

P①

24.06.2020

LECTURE NO 4Effect of pH on Rate of Corrosion

— Rate of corrosion is much faster in Acid medium than alkaline or neutral medium.

Reason:

Corrosion Rate increase with increase in acidity.

Increase in H^+ ions
Increase the solubility of most potentially corrosive products.

This can be further understood by discussing

POURBAIX DIAGRAM

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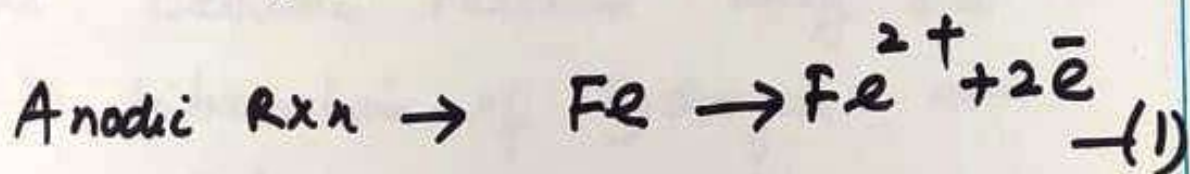
Effect of pH and potential for IRON (POURBAIX DIAGRAM)

POLARISATION CURVE OF IRON

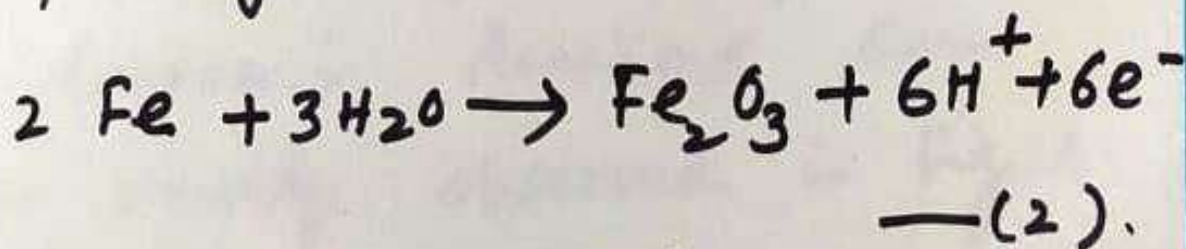
- Corrosion is rxn of metal and alloys w/ environment
- pH is one of the environmental factors which affect corrosion
- There are two rxns involved

Cathodic rxn

Anodic rxn



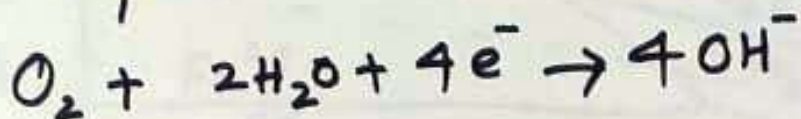
In solution with higher pH, anodic rxn produces a surface film of ferric oxide according to following rxn



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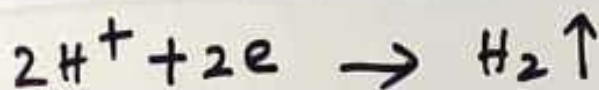
Cathodic Reactions

Most common cathodic rxn is the electrochemical reduction of dissolved oxygen according to the equations:



Hence, the reduction of oxygen at an electrode will cause a rise in pH due to hydroxide ion production.

If the medium is acidic, then the cathodic reaction may be the liberation of hydrogen at the cathode.



Role of the electrode potential E in defining the products of corrosion reactions can be readily observed in Fig A.

