Chemical Attack

Chloride Attack

Chloride attack is one of the most important aspects while dealing with durability of concrete. It primarily causes corrosion of reinforcement. Statistics have indicated that over 40% of failure of structures is due to corrosion of steel.

Concrete and the Passive Layer

The strongly alkaline nature of $Ca(OH)_2$ (pH of about 13) prevents the corrosion of the steel by the formation of a thin protective film of iron oxide on the metal surface. This protection is known as passivity.

If the concrete is permeable to such an extend that soluble chlorides penetrate right up to the reinforcement and water & oxygen is also present, then the corrosion of steel will take place. This layer can also be lost due to carbonation.

Role of Chloride Ions

Chloride enters the concrete from the cement, water, aggregate and sometimes from admixtures. This can also enter by diffusion from environment if concrete is permeable.

The Bureau of Indian Standard had specified the maximum chloride content in cement as 0.1%.

The amount of chloride required for initiating corrosion is partly dependent on the pH value of the pore water in concrete. At a pH value less than 11.5 corrosion may occur without the presence of chloride.

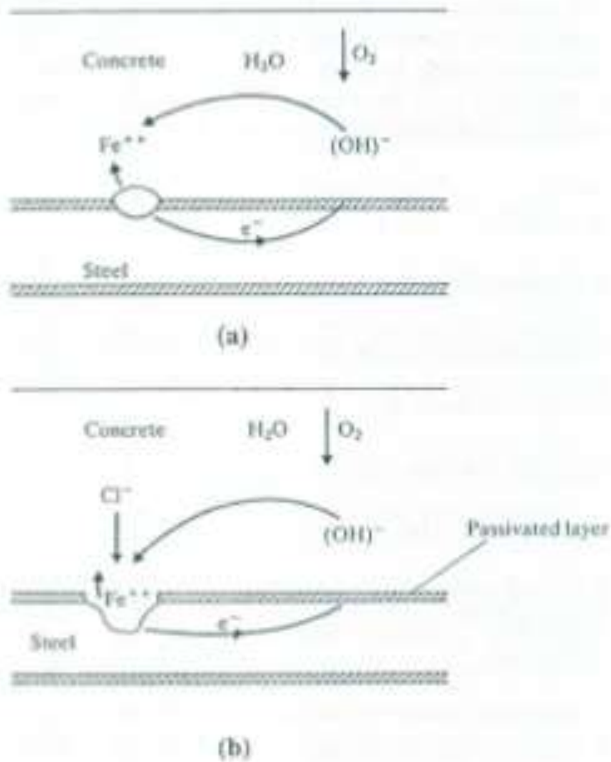
Corrosion

For corrosion to occur, these elements must be present:

~There must be at least two metals (or two locations on a single metal) at different energy levels
~ an electrolyte
~ a metallic connection

In reinforced concrete, the rebar may have many separate areas at different energy levels. Concrete acts as the electrolyte, and the metallic connection is provided by wire ties, chair supports, or the rebar itself.

Corrosion of steel (Chloride induced)



Schematic representation of electro-chemical corrosion: (a) electro-chemical process, and (b) electro-chemical corrosion in the presence of chlorides

Anodic reactions

$$Fe \rightarrow Fe^{++} + 2e^-$$

$$Fe^{++} + 2(OH)^- \rightarrow Fe(OH)_2 \text{ (Ferrous Hydroxide)}$$

$$Fe(OH)_2 + 2H_20 + 0_2 \rightarrow Fe(OH)_3 \text{ (Ferric hydroxide)}$$

Cathodic reaction

$$4e^- + 2H_20 + O_2 \rightarrow 4(OH)^-$$

It can be noticed that no corrosion takes place if the concrete is dry or probably below relative humidity of 60% because enough water is not there to promote corrosion. If concrete is fully submersed into water corrosion does not take place because diffusion of oxygen does not take place into the concrete. Probably the optimum relative humidity for corrosion is 70 to 80%.

