

VARIOUS FORMS OF WATER SIDE CORROSION : CAUSES AND PREVENTION

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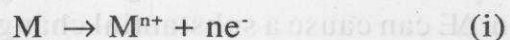
During operation and idle period of boilers, various types of corrosion problems are encountered. These problems arise mainly due to the interaction of metal with the fluids (water, steam, condensate, air) circulating in the boiler. The outside i.e., the fire side corrosion problems occur mainly due to the interaction of constituents of fuel with metal surface. These corrosive constituents interact with the metal surface to form low melting point compounds which results in catastrophic failure of the components of the boiler. The fire side corrosion problem has been discussed by the other speakers. The present talk will be limited to the various forms of corrosion problems experienced in water side of boilers; their causes, mechanism and control. Before, I go in detail about the subject, it will be *pertinent* here to describe in brief the corrosion reactions that occur at the interface of a metal and electrolyte.

Causes of Corrosion

Except certain noble metals such as gold and platinum, most of the metals are found in nature in form of their compounds. This due to

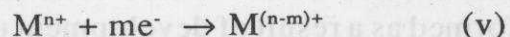
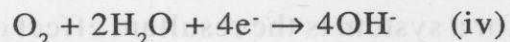
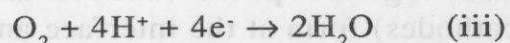
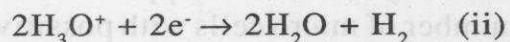
the fact that the metals in their compounds form are thermodynamically more stable compared to in elemental form. All the metals have an inherent property to interact with their surroundings and form a stable compound. In order that a metal interacts with its surroundings, two conditions must be fulfilled :

- a) An anodic reaction i.e., the ionization of metal into metal cations and electrons, must take place;



- b) A cathodic reaction involving the consumption of electrons should take place at the same rate as in (i)

The various cathodic reactions that are encountered during the water side boiler corrosion are :



Development of Potential Difference at the Interface

The above reactions as stated at (i) - (v) which are encountered during the corrosion process take place under the influence of a potential gradient which develops at the interface of metal-electrolyte. The activation energy required to overcome the barrier of the above reactions is derived from the potential gradient developed at the interface. A double layer is formed at the interface which can be schematically illustrated as shown in figure 1. This double layer formation occurs owing to the accumulation of opposite charges at the interface. The potential difference across the interface (ΔE) and corrosion current (I) are interrelated with a mathematical expression :

$$I_{\text{corr}} = A e^{\frac{V}{RT}}$$

It is evident from the above expression that even a slight change in ΔE can cause a substantial change in corrosion current i.e., the corrosion rate.

Formation of Corrosion Cells

From the above description it is evident that the corrosion takes place only because of the development of potential gradient at the interface. If corroding metal is observed minutely, it would appear that a number of micro cells with positive and negative poles (anodes and cathodes) form at the interface and the corrosion rate that we observe for a system is the resultant effect of these micro cells. These cells are formed as a result of development of

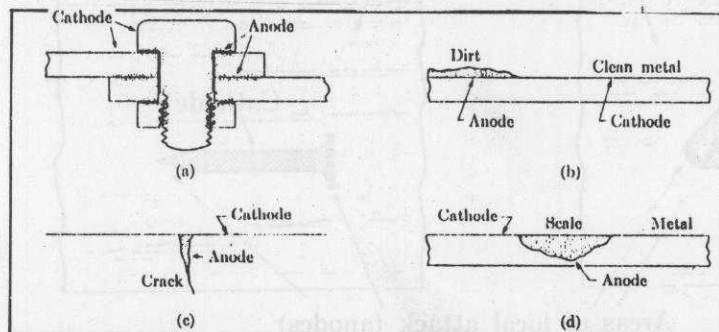
inhomogeneities at the interface. Some important types of cells that develop on the metals surfaces exposed to a corrosive environment and are of interest to the present audience are described below :

Oxidation Cells : This type of cells are formed when inhomogeneities occur due to the availability of oxygen at the corrosive surface. The examples are shown in Fig. 2.^(a-d) The portion which has poor accessibility of oxygen becomes anodic compared to the parts having plenty supply of oxygen.