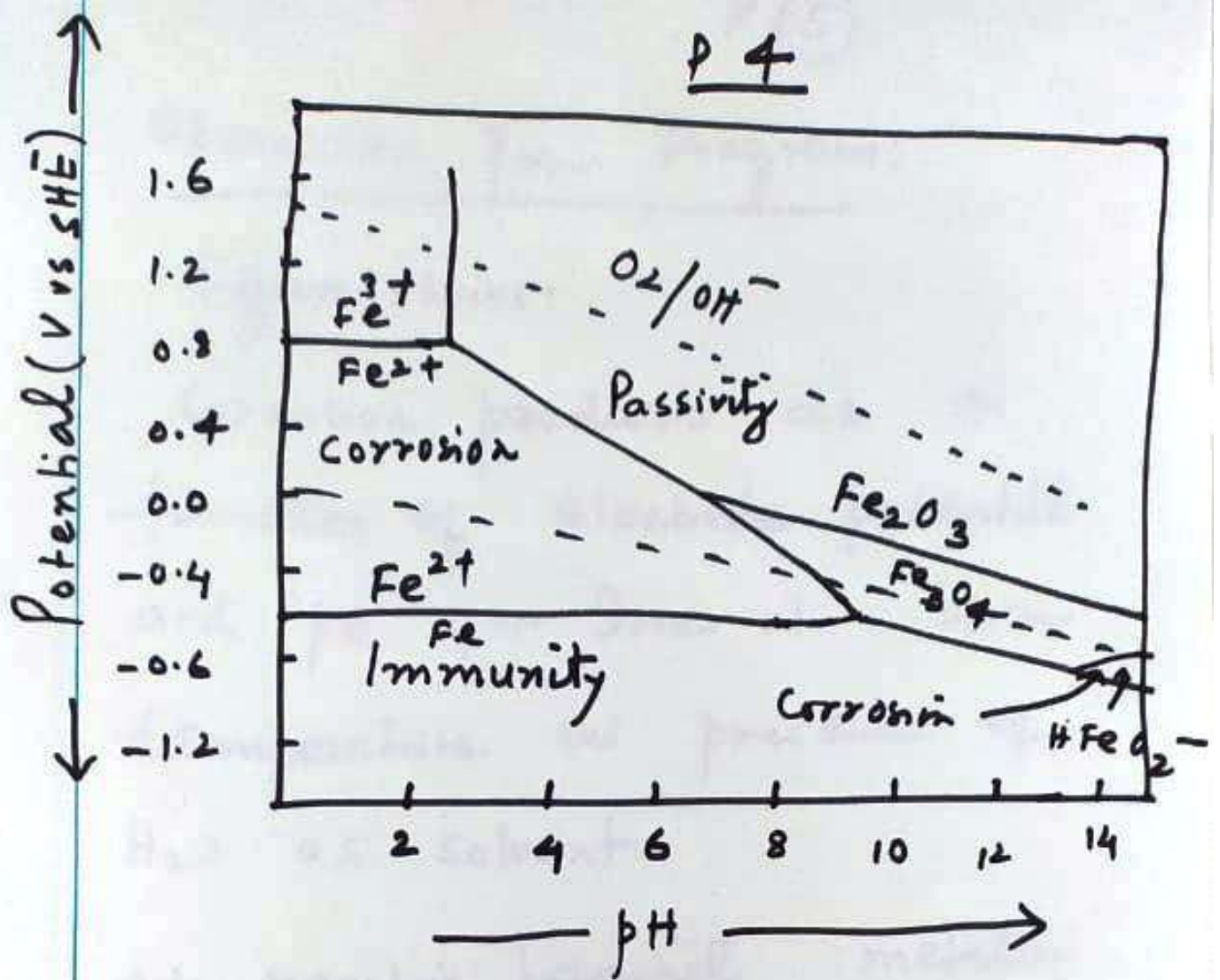


Fig A: Simplified potential - pH diagram for Iron in a solution containing dissolved iron at 25°C.

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Observations from Diagram:

Figure shows:

Corrosion products as a function of electrode potential and pH for Iron at room temperature in presence of H_2O as solvent.

- At negative potential, metallic iron is itself stable form, hence in this region no corrosion is possible, this is referred as Immunity, Corrosion - Immune Range ~~Immune~~ Immune Atmosphere.

This figure shows stable forms of the iron element as a function of E and pH.

- If pH lies on the alkaline side then insoluble surface oxides will form.

The oxide Fe_3O_4 , known as magnetite or black iron oxide, is produced at low electrode potential.

- Low potentials are relatively stagnant conditions with a low oxygen partial pressure.

- At more positive potentials the oxide formed is Fe_2O_3 and this is usually present as a thin adherent film.

Since this oxide forms at the surface, its presence

blocks the surface rxn and hence corrosion rates are reduced.

This is called passivation and the oxide film on the surface is known as passive layer.

The corrosion rate is very low in the passivation region of the diagram.

Further to understand the rate of corrosion process let us examine the electrochemical polarisation curves of the electrode rxns which

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takes place on the metal surfaces.

Fig B shows the polarisation curve of iron in an acidic solution at room temperature.

