Corrosion of iron.

The corrosion rxn for iron in acid can be broken into two thus, oxidation

$Fe = Fe^{2+} + 2e^{-}$ …… 1 and reduction,

$2H^{+} + 2e^{-} = H_2$ ……. 2

The summation of reactions 1 and 2 will give,

$Fe + 2H^{+} = Fe^{2+} + H_2$ …. 3

Electrons released in 1 is taken up in 2 ie rate of 1= rate of 2. D4 can control by interfering with either rxn. All corr control techs are based on this fact.

Cathodic protection

- Draw E/logi diagram.
- Raise E_{cor} to A, Fe dissolves more ie anodic rxn increases, cathodic rxn decreases.
- Flood corroding surface with electrons ie depress E_{cor} to B, anodic rxn decreases, & cathodic rxn increases.
- Depress E_{cor} further to E_{fe} iron will not corrode.
- This is the principle of CATHODIC PROTECTION

Overprotection

- However, lowering of the potential below E_{Fe} leads to over protection. Such is of no benefit in as much as corrosion control is concerned. In addition, a greater expenditure on current than required for full protection is needed.

Cathodic protection & coatings

- Usually, cathodic protection is used in conjunction with coatings. In such instance, the current demand for protection is low. While the coating affords the majority of the protection, current from the cathodic protection system protects flawed and damaged regions of the coatings where the bare metal is exposed to the corrosive environment.

Powerful tools in corrosion control

- As the coating deteriorates with time in service, the cathodic protection is activated to provide more current to protect the damaged regions. Thus, the conjoint use of coatings and cathodic protection is an eminently powerful tool in corrosion control.
- The rates of both cathodic reactions i.e. hydrogen evolution and oxygen reduction, are increased during cathodic protection.

Avoidable problems with CP & Coatings

- Since rates of both cathodic rxns increase, the environment becomes more alkaline.
- D4 avoid use of alkyds & oil based paints. They are saponified by alakalis. Instead use epoxy coatings and bituminous paints.
- when hydrogen evolution is the cathodic reaction. Rxn takes place on the bare metal at holidays in the coatings. Rapid evolution of hydrogen during over-protection can cause the coating to be blown off, thus creating larger regions to be cathodically protected.

More associated problem

- In high strength steels, hydrogen generated on such surfaces may enter into the metal causing what is known as hydrogen embrittlement. These problems only occur when the cathodic protection is badly designed or during an over enthusiastic operation of the system which normally leads to wasteful over-protection.

Metals that can be Cathodically Protected.

- Noble metals- do not corrode. No need
- All other metals in use where there are electrolytic conducting media can be cathodically protected even in de-aerated environments.
- Passive-base metals e.g, stainless steel and aluminium & its alloys- can be cathodically protected as well.

Environments where Cathodic Protection is Applicable

Aqueous environments i.e. electrolytic conducting environments. For example, structures in sea water such as piers, jetties, pipelines, production platforms, ships.

Process fluids in chemical plants and cooling water systems. Cathodic protection will not be useful in strong acids.

Soils – Buried pipelines, piling of buildings etc.

- In all cases cathodic protection can be used to protect against general, microbial, stress corrosion cracking, pitting, and cavitations etc.

Application of cathodic protection

- Two methods: Impressed current technique and sacrificial anode method.
- Impressed current- the current is forced in, or impressed through an auxiliary anode from an external source of power.
- Sacrificial anode- practical use of Galvanic corrosion.

Impressed current

- The current is delivered to the structure in this technique from a dc power source through an auxiliary anode.
- Structure will act as a cathode in the cell formed and, in the presence of an anaerobic aqueous environment will sustain the hydrogen evolution reaction.
- If the solution is aerated, the reduction of oxygen becomes possible and may occur in place of, or together with the hydrogen evolution reaction depending on the potential to which the structure is depressed.

Anodic Rxns for impressed current

- Auxiliary electrode will become an anode in the cell. If this electrode is a base metal then the anodic reaction will be: M ⌖ $M^{n+} + ne^-$ the electrode will be consumed steadily.
- a noble metal or electrochemically inert, but electrically conducting material, oxidation of the environment will occur in preference. Thus, in water the reaction will be:
- $2H_2O$ ⌖ $O_2 + 4H^+ + 4e^-$ or in brine possibly,
- $2Cl^-$ ⌖ $Cl_2 + 2e^-$
- In either case the electrode will not normally be consumed.

Disadvantages

- Consumable electrodes are cheap (scrap iron may be used for example)
- must be replaced at intervals
- they contaminate the environment with dissolution products,
- they cannot sustain high current densities and must therefore be rather bulky.
- These disadvantages may be avoided by the use of non-consumable electrodes (silicon-iron, lead-antimony-silver, platinum-titanium or platinum-tantalum), but with an unavoidable increase in first cost.

Magnitude of driving voltage

- magnitude of the driving voltage required from the dc source depends on a number of factors, including:
- conductivity of the environment
- the area of structure to be protected
- the nature of the electrode reaction at the auxiliary electrode
- the resistance of the auxiliary electrode.
- In most cases, conductivity is the controlling factor, and the electrode reaction of least importance. Clearly, if the environment does not have reasonable conductivity large IR (or voltage) drops will occur creating the need for a high driving voltage

Sacrificial anode

- Galvanic cell is formed between the structure and the sacrificial anode in which electrons pass spontaneously from the latter to the former. Thus the source of the electrons (the sacrificial anode) must have a more negative electrode potential than the structure.
- When sacrificial anode is attached to the structure, which now bicoms the cathode will sustain the hydrogen evolution and/or the oxygen reduction reaction.
- The anode dissolves and may be said to be scarified in favour of protecting the structure.
- Hydrogen evolution will usually only occur when magnesium alloy anodes are used.

Sacrificial anode materials

- Mg alloy- used where high driving voltage is impt.-soils, fresh and brackish waters. Gives sparks when struck with rusting iron.
- Zinc- used where sparking is a problem, sea water, where there is high conductivity. Has toxic dissolution products.
- Al alloys-used exclusively in sea water, has sparking problems. Passivate when used in the cold and in mud. Gives poisonous dissolution products