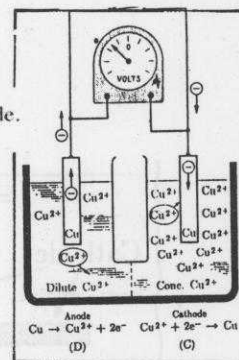
Stress Cells : The types of cells formed as in Fig. 3^(a&b) come under this category. The strain hardened portion of the component becomes anodic compared to the *annealed* part. The formation of this type of cells cause stress corrosion cracking, corrosion fatigue and other stress assisted corrosion cracking.

Galvanic Cells : The cells formed due to the availability of two or more types of metals at the corrosive surface, are called galvanic cells. Two common examples which are experienced in our day to day life are shown in Fig. 4. Since zinc is more active than iron, it corrodes preferentially to iron in situation of breakdown of galvanized coating. Tin, on the other hand, is protected at the cost of iron as former is nobler than iron. Similar is the case with other alloys where a preferential attack on active compo-

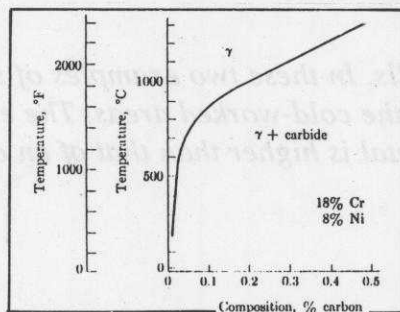
Fig. 2 : Examples of various forms of corrosion cells



Concentration cell, when the electrolyte is not homogeneous, the less concentrated area becomes the anode.

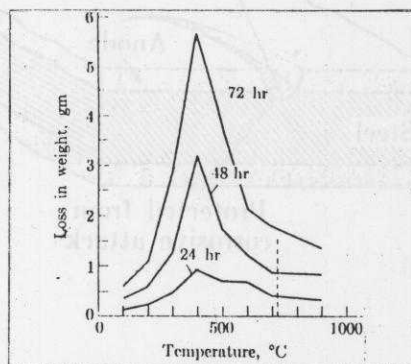


Oxidation cells. Inaccessible locations with low oxygen concentrations become anodic. This situation arises because the mobility of electrons and metal ions is greater than that of oxygen or oxygen ions.

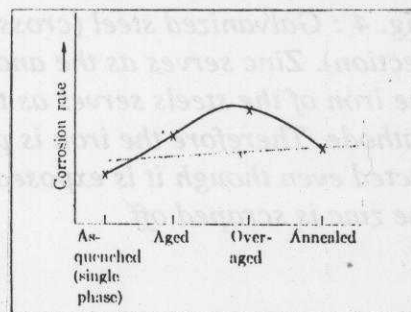


Carbon solubility in austenitic stainless steel. The carbon solubility in an 18-8 type stainless steel decreases markedly with temperature. Consequently, the carbon will precipitate if cooling is not rapid. The precipitated carbide is rich in chromium. (Adapted from E.E. Thum, *Book of Stainless Steels*, American Society for Metals)

Fig. Microcells and corrosion. After quenching, only martensite exists. After intermediate-temperature tempering, many small galvanic cells exist as a result of the fine (α + carbide) structure in tempered martensite. After high-temperature tempering, the carbide is agglomerated and fewer galvanic cells are present. (Adapted for F.N. Speller, *Corrosion: Causes and Prevention*, McGraw-Hill).



Age-hardening and corrosion (schematic). The single-phase, quenched alloy has a lower corrosion rate than the subsequent two-phase modifications.