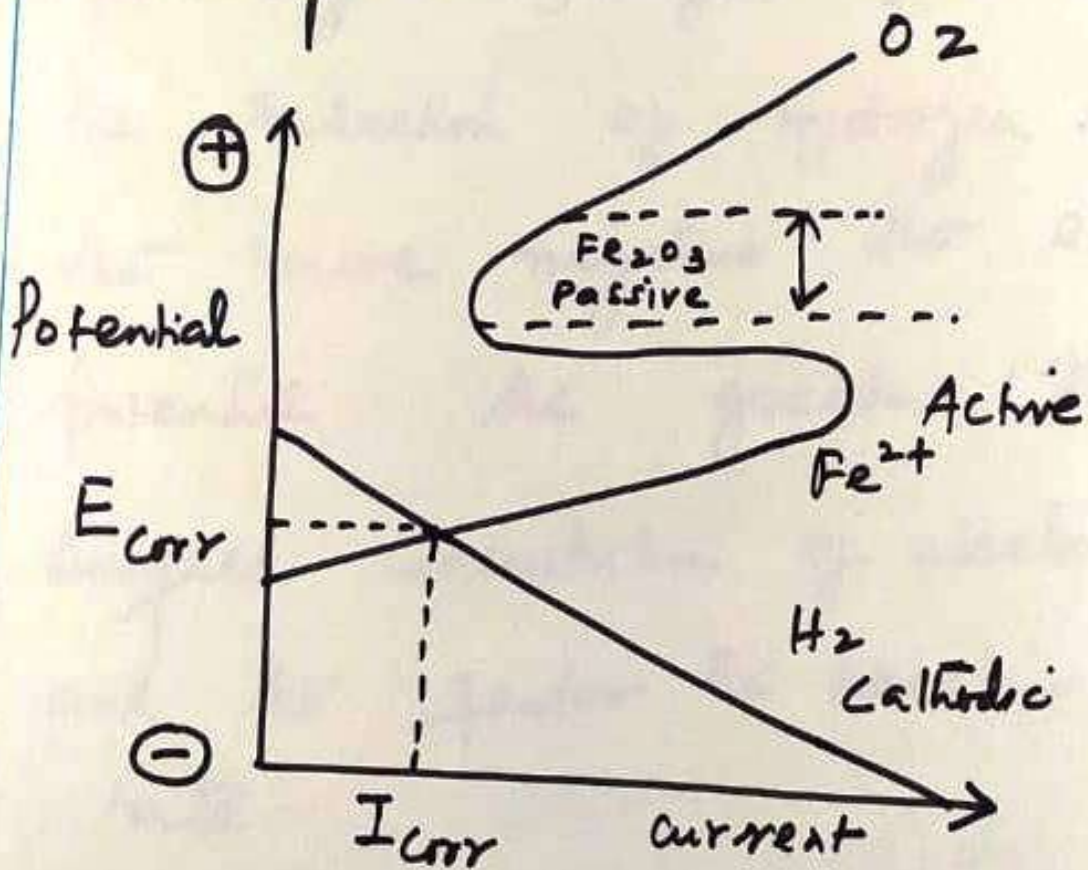


Fig B: Polarisation curve of Iron

P (9)

The rates of the electrode processes are controlled by the value of potential E .

Thus, for a cathodic process in acidic solution producing hydrogen gas by the reduction of hydrogen ions, the more negative the electrode potential the greater the surface concentration of electrons and the faster the reaction rate.



Since the reaction rate is proportional to the flow of electrons (measure as current I) the diagram shows the magnitude of I as a function of E .

The polarisation curve ^{Fig B} of iron shows how the potential, E , of the metal determines the electrochemical reaction rate and corrosion products. Anodic reactions are accelerated by increasing potential in the positive sense. Ferrous ions are produced in the active state and this is the region in which corrosion will take place freely.

At higher potentials, the reaction passes into the passivation region and passivation occurs. This is observed as a very small current flowing in this region.

The metal is protected by the passive film of ferric oxide on the surface.

⇒ At very positive potential, passive electrode surface will act as an anode to oxidise H_2O to O_2 gas, but this does not occur in normal corroding systems.

To find the corrosion rate under normal conditions it can be observed that for
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The point on the diagram where the anodic and cathodic reactions intersect (Tafel Plot), etc of anodic and cathodic rates are equal and the system is behaving as a closed circuit with all the electrons produced in the anode reaction being consumed in the cathodic reaction
