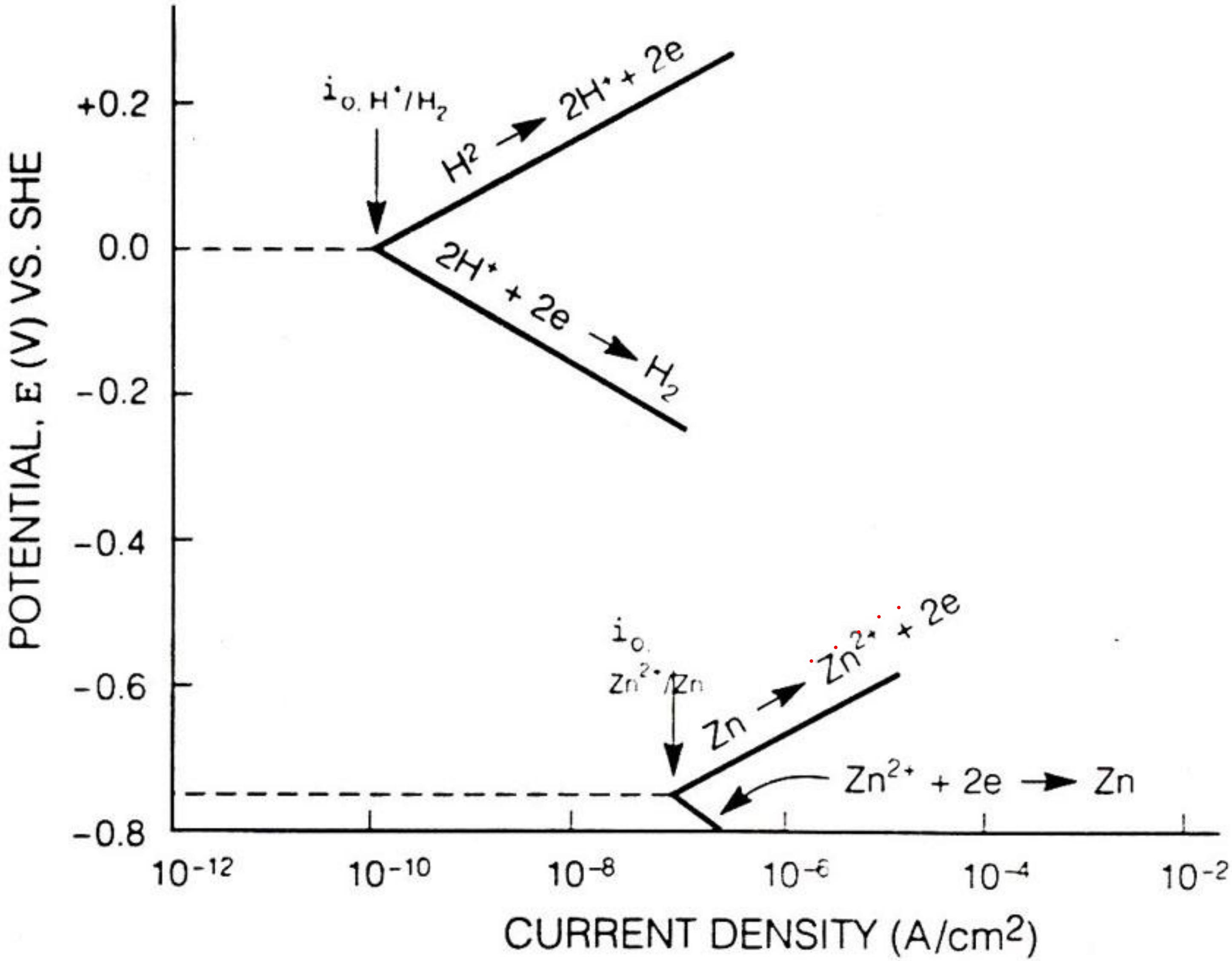
$$E_{Zn/Zn^{2+}}$$

$$E_{H^{+}/H_2}$$

cannot exist separately on a conductive surface ……

They must change to a common *intermediate* potential called:

the "mixed potential" or "corrosion potential" E_{corr}

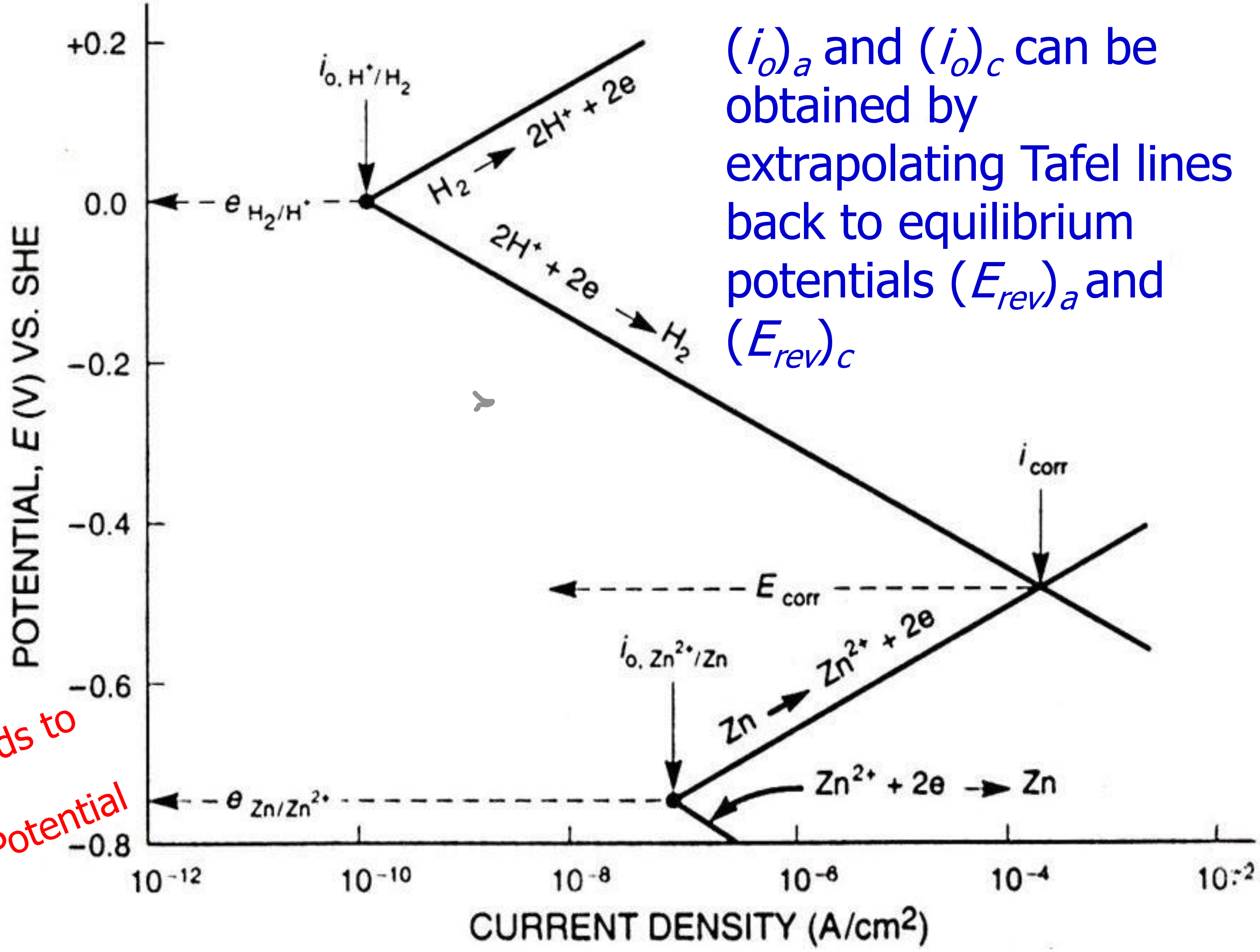


Anodic and cathodic half-cell reactions present simultaneously on a corroding zinc surface.

Evans Diagrams

The bigger the difference in equilibrium potentials (ΔE_{rev}), the bigger i_{corr}

$(i_o)_a$ and $(i_o)_c$ can be obtained by extrapolating Tafel lines back to equilibrium potentials $(E_{rev})_a$ and $(E_{rev})_c$



Io corresponds to Standard Electrode Potential

Polarization of anodic and cathodic half-cell reactions for zinc in acid solution to give a mixed potential, E_{corr}, and a corrosion rate (current density), i_{corr}.

Evans Diagrams

1. In the Evans diagram, the intersection of the two polarization curves occurs @ the corrosion current, i_{corr} (as shown in the previous plot)..
2. The exchange currents, $(i_o)_a$ and $(i_o)_c$ can be obtained by extrapolating the Tafel lines back to the ***equilibrium potentials*** $(E_{rev})_a$ and $(E_{rev})_c$ …

   $$E_{rev} = E_{equ} = E_o - (RT)/(nF). \ln(\text{activity quotient})$$

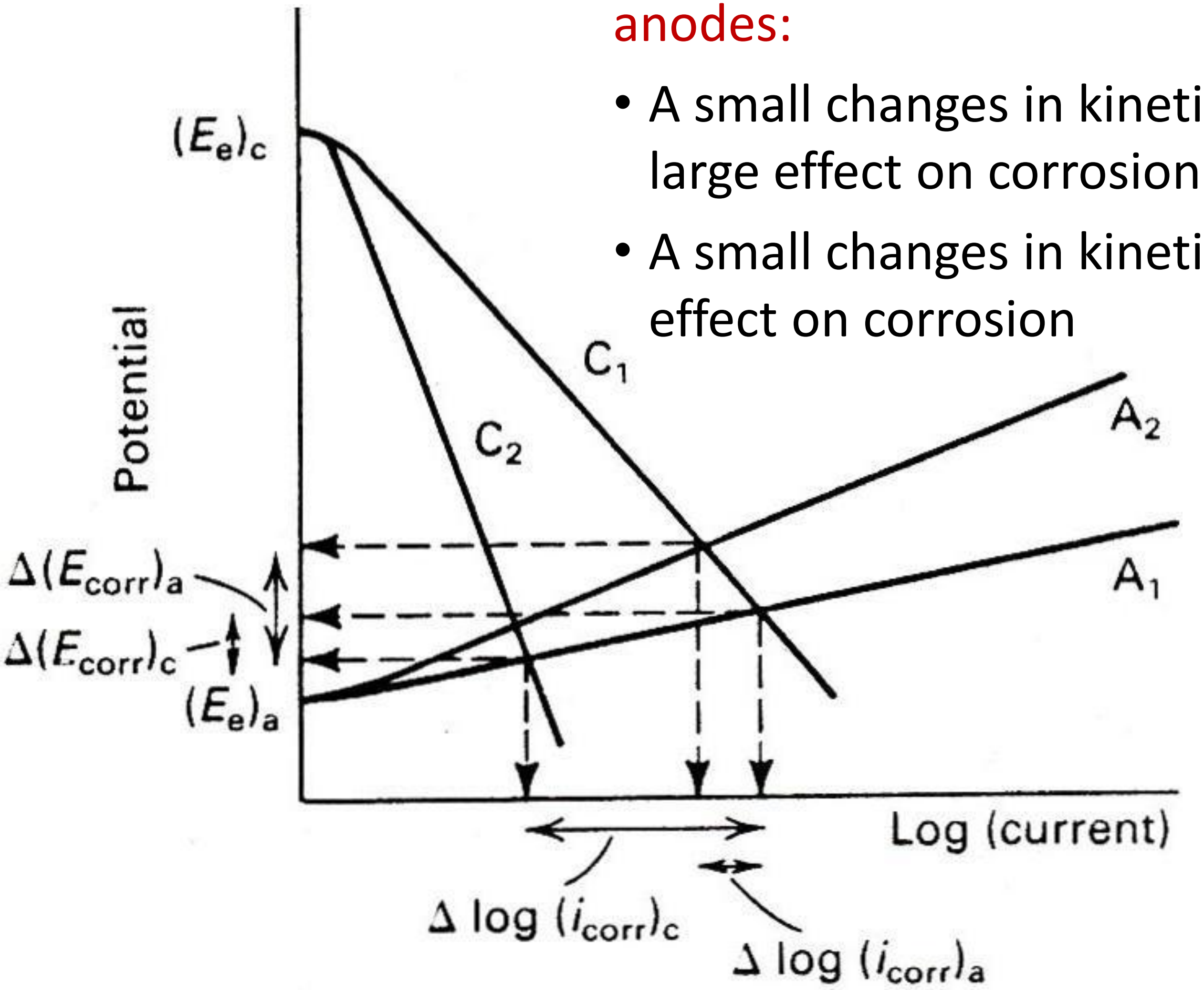
3. The origin ($i = 0$) is not shown on a logarithmic plot.
4. The bigger the difference in equilibrium potentials (bigger ΔE_{rev}), the bigger the value of i_{corr} (or the greater the corrosion rate)…

Evans Diagrams

- The slowest reaction controls the rate of corrosion. Normally this is the cathodic reaction.