Corrosion of steel due to Carbonation

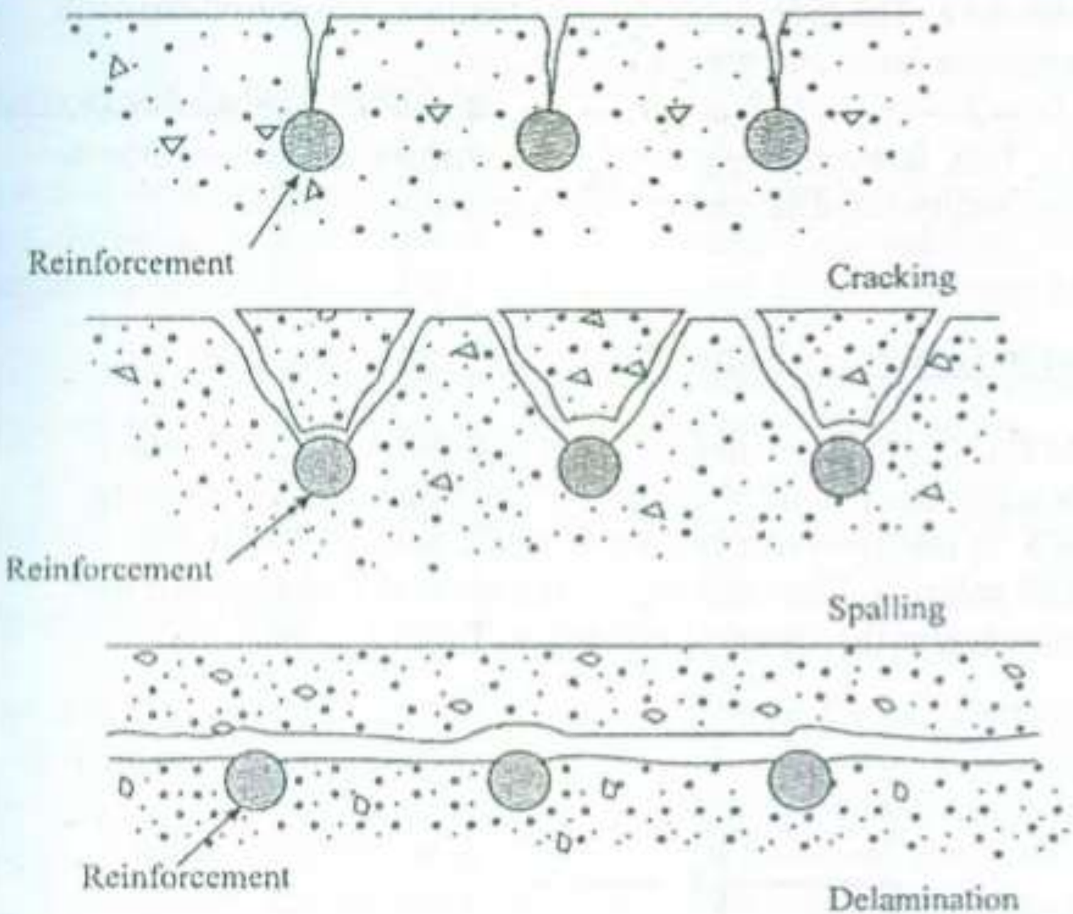
The passive layer can be lost by carbonation due to reduction in alkalinity of the concrete.
In the presence of moisture and CO_2 reacts as

$$CO_2 + H_2O \rightarrow H_2CO_3 \text{ (Dil. Carbonic acid)}$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

H_2C0_3 reacts with $Ca(OH)_2$ and carbonation of concrete takes place. This reduce the alkalinity of concrete. When pH of concrete reduces below 8.3, then passive layer destroyed and corrosion takes place.

The products of corrosion occupy a volume as much as six times the original volume of steel. This exert thrust on cover concrete resulting in cracks, spalling or delamination of concrete. (It is a result of water entering brick, concrete or natural stone and forcing the surface to peel, pop out or flake off).



Diagrammatic representation of damage induced by corrosion: cracking, spalling, and delamination

Sulphate Attack

Most soils contain sulphate in the form of calcium, sodium, potassium and magnesium. They occur in soils or ground water. Ammonium sulphate is frequently present in agricultural soil and water from use of fertilizers or from sewage and industrial effluents.

Decay of organic matters in marshy lands, shallow lakes often leads to formation of H_2S which can be transformed into sulphuric acid by bacterial action.

Therefore sulphate attack is common occurrence in natural and industrial situations.

Sulphate Attack

The main reactions of sulphate attack on concrete are as under;

1. Formation of sulphoaluminates (ettringite) by reaction of sulphate salts and the C_3A - phase in cement;

$$C_3A + 3\,CS\,H_2 + 26\,H \rightarrow C_3A(CS)_3H_{32}$$

Increase in volume of reaction products causes expansion and spalling.