Figure: Consider one anode with two alternative cathodes & one cathode with two alternative anodes:

- A small changes in kinetics of cathode have a large effect on corrosion rate.
- A small changes in kinetics of anode have small effect on corrosion



Corrosion Tendency vs. Corrosion Rate

$$\eta_A = b_a \log \frac{i_a}{i_o}$$

$$\eta_c = b_c \log \frac{i_c}{i_o}$$

Standard potentials of Fe and Zn oxidation:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad \text{(-0.44V SHE)}$$

$$Zn \rightarrow Zn^{2+} + 2e^{-} \quad \text{(-0.76V SHE)}$$

- Zn corrosion would be more prevalent than Fe corrosion based on thermodynamic considerations (emf series of potentials).

- However, due to *kinetics* considerations:

  1. low exchange current density for **hydrogen reduction** on zinc (10^{-11} A/cm^2) "higher η_{act}", compared to that of H_2 reduction on iron (10^{-6} A/cm^2),

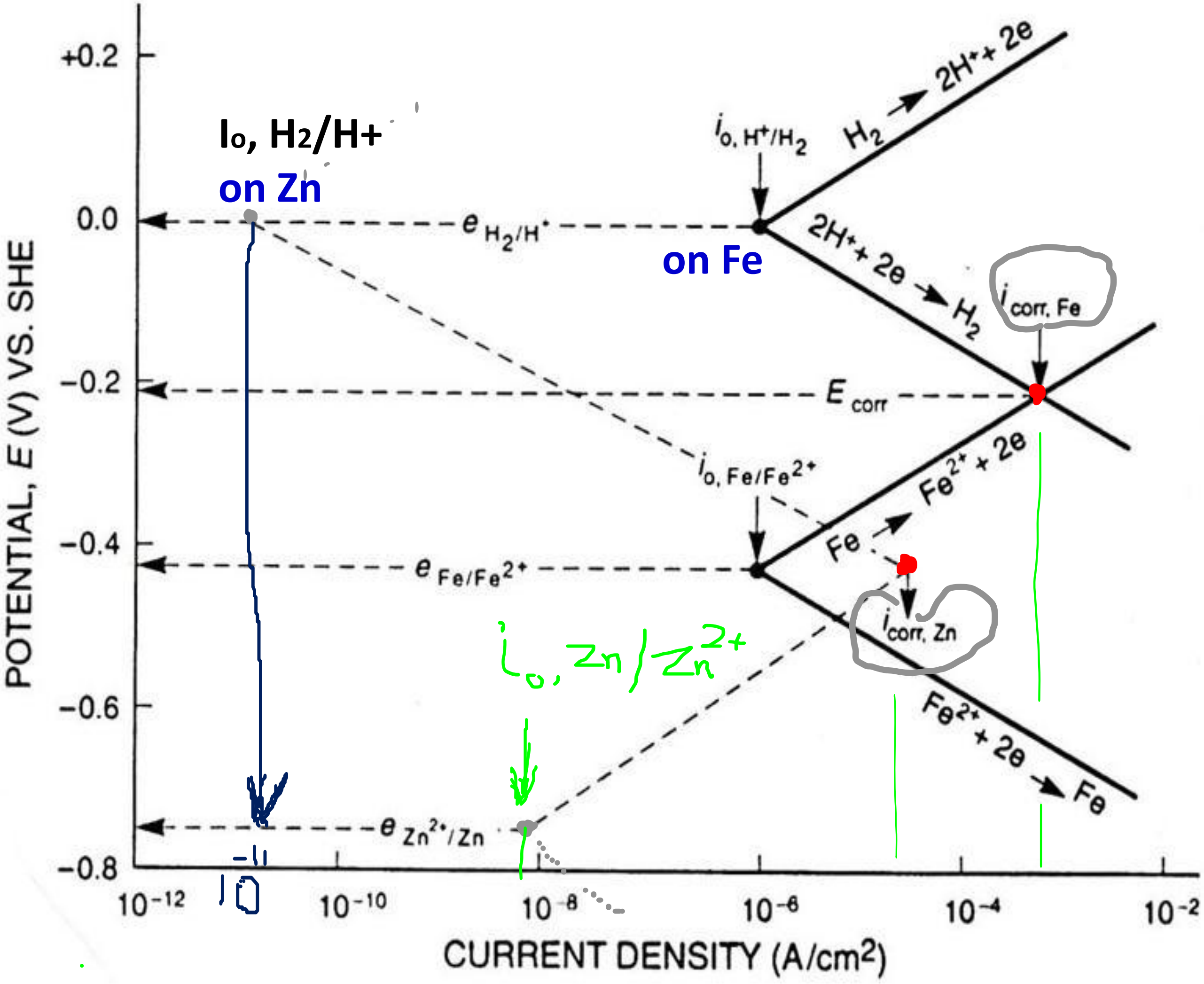
  2. lower exchange current density for **zinc dissolution** (10^{-8} A/cm^2) "higher η_{act}", compared to iron dissolution (10^{-6} A/cm^2), then

the corrosion rate of Fe is faster than that of zinc: $i_{corr, Fe} > i_{corr, Zn}$

(lower i_o means higher η (see Tafel's equation)

Conclusion: Iron is better a catalyst for H_2 evolution from acid than Zn.

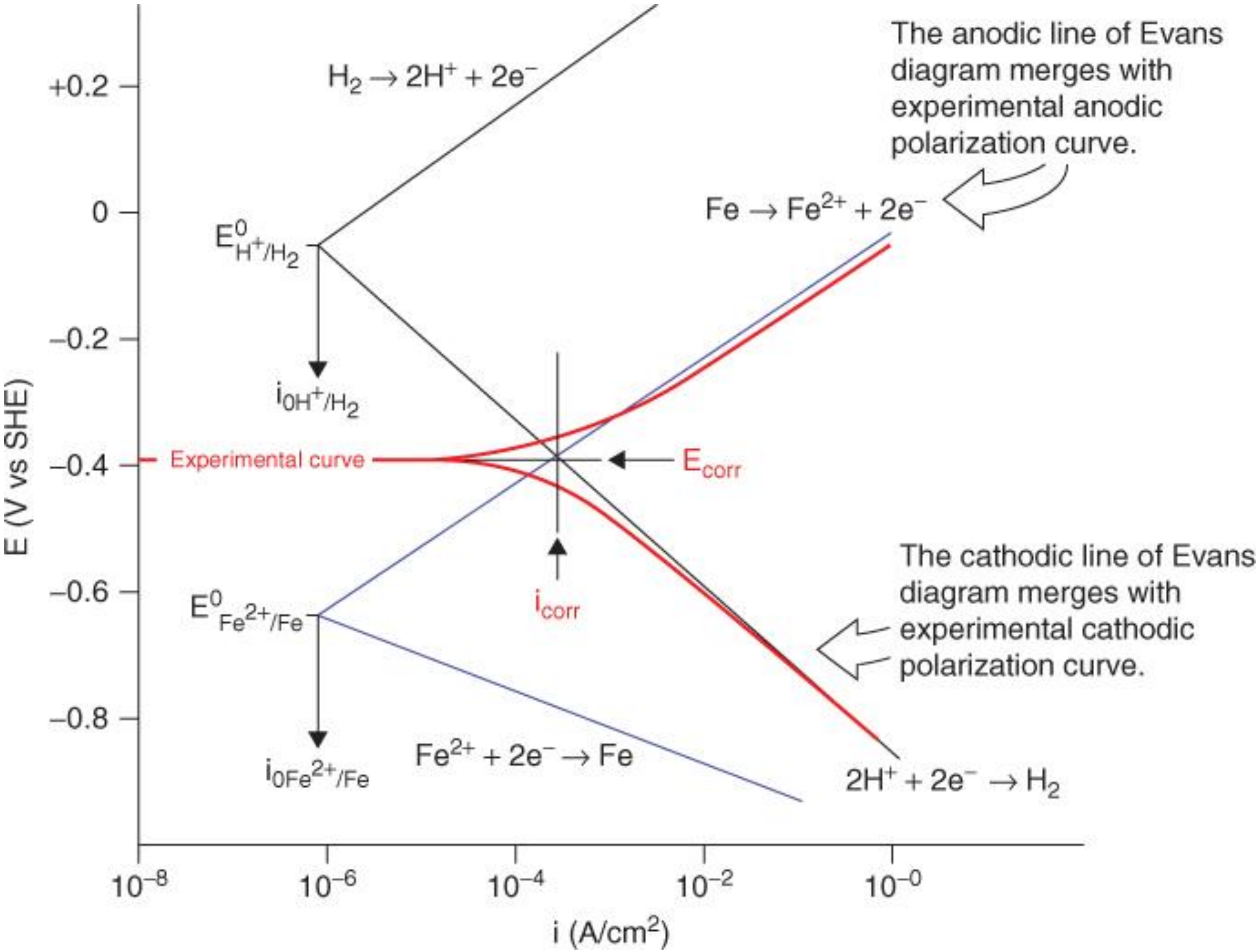
Evans Diagrams



Comparison of electrochemical parameters for iron and zinc in acid solution, demonstrating the importance of i_o on determination of corrosion rates.

N.B. Currents must balance for the coupled reactions. Current densities are equivalent to currents when surface areas are accounted for.

Tafel Extrapolation & Evans Diagram: Fe in acid



The anodic line of Evans diagram merges with experimental anodic polarization curve.

The cathodic line of Evans diagram merges with experimental cathodic polarization curve.

Environment & Material Effects

1. Effect of Galvanic Coupling
2. Effect of Electrode Area
3. Effect Oxidizers
4. Effect of Aeration (presence of oxygen)
5. Effect of Velocity
6. Effect of Temperature
7. Effect of Corrosive Concentration
8. Effect of Inhibitors and Coating

Refer to the textbook of Mars Fontana:
Corrosion Engineering, 3rd edition, 1986

1. Effect of Galvanic Coupling-1

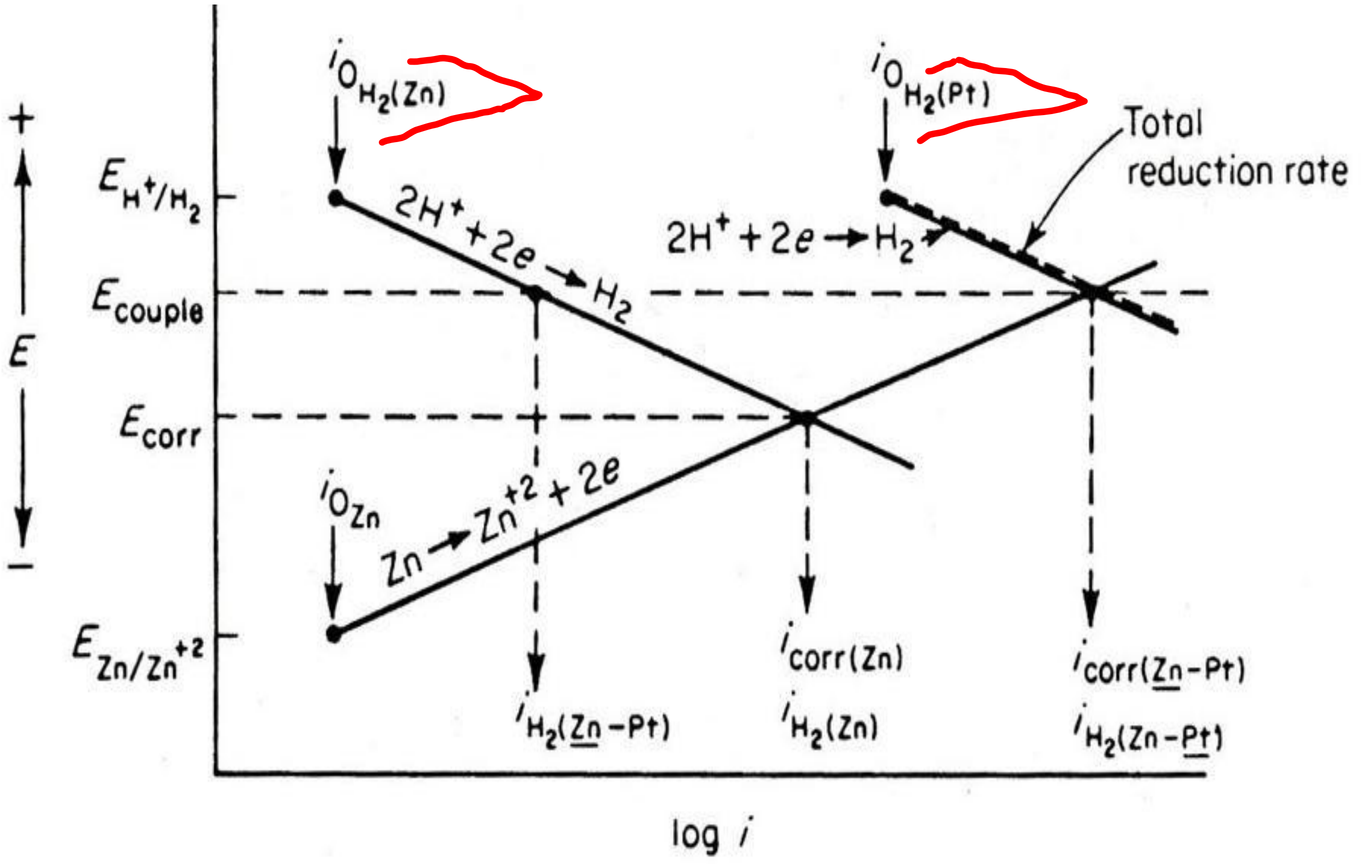
- Isolated zinc corrodes in acid …

$$Zn \rightarrow Zn^{2+} + 2e$$

$$2H^{+} + 2e \rightarrow H_2$$

- Platinum is inert in acid.
- When Zn & Pt are coupled:
  1) zinc corrosion increases
  2) H_2 evolution occurs on platinum rather than on zinc:
     - Activation polarization of H_2 reduction $\eta_{H2/Pt}$ is less than $\eta_{H2/Zn}$
     - Pt is a good catalyst for H2 evolution; Zn is not.

1. Effect of Galvanic Coupling



NOTE: the thermodynamic driving force remains the same

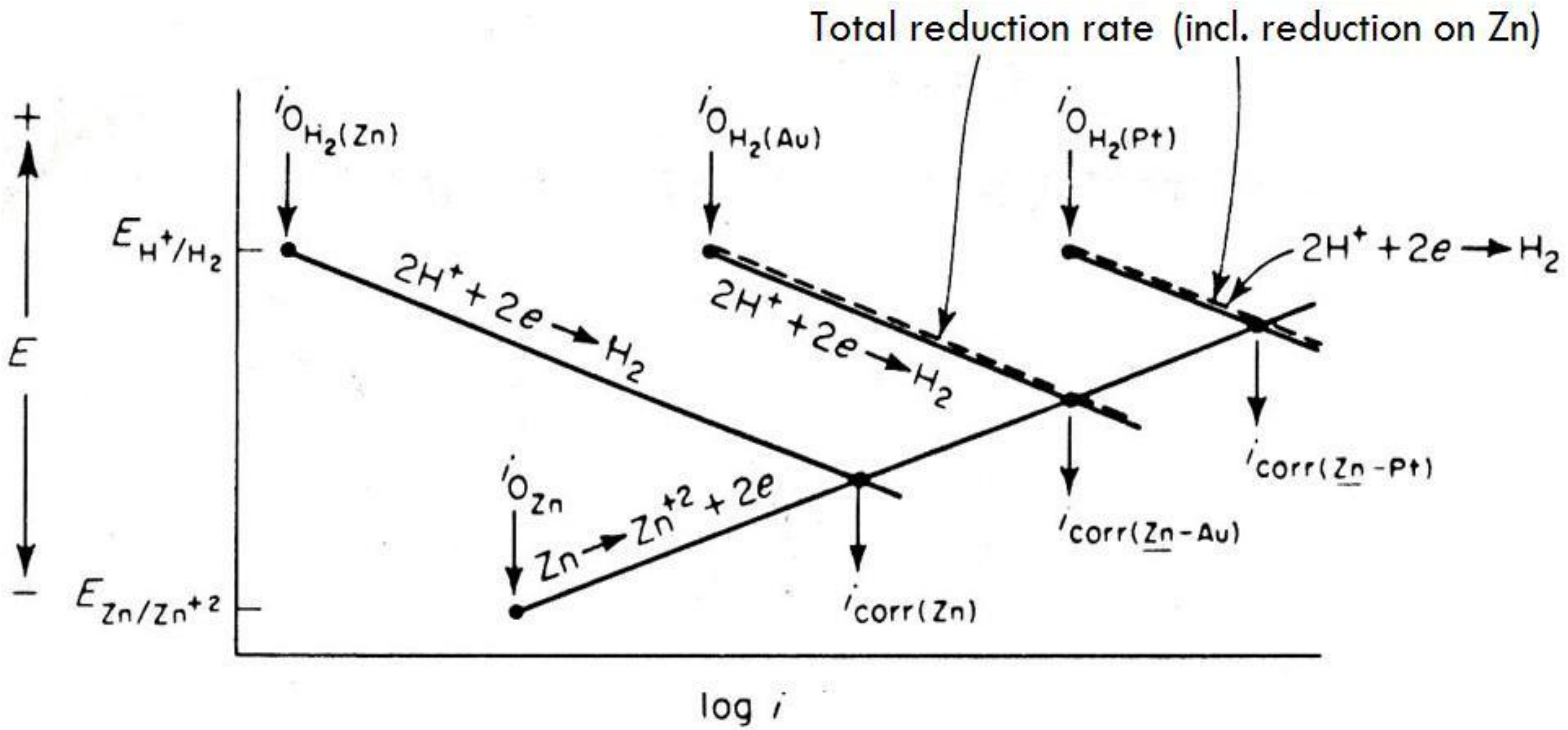
$$\left(\Delta E_{therm} = (E_e)_{H^+/H_2} - (E_e)_{Zn/Zn^{2+}}\right)$$; but the kinetics change !

Exchange currents on Zn and Pt are different:

1. $E_{Corr,couple} > E_{Corr,Zn}$ 2. H_2 evolution on Zn decreases. 3. $i_{Corr,couple} > i_{Corr,Zn}$

1. Effect of Galvanic Coupling

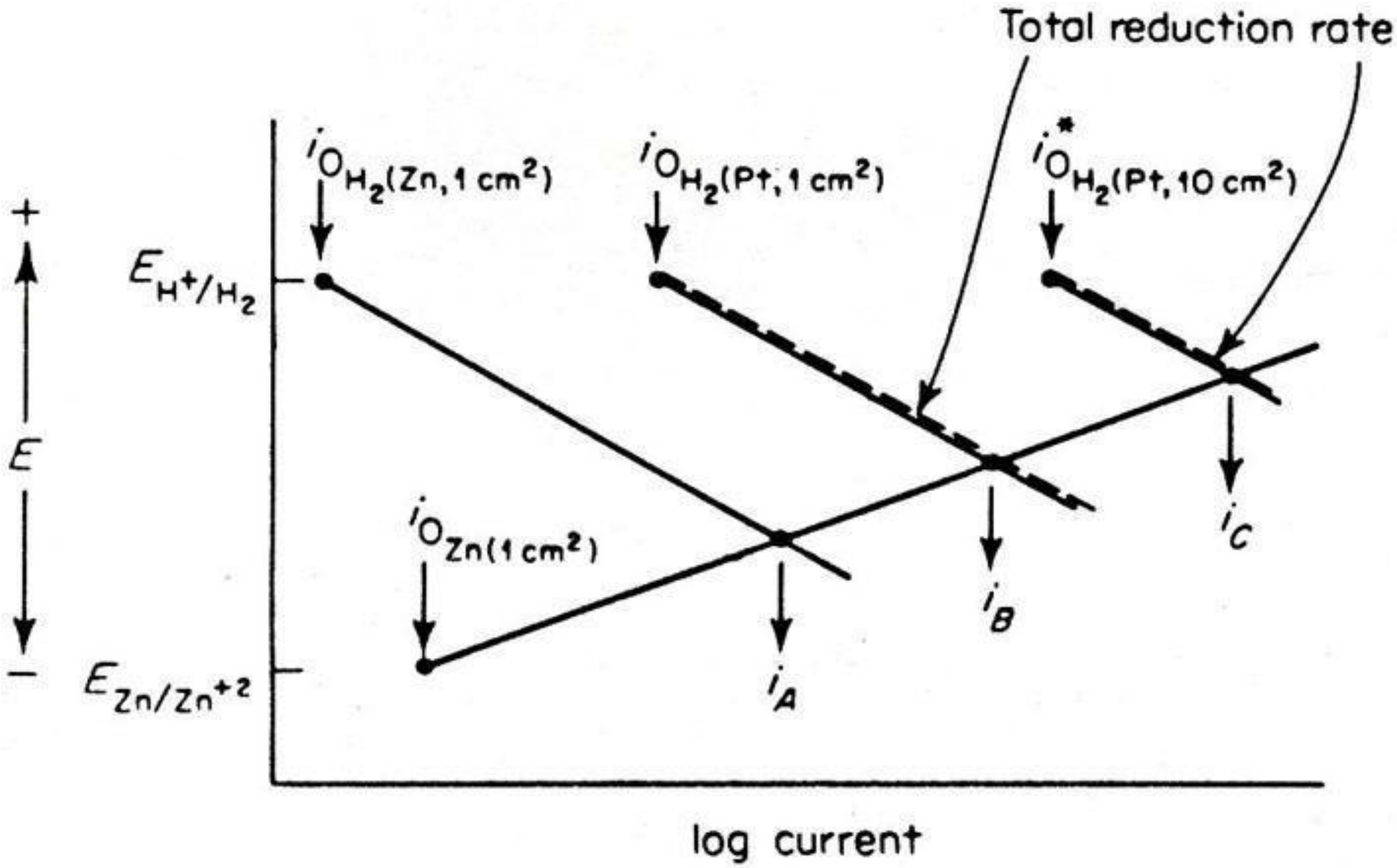
The more efficient the hydrogen evolution process (i.e., the higher the exchange current), the larger the effect of galvanic coupling …



Comparison of zinc-platinum and zinc-gold couples (equal areas).

Pt is more efficient a cathode for H_2 evolution than Au

2. Effect of Electrode Area



Galvanic corrosion of zinc-platinum couples at different cathode (Pt) areas

3. Effect of Oxygen and Oxidizers

What happens if we add an *oxidizer with a half-cell electrode potential much more noble* than any others present (e.g. adding ferric-ferrous salts to a metal M in an acid solution).

Experimental observations:

1. *Corrosion potential E_{corr} shifts to more positive values*
2. *Corrosion rate increases*
3. *Hydrogen evolution rate is reduced*

Use charge conservation and find E_{corr} as the point where the two oxidation and reduction *current densities* are equal.

3.Effect of Oxygen and Oxidizers-2

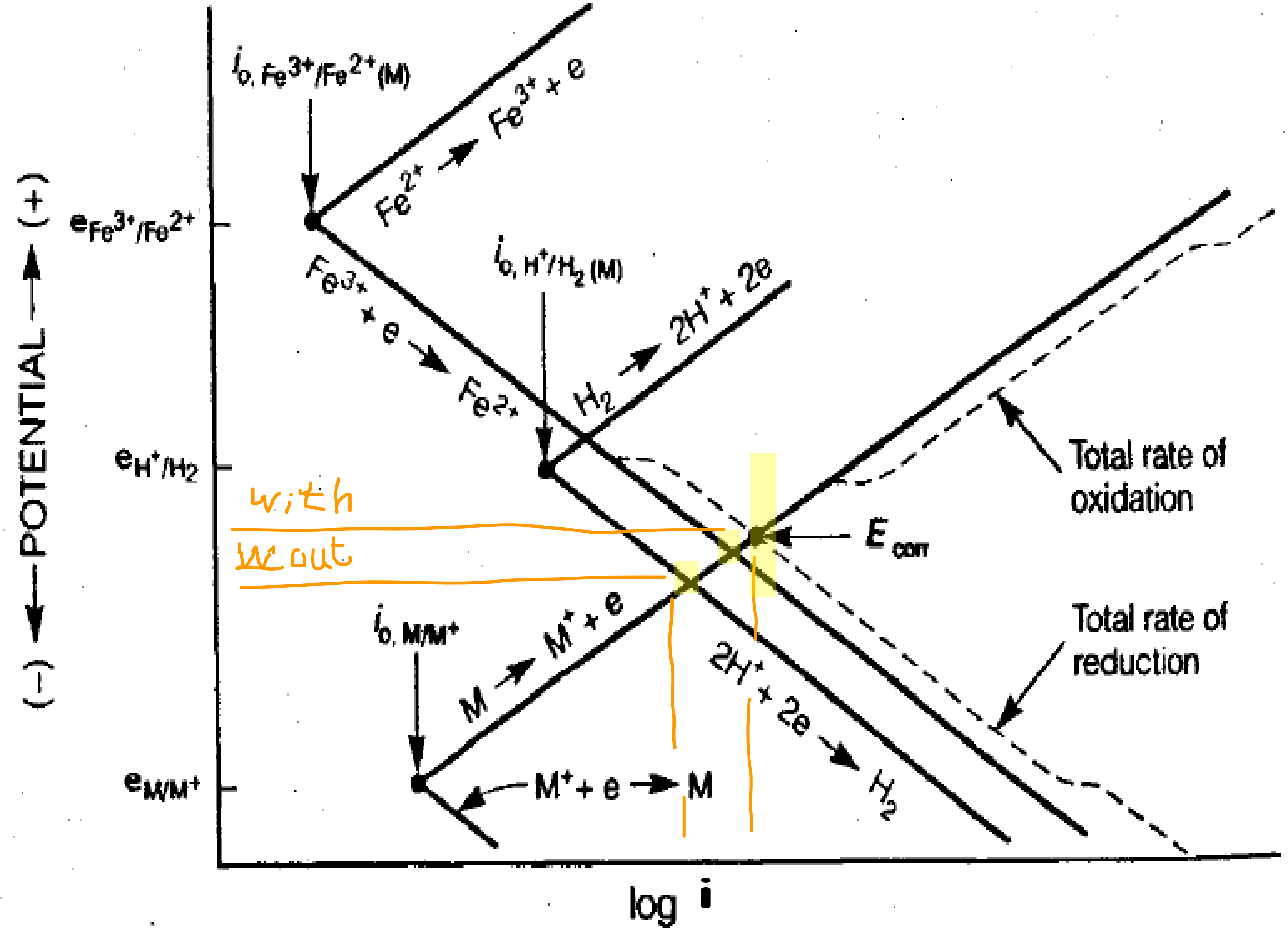
- Total rate of reduction is the *sum of all three* possible reduction reactions at any given potential