2. Formation of calcium sulphate (gypsum) in reaction with lime (CH) formed by hydration of cement

$$NS + CH + 2H \rightarrow NH + CS\,H_2$$

Increase in volume of reaction products causes expansion and spalling.

3. Magnesium sulphate is more aggressive than sodium or calcium salts.

4. There are some other reactions also.

Spalling

Spalling (Concrete flakes)

Spalling

Carbonation

Carbon dioxide in air or dissolved in water reacts with hydrated cement systems.

The main concern is the reaction of carbon dioxide with the lime (CH) - phase. It gives rise to calcium carbonate;

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

In severe cases, the C-S-H phase, which gives strength, can also be attacked.

In all such reactions, OH^- is consumed, thus lowering down the pH of concrete. If pH is lowered very much, protection to steel reinforcement against corrosion may be lost.

Carbonation is highest in pH between 50 to 80 percent.

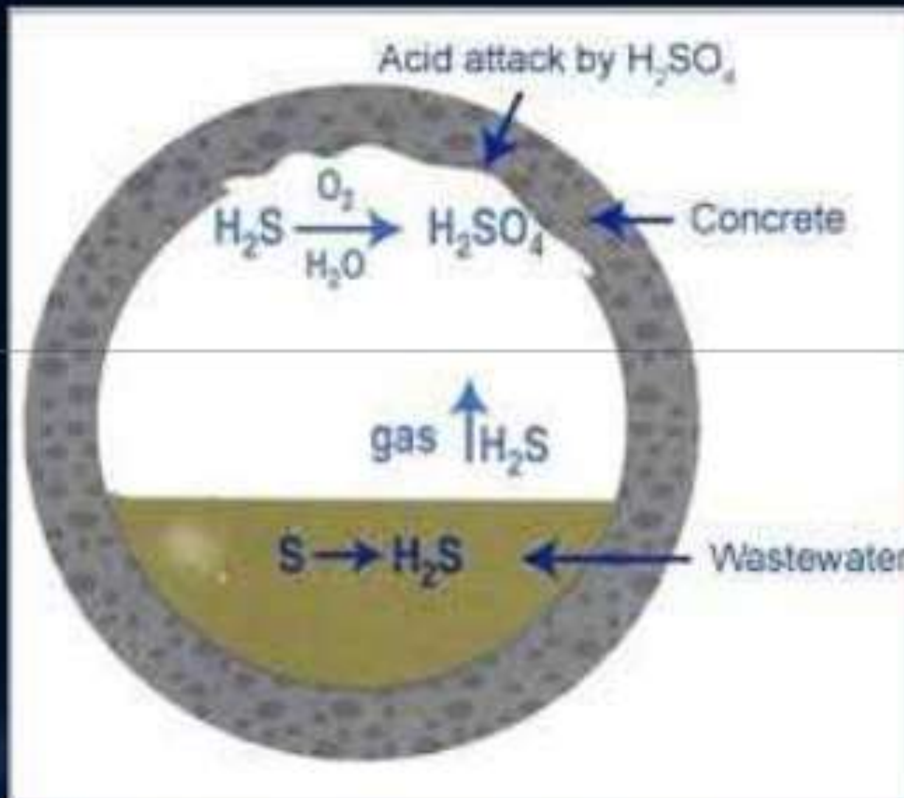
Carbonation
in concrete

ACID ATTACK

- Most acid solutions will slowly or rapidly disintegrate the cement depending upon type and concentration.
- Most vulnerable part of cement is $Ca(OH)_2$, but C-S-H gel can also be attacked.
- Siliceous aggregates are more resistant than calcareous aggregates.
- Concrete can be attacked by acids with **pH < 6.5**
- As the attack proceeds, all the cement compounds eventually broken down and leached away, together with any carbonate aggregate material.
- With sulphuric acid attack, calcium sulphate formed can proceed to react with calcium aluminate phase in cement to form calcium sulphoaluminate , which cause expansion and disruption of concrete.

Ph Value	Cause
<6.5	Possibility of acid attack
4.5-5.5	severe
<4.5	Very severe

❑Acid attack in the sewer line:



CONCLUSION:

- **Factors responsible for chemical attack:**
  - Exposure conditions
  - Depth of cover
  - Quality and quantity of aggregates
  - Inadequate design
  - Improper use of structure
  - Quality of workmanship
- **Remedial measures:**
  - Use higher grade of concrete
  - Use Portland pozzolana cement
  - Low water cement ratio
  - Use proper cover to the reinforcement
  - Provide protective coating