- Total rate of oxidation is the *sum of all three* possible oxidation reactions at any given potential

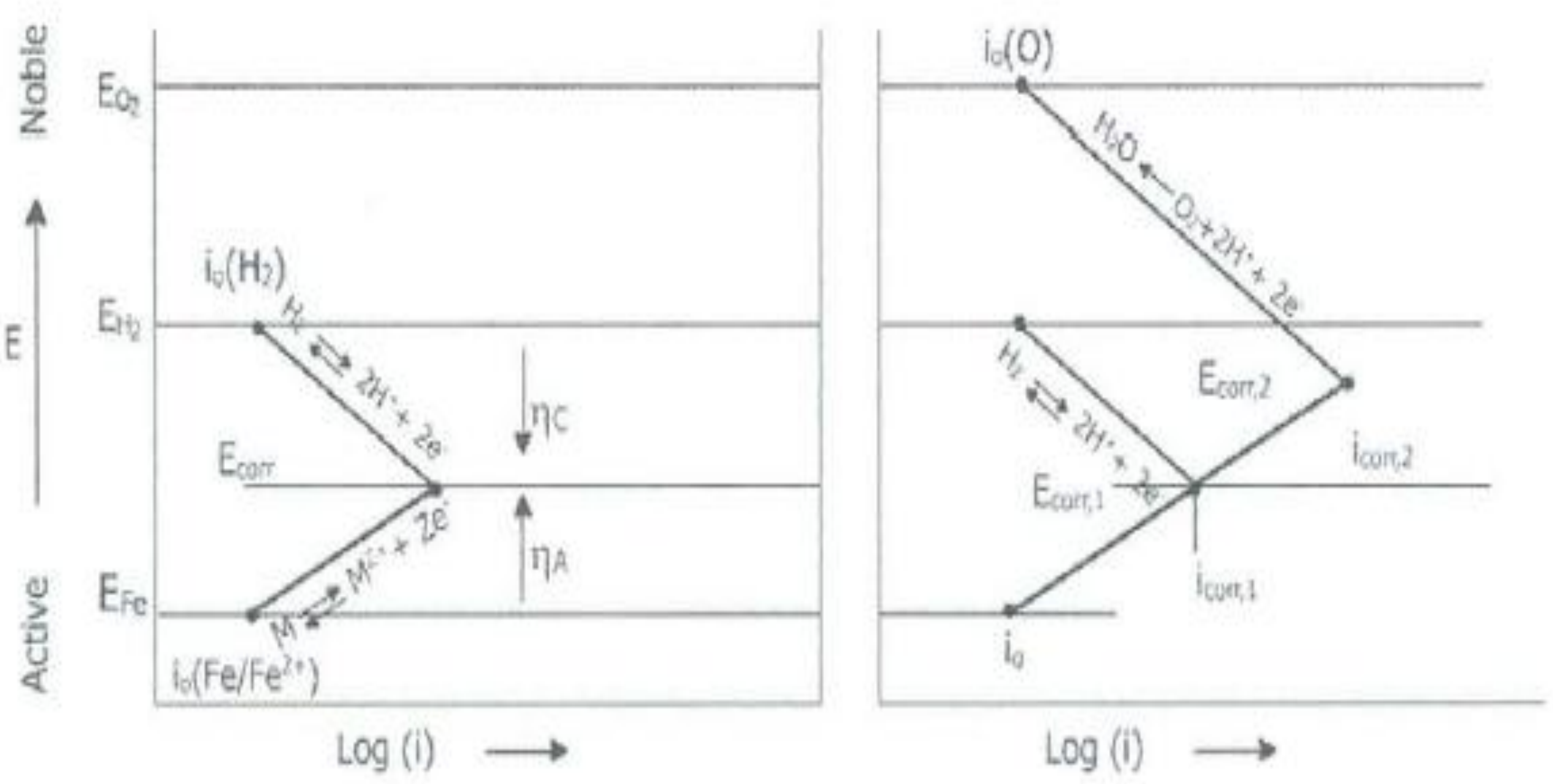
- E_{corr} is defined by the intersection of the *total* oxidation and *total* reduction lines

- In the example (Figure on next slide):
  - *At E_{corr} the metal oxidation is the only oxidation so the total oxidation current density is the corrosion rate*
  - *The total reduction current is the sum of the iron and hydrogen reduction*
- Determine the mixed potential E_{corr} for a corroding metal M exposed to acid solution with a second oxidizer, Fe^{3+}/Fe^{2+} , present.

3. Effect of Oxygen and Oxidizers-3



4. Effect of Aeration (Presence of oxygen)



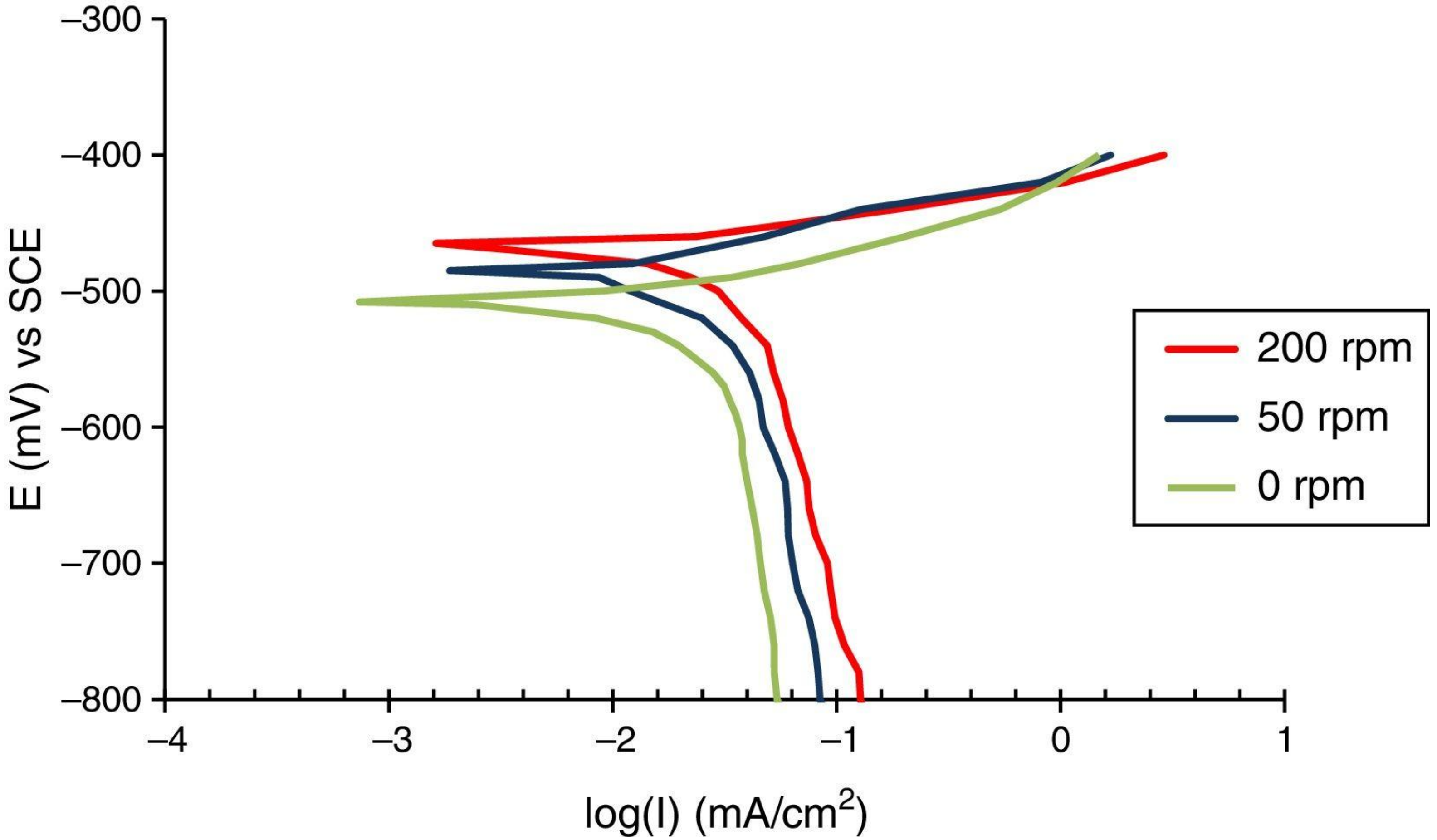
(a) Deaerated solution

(b) Aerated solution

Figure 3.14 Effect of aeration and deaeration

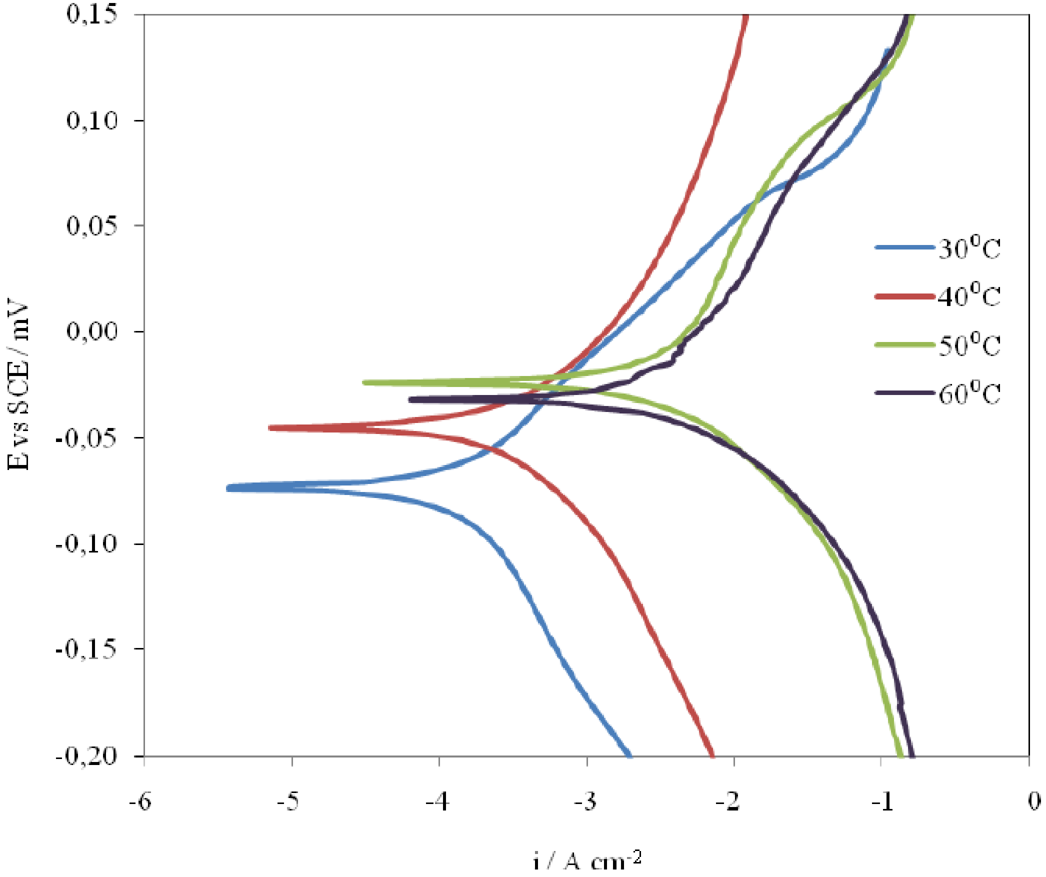
5. Effect of Velocity

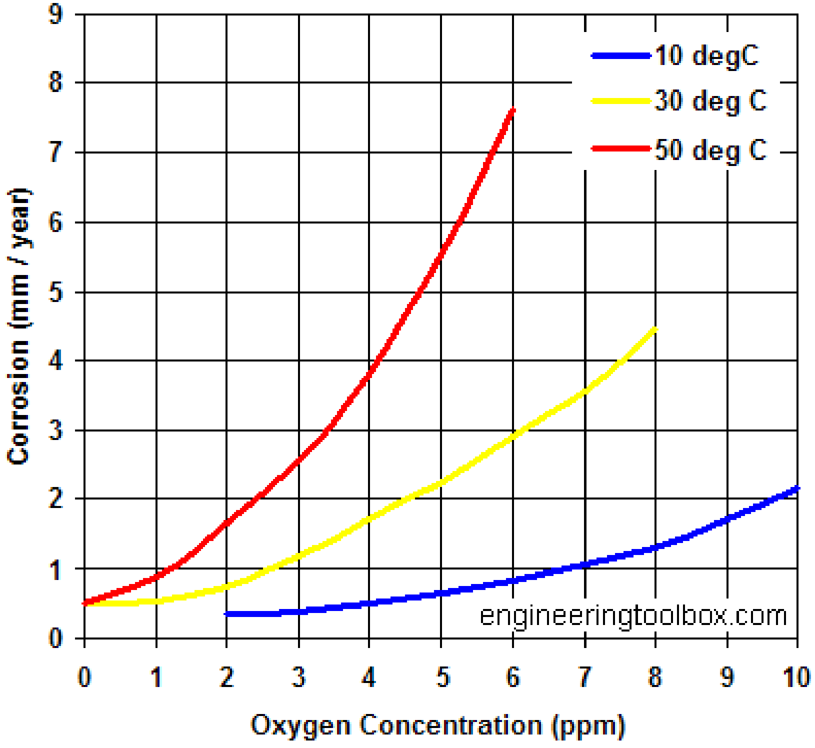
- Polarization curves for the corrosion of Fe in 1% $MgCl_2$ at fixed temperature of 30°C.



6. Effect of Temperature

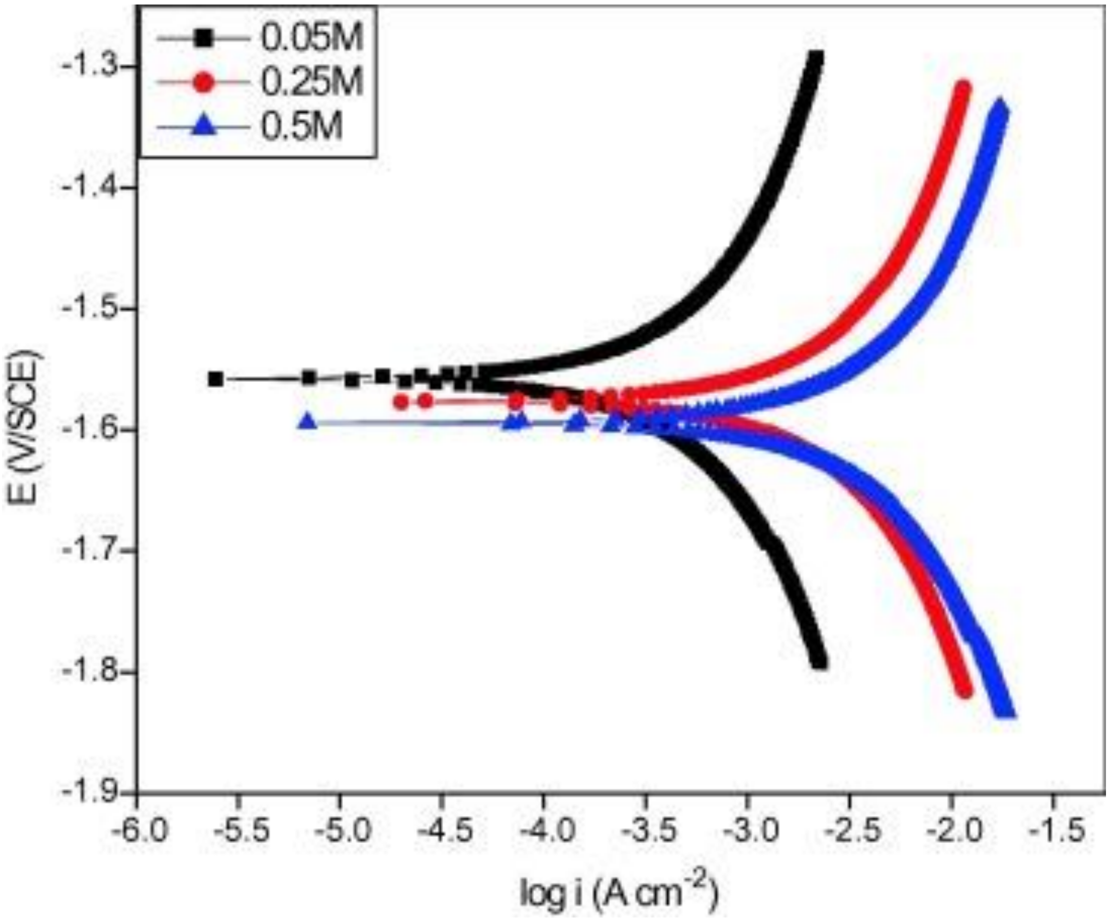
- Temperature increase promotes corrosion, specially in oxygenated media





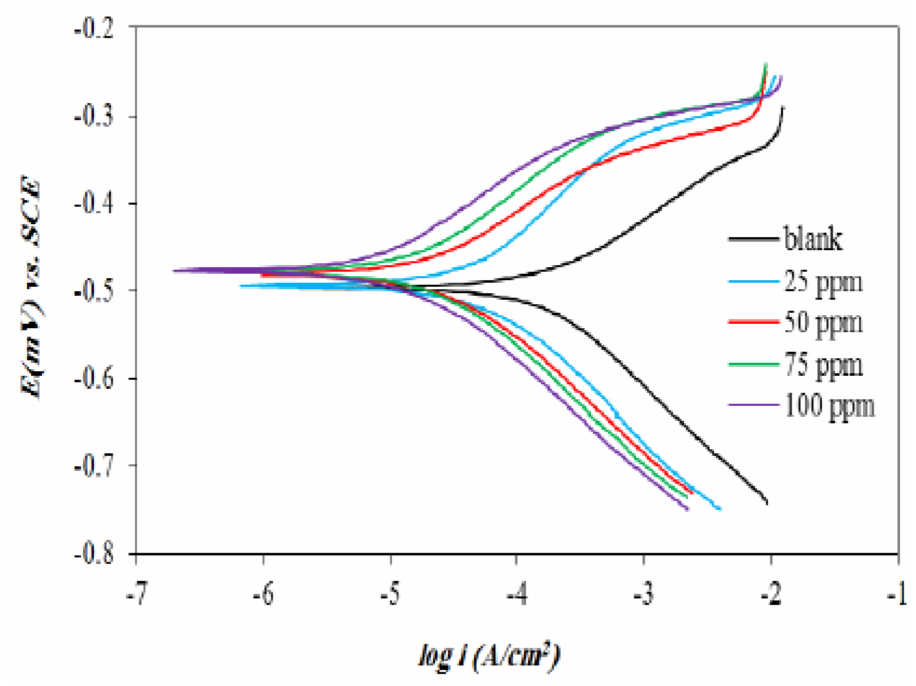
Substrate: Steel pipes

7. Effect of Corrosive Medium Concentration



Tafel polarization curves for 6063 aluminium alloy in different concentrations of NaOH at 30°C.

8. Effect of Inhibitors and Coating



Polarization curves for **mild steel** obtained in 1.0 M HCl solution containing different concentrations of chemical inhibitor

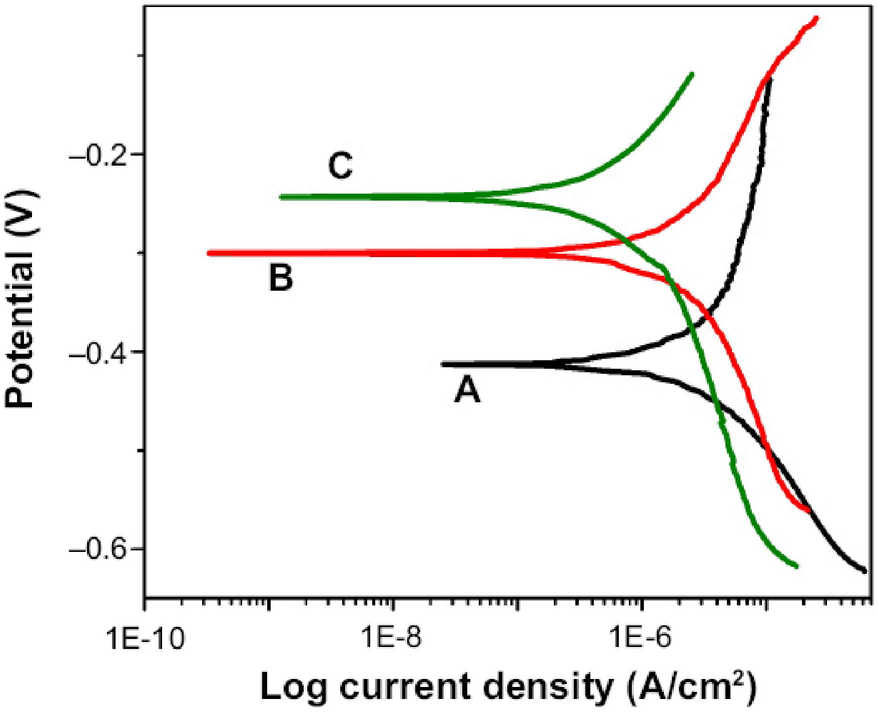
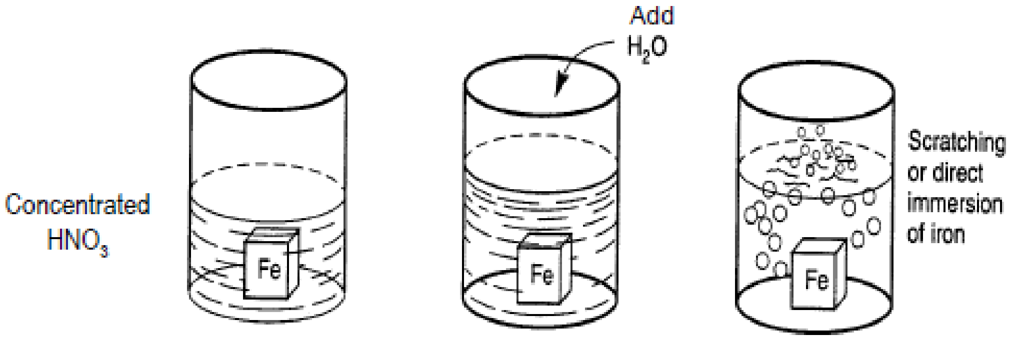


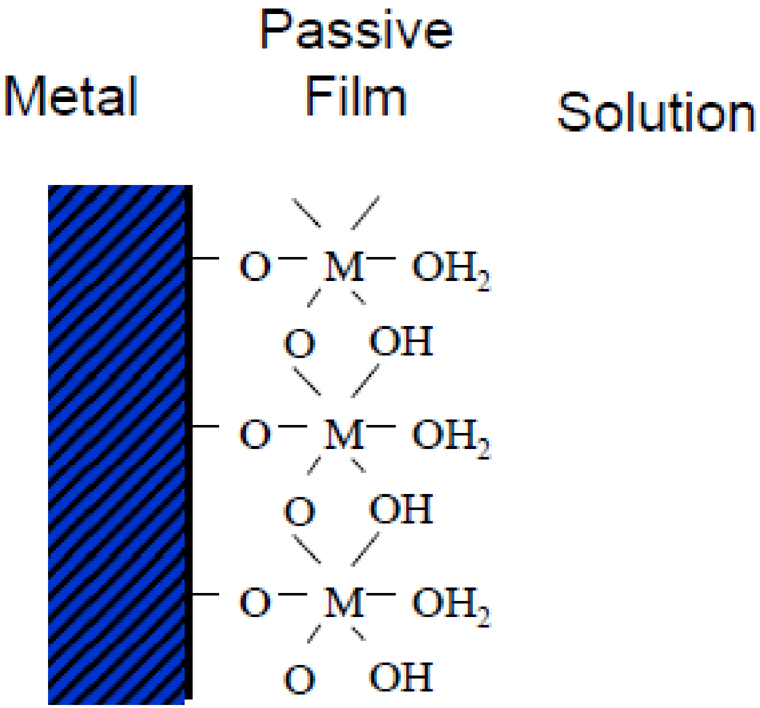
Figure 7 Tafel plots for (**A**) blank stainless steel substrate, (**B**) 1.5 µm thick thin film metallic glass-coated stainless steel, and (**C**) 3 µm thick thin film metallic glass-coated stainless steel in simulated body fluid.

Metal Passivity

- Historical perspective on passivity - in 1836 Michael Faraday described the behavior of Fe in nitric acid:



- Composition and thickness of the passive film are functions of potential and solution composition.
- For alloys, usually one element is enriched in the film (films on Fe-Cr alloys are enriched in Cr).
- Passive films can be either crystalline or amorphous.
- Films can be either insulators (e.g., Al, Ti, and Ta) or semiconductors (e.g., Fe and Ni).



Metal Passivity

- Metallic passivity was discovered in 1790 by Keir, who found that metallic iron violently corroding in the active state in concentrated nitric acid solution suddenly turned into the passive state where almost no corrosion was observed. It was not until 1960s that we confirmed the presence of an oxide film several nanometers thick on the surface of passivated metals.

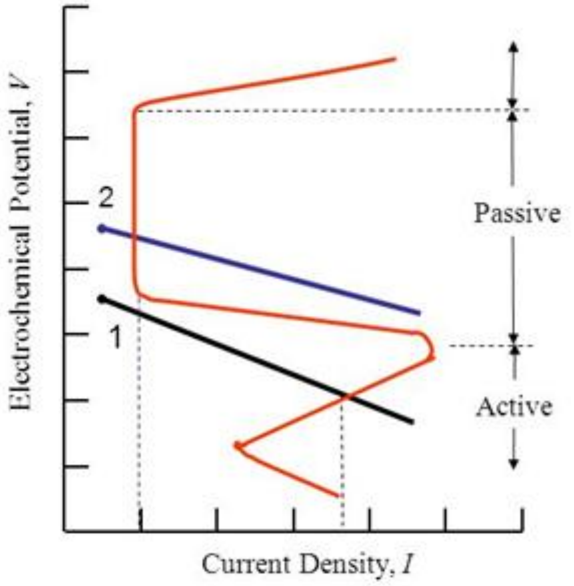
- A passive metal is one that is active in the EMF series but which corrodes at a very low rate due to formation of very thin, oxidized and protective films on its surface in corrosive solutions: **e.g.** **Fe, Ni, Cr, Al, Ti, Zr, Nb and their alloys.**

- Definition: A metal is passive if it substantially resists corrosion in a given environment resulting from marked anodic polarization despite of a marked thermodynamic tendency to react.

Metal Passivity: Steel & Stainless Steel

- Chrome is more anodic than Iron
  - Why do we chrome plate things for corrosion protection?

- form very stable oxides on the surface
  Cr_2O_3

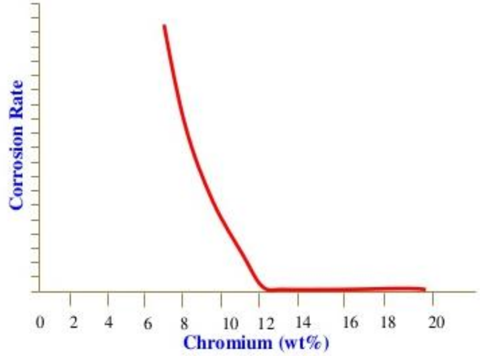


Same material can experience both active and passive behaviors depending on the corrosion environment.

Reaction at Interface	Half-cell Potential (E^o)
$Al^{3+} + 3e^- \rightarrow Al$	-1.706 V
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.763 V
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.744
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.409V
$Cd^{2+} + 2e^- \rightarrow Cd$	-0.401 V
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.230 V
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126 V
$2H^+ + 2e^- \rightarrow H_2$	0.00 V

- Under most conditions, iron is not very corrosion resistant. Alloying with >12% Cr to make stainless steel greatly improves corrosion resistance owing to the formation of protective Cr-rich passive film

Passivity in iron alloys



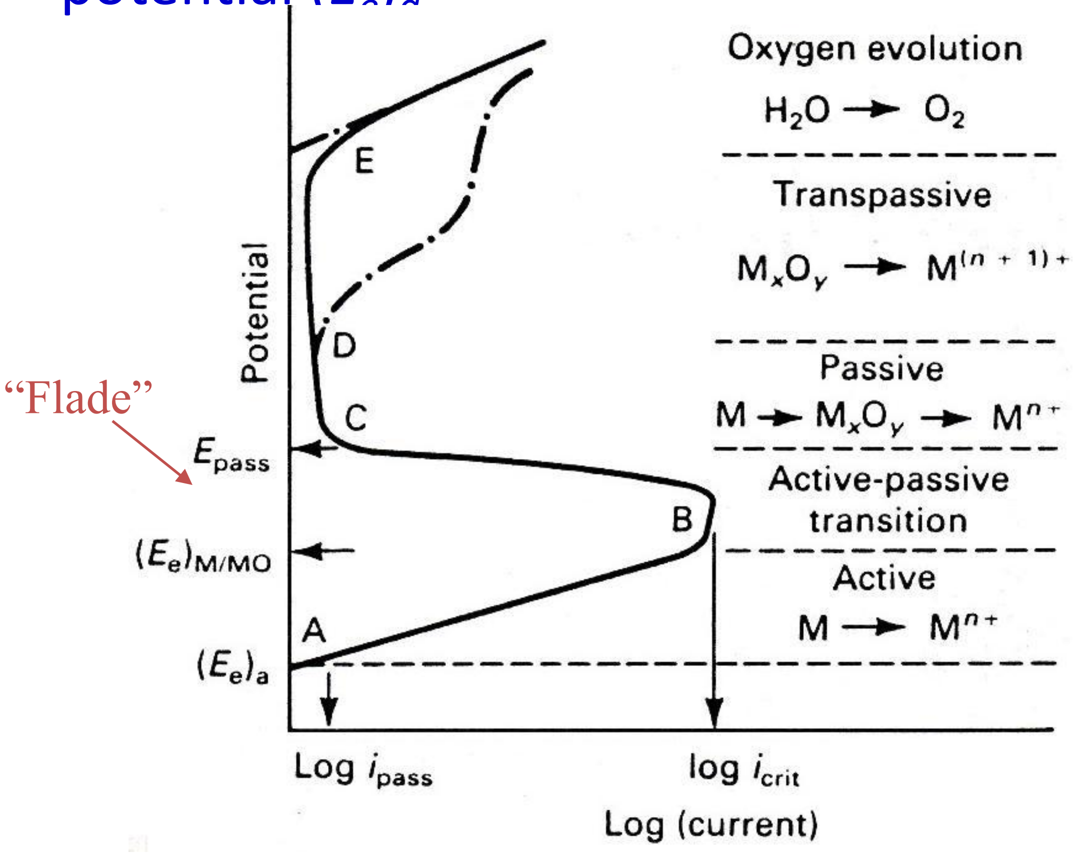
Fe alone is not naturally passive (*i.e.* corrodes in short time)

Cr is a naturally passive metal (*i.e.* remains bright & tarnish-free)

Fe-alloy have passive property when at least **12% Cr** is there

Passivity

The polarization curve for the anodic reaction of a passivating metal drawn for potentials more noble than the equilibrium potential $(E_e)_a$.



Oxidative dissolution of oxide (e.g., $Cr_2O_3 \rightarrow CrO_4^{2-}$)

$(E_e)_{M/MO}$ is the equilibrium potential for oxide/hydroxide formation

Tafel region
(i_{crit} is min. reaction rate required to initiate film growth by precipitation of M^{n+})

The region attained by the metal in a given environment depends upon the cathodic reaction i.e., where the cathodic curve cuts the above anodic curve.

Theories of Metal Passivation

1) Oxide film theory : The passive film is always a diffusion-barrier layer of reaction products, e.g, metal oxide or other compound which separates metal from its environment and which slows down the rate of reaction. According to this model, the following processes are driven by the electric field across the film:

- Transport of the metal cations or of oxygen anions through the oxide.
- Dissolution of metal cations from the film at the film/ environment interface.

Properties required for protective passive film:

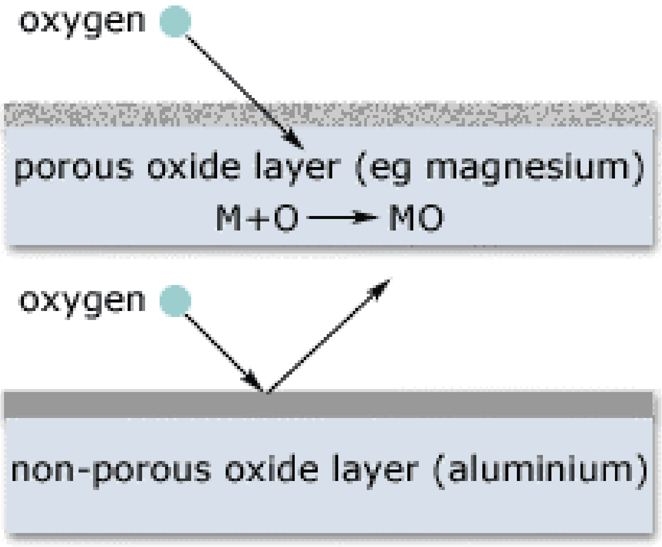
- Stability over a wide potential range.
- Mechanical integrity.
- Low ionic conductivity.
- Low solubility and slow dissolution in the aqueous medium.

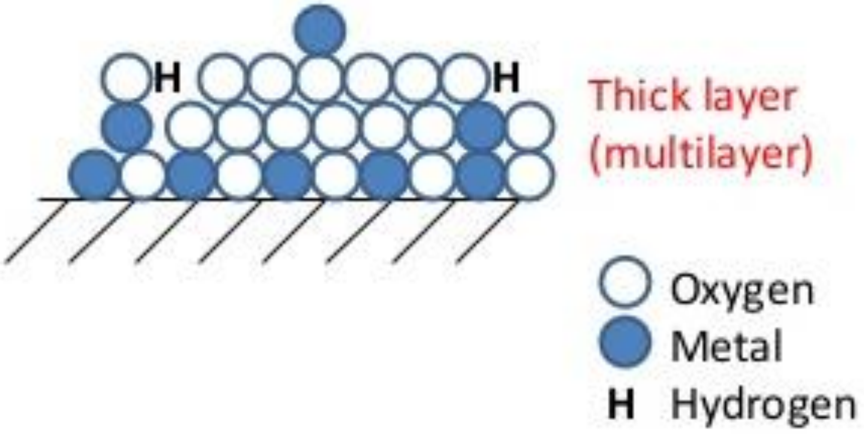
Theories of Metal Passivation

2) Adsorption theory : A chemisorbed layer of oxygen displaces the normally adsorbed H_2O molecules and slows down the rate of anodic dissolution involving hydration of metal ions. Adsorbed oxygen decreases the exchange current density of metal:

$$M + (H_2O)_{ads} \rightarrow [M(O^{2-})]_{ads} + 2\ H^+$$

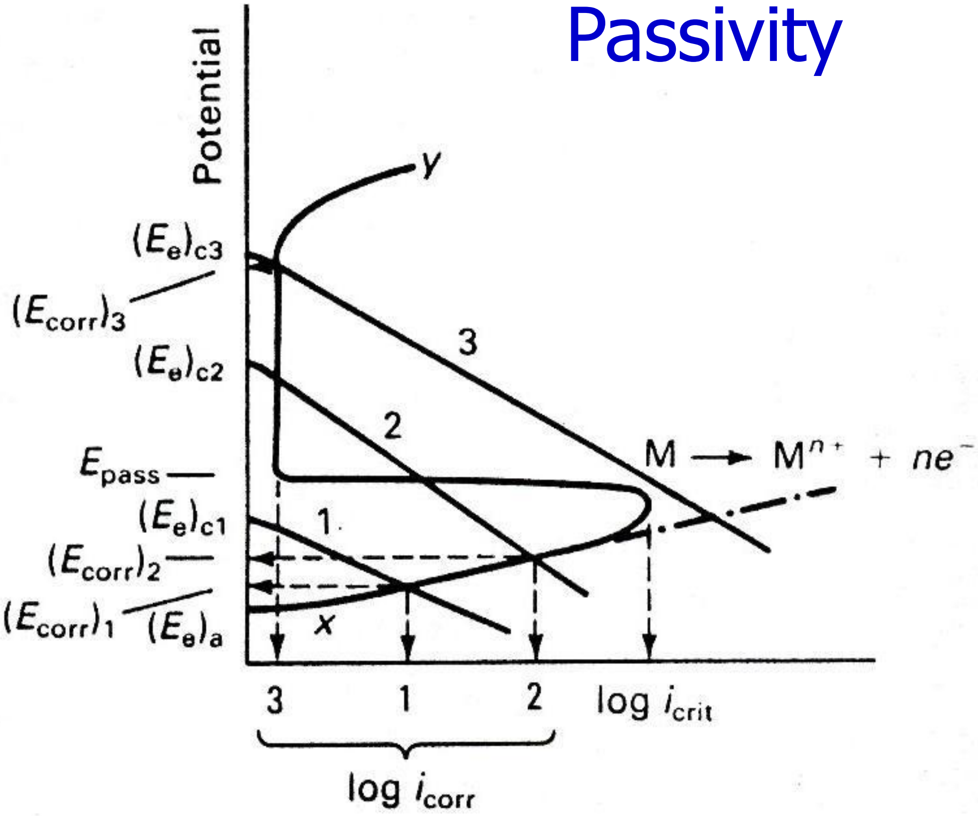
The two theories are valid due to different surface chemistry of the various metal/solution systems as well as mechanisms of film formation.





Passivity

Impact of various cathodic reactions on the corrosion current and potential for a metal capable of undergoing an active-passive transition



Cathodic Reaction C1:

$(E_e)_{C1} < E_{pp}$

$(E_{corr})1 < E_{pp}$ …

… metal corrodes actively

Example: Titanium in HCl or H_2SO_4

Cathodic Reaction C2: $(E_e)_{C2} > E_{pp}$

However, curve intersects Tafel line for anodic reaction below $i_{critical}$

Passive film cannot form. … metal corrodes actively.

Examples: Chromium in air-free H_2SO_4; Fe in dilute HNO_3.

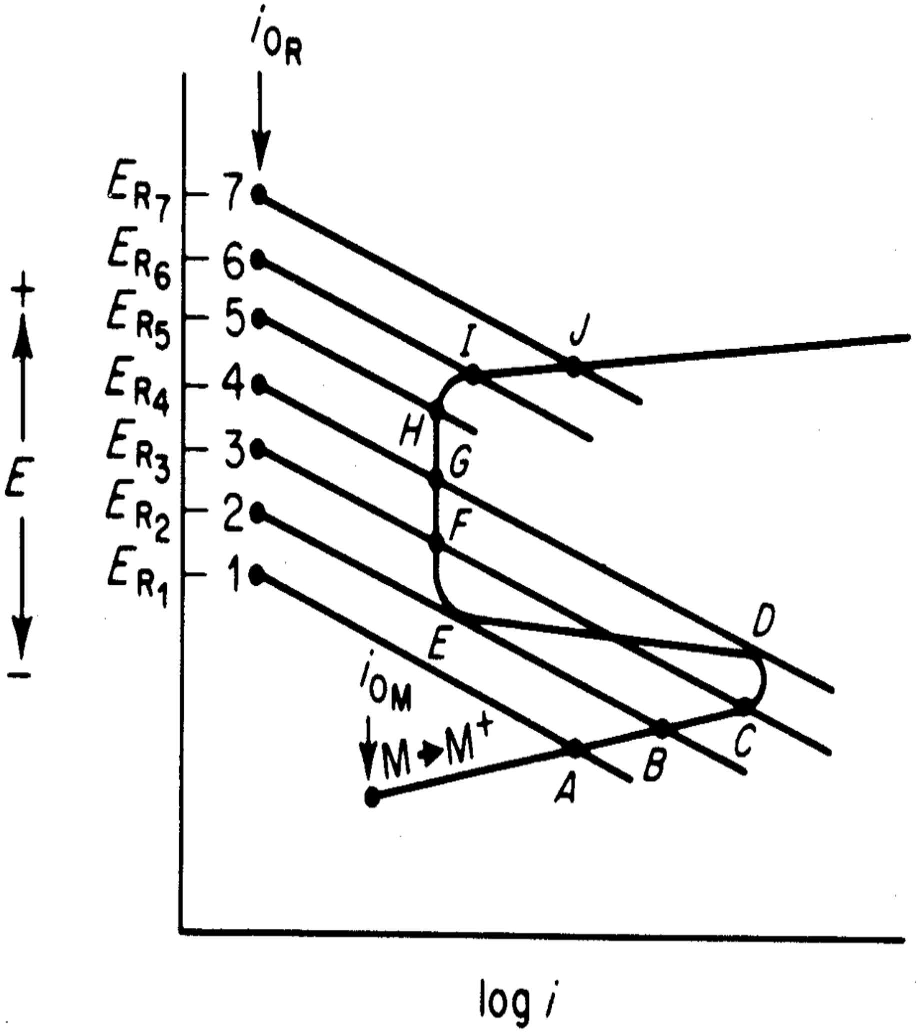
Cathodic Reaction C3: both passivating conditions are met:

$(E_e)_{C3} > E_{pp}$ and i (intersecting Tafel line) $> i_{crit}$) … metal passivates.

Examples: Stainless steels & titanium in acid solutions containing oxidizers.

Effect of oxidizer

Oxidizer undergoes the reduction reaction. Increasing the concentration of an oxidizer moves the cathodic curves from 1 to 7.



To safely maintain passivity, oxidizer concentration should be greater than the minimum amount necessary to produce spontaneous passivation

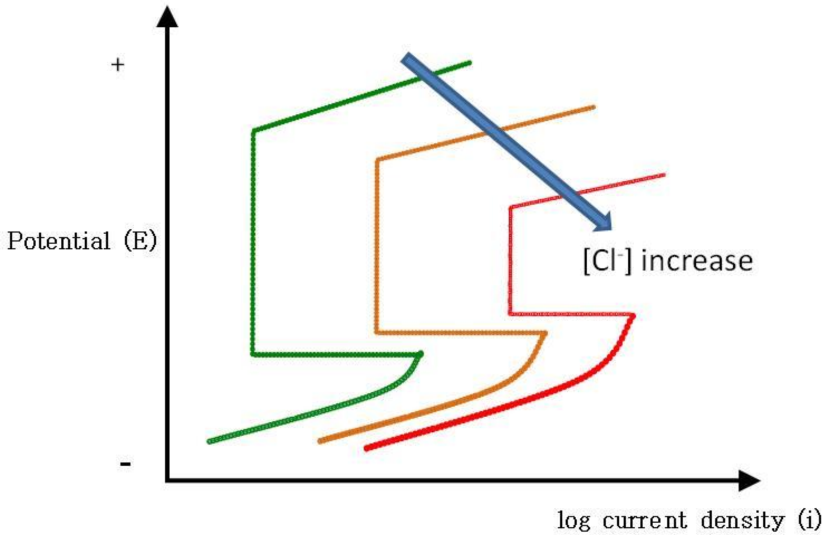
(that is, 5)

Effect of chloride ions

1. Chloride ions damage the protective films and cause the metal surface to be pitted.

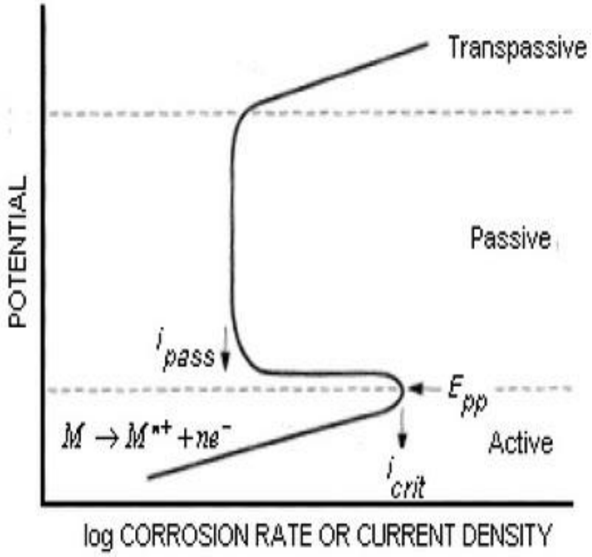
Examples: Stainless steel is subjected to serious pitting by stagnant water containing a high concentration of chloride ions, AND Steel pipes are subjected to pitting in brackish water and seawater.

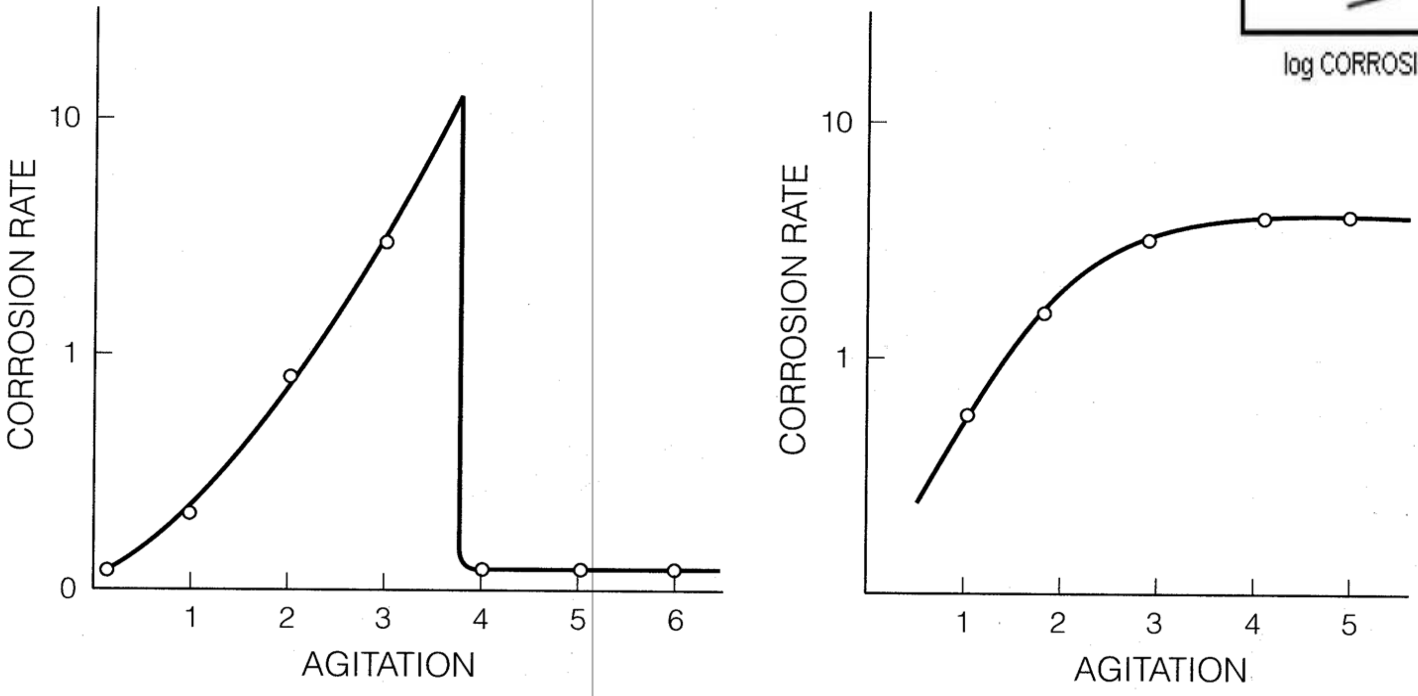
2. The higher the concentration of chloride the greater is the tendency of pitting.
3. The effect of chloride concentration on the passivation of steel is shown in Figure.
4. Chloride ions break down the passivity and increase the rate of anodic dissolution.



pitting

Effect of solution velocity





(a)

(b)

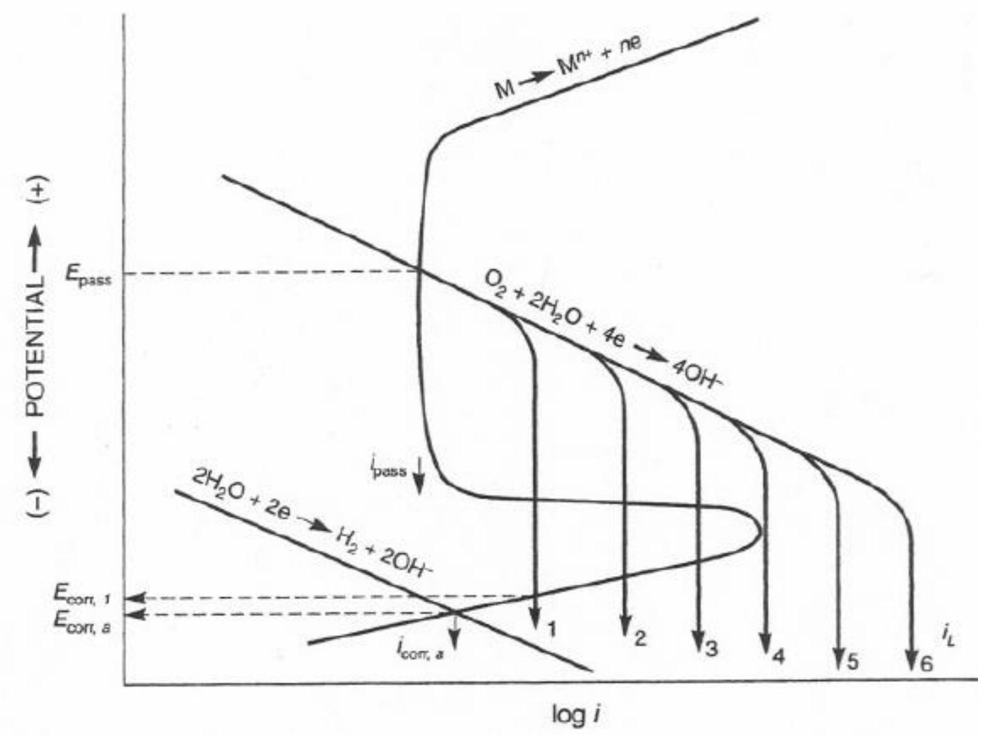
FIGURE 4.8 Effect of stirring or solution velocity on corrosion rate for (a) active–passive stainless steel, derived from Figure 4.6, and (b) normal active metal, reproduced from Figure 3.12b.

Passivity: aeration, deaeration & Stirring

In deaerated solutions, the only available cathodic reaction is

$$2H_2O + 2e^- = H_2 + 2OH^-$$

and the metal corrodes in the active state



In partial aeration, reduction of dissolved oxygen occurs

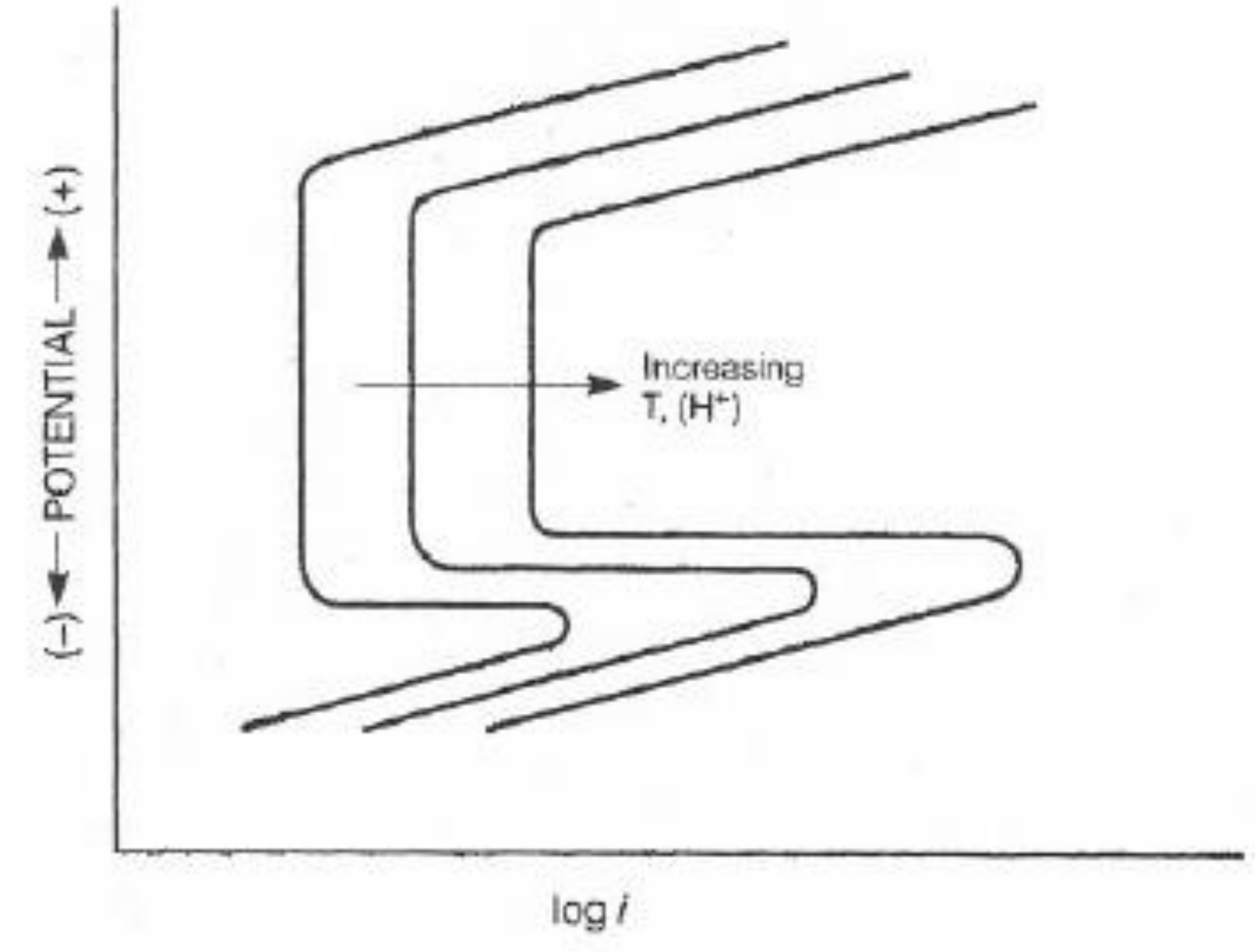
$$O_2 + 2H_2O + 4e^- = 4OH^-$$

- At low velocity (curve 1), the limiting oxygen concentration keeps the corrosion in the active state.

- On curve 4, the limiting current has increased and pushed the system into the passive region with potential E_{corr}.

Effect of T and pH

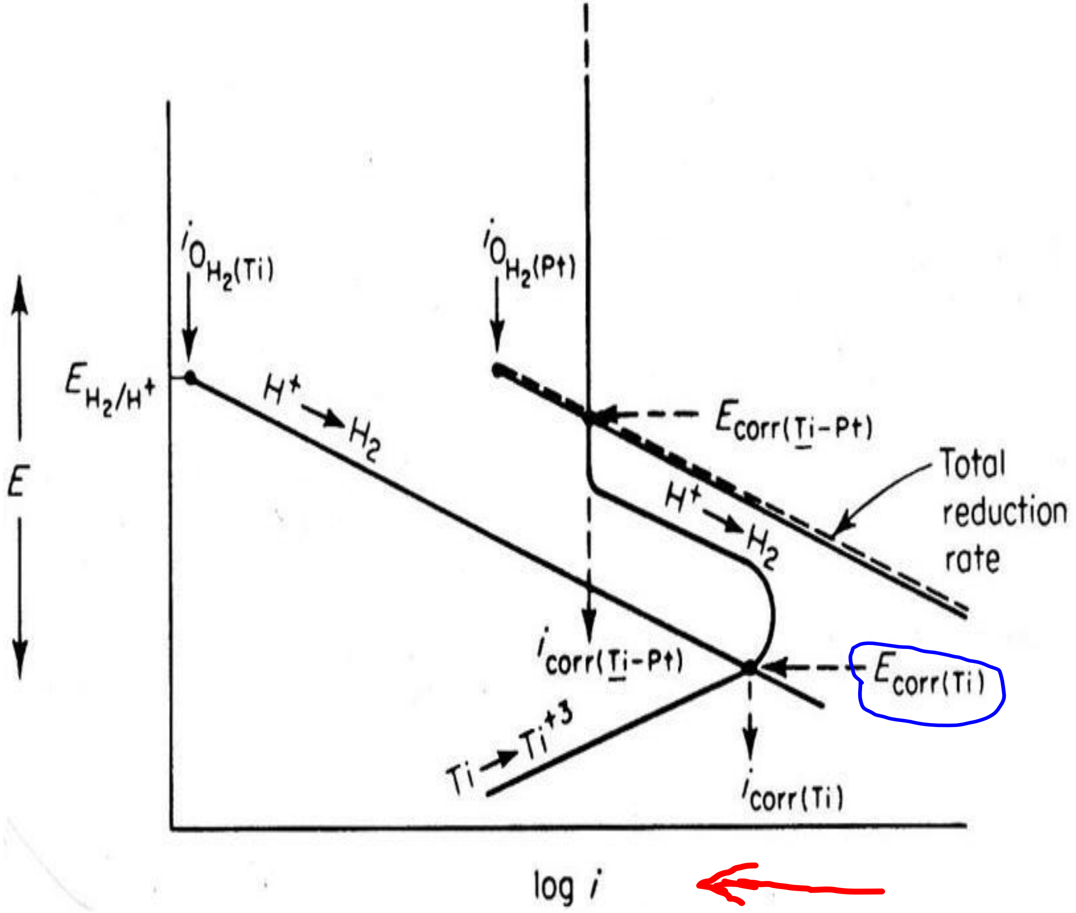
Passive region decreases with increasing temperature and higher acidity (H^+)



Coupling

Passivation (of Ti) by galvanic coupling (to Pt) in acid solution raises the possibility of anodic protection.

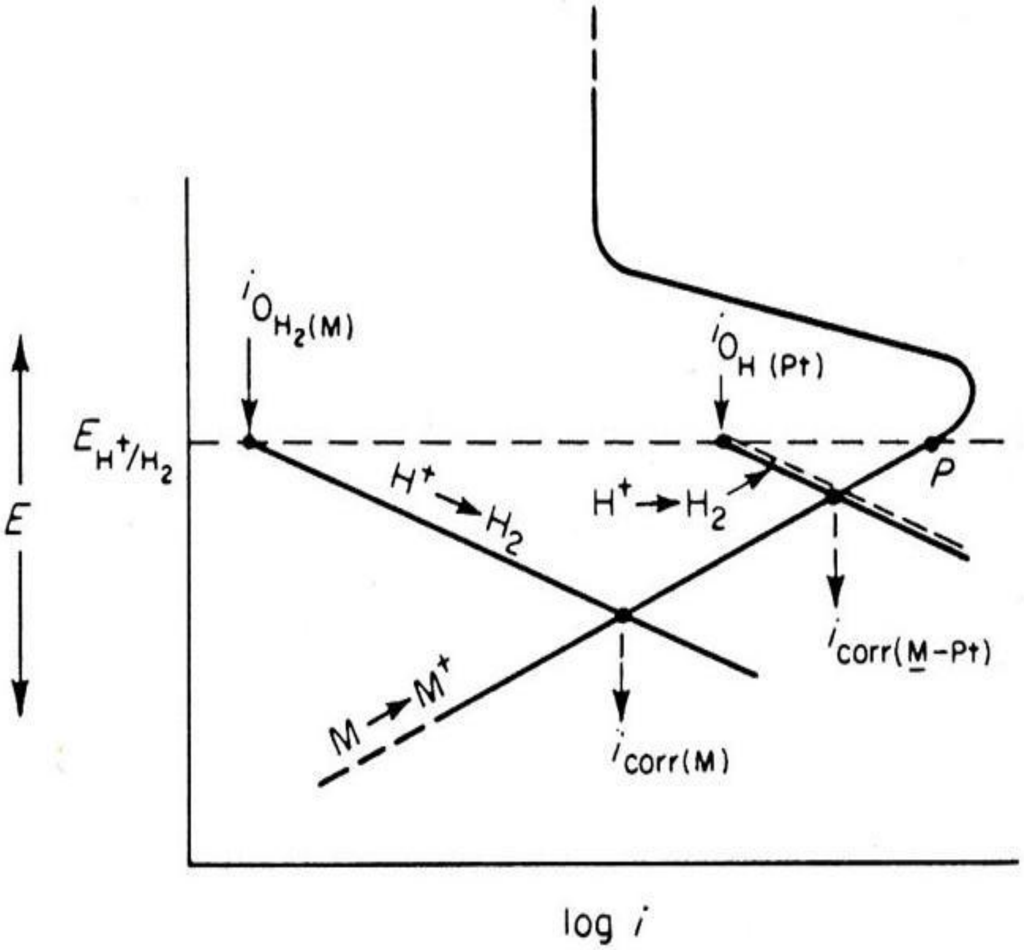
- Titanium does not exhibit a transpassive region.
- Corrosion rate is obtained by intersection of cathodic (H_2 evolution) line with anodic passivation curve of titanium.



Coupling

Galvanic couple between an active-passive metal (Cr) and platinum (Pt) in air-free acid solution (no oxygen):

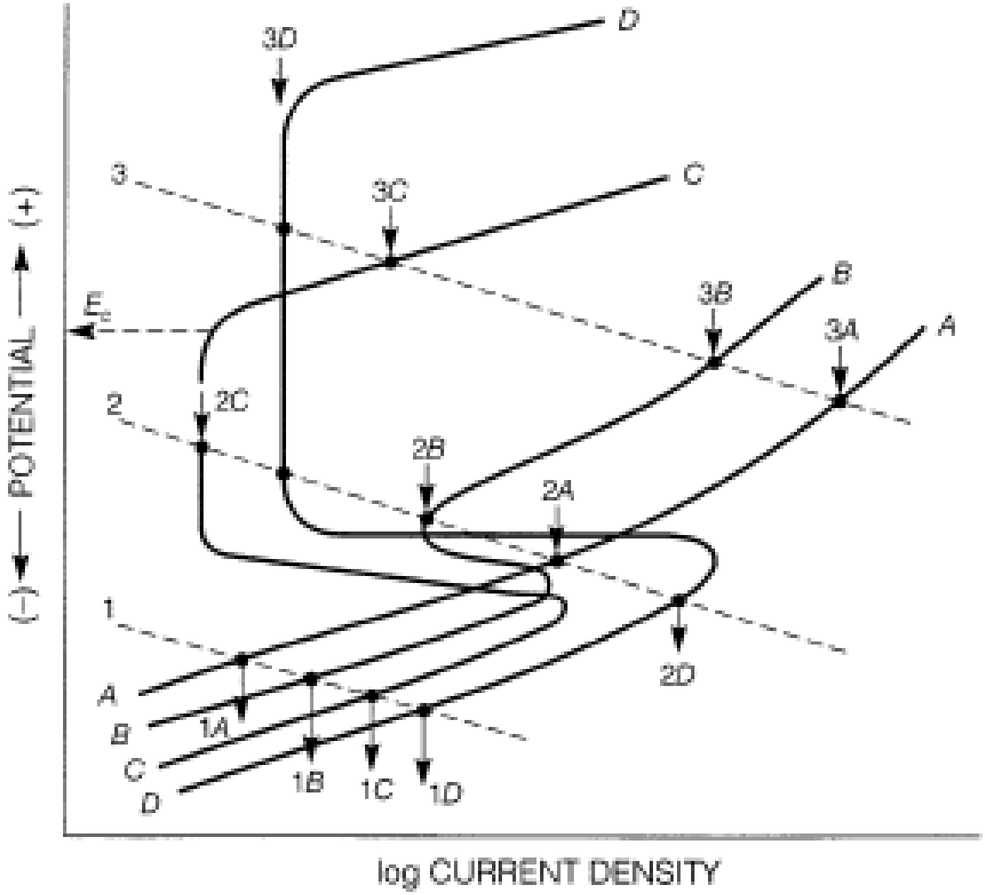
Passivating potential too noble (highly +ve) for couple to passivate metal. If very large Pt cathode area is used, active anode potential can be increased to P.



In aerated acid solutions, i_o of oxygen absorption will shift the intersection to the passive region and reduces the corrosion rate.

General Passivity Curves

Alloys with different electrochemical behavior would be preferred for environments with different oxidizing power:



Schematic anodic polarization curves for hypothetical alloys *A*, *B*, *C*, and *D*, illustrating evaluation in various chemical conditions: 1, reducing; 2, moderately oxidizing; 3, highly oxidizing.

CONCLUSIONS

- Rates of individual processes are determined by mixed potential theory.
- Corrosion [mixed] potential are determined by point where total oxidation rate equals total reduction rate.
- Increasing cathode area/anode area ration increases corrosion rate
- To control corrosion, cathode area /anode ratio should be low

  ($i_a = I/A_a$; high corrosion current if anode area is low)
- Passivity is a property of certain metals that make them individually or as part of alloy more resistant to corrosion due to formation of natural protective them.
- Passive films can be oxides or other chemical forms and are self repairing in appropriate media and conditions.
- Tafel polarization curves describe accurately when a given material /medium system under certain conditions is immune to corrosion or not and give the corrosion rate (current).