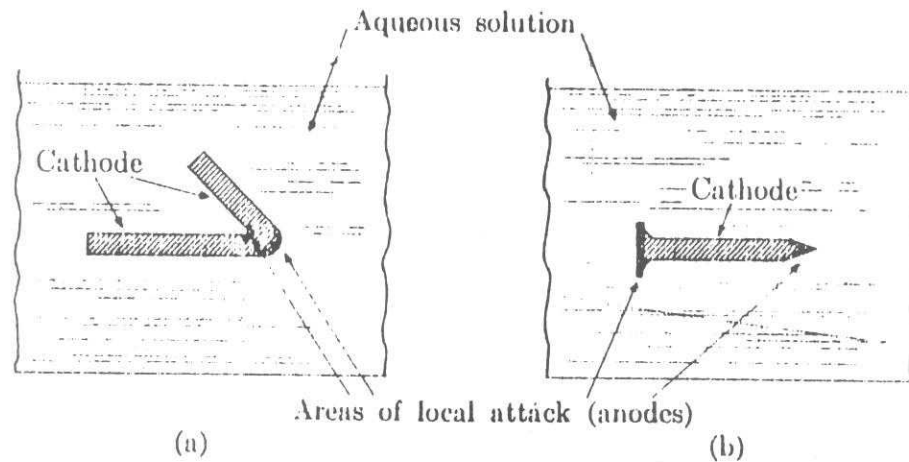


Fig. 3 : Stress cells. In these two examples of strain hardening, the anodes are in the cold-worked areas. The electrode potential of a strained metal is higher than that of an annealed metal.

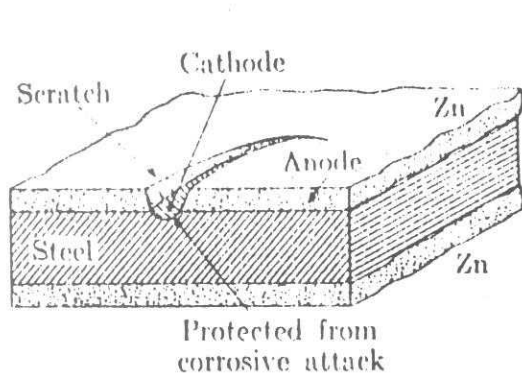


Fig. 4 : Galvanized steel (cross Section). Zinc serves as the anode; the iron of the steels serves as the cathode. Therefore the iron is protected even though it is exposed where the zinc is scraped off.

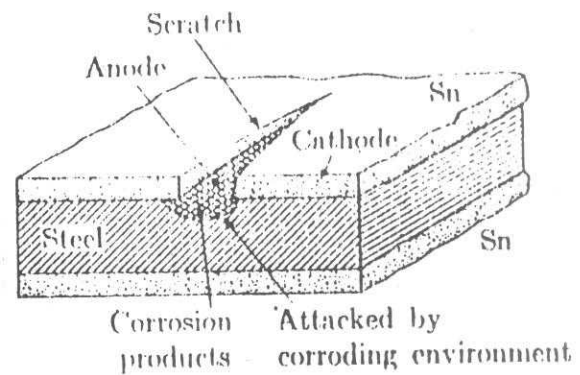


Fig. 4 : Tinplate (cross section) The tin protects the iron while the coating is continuous. When the coating is broken, the iron of steel becomes the anode and is subject to accelerated corrosion

ment of the alloy takes place. Formation of galvanic cells at the grain boundaries due to the precipitation of chromium carbide (eq. in stainless steels) is another example of formation of galvanic cell.

Forms of Corrosion

Depending upon the type of failure, corrosion product and appearance of corroded structures, the corrosion can be classified in the different groups. Some of the forms which are very common are :

Uniform Corrosion : when corrosion product is highly soluble in the corroding electrolyte.

Galvanic Corrosion : Dissimilar metals are in contact corroding electrolyte

Crevice Corrosion : oxygen availability is not uniform on corroding surface.

Pitting : Cathode to anode area ratio is very high

Intergranular : inhomogeneities at the grain boundary

Selective leaching : as stated in galvanic corrosion

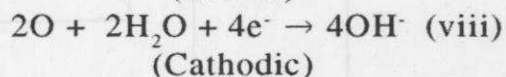
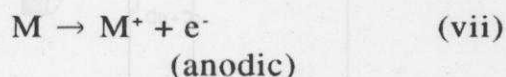
Stress assisted cracking : conjoint action of stress and corrosion.

Out of the above forms of corrosion, crevice, pitting, intergranular and stress assisted corrosion cracking are

more common in water side of boilers. A brief description of these types of corrosion therefore, would be useful here.

Crevice Corrosion

This is a kind of intensive localized corrosion which frequently occurs within crevices and other shielded areas on metal surface exposed to corrosives. This type of attack is usually associated with small volume of stagnant solution caused by holes, gasket, tap joints, surface deposits and crevices under it and rivet heads. Contact between metal and non-metallic surfaces can also cause crevice corrosion. The electrochemical reactions like :



occur at the crevice area. Since the area suffering from crevice attack is very small, the depletion of oxygen from this area as a consequence of reaction (viii) is very rapid. In order to maintain electroneutrality of the crevices, Cl ions (if present) would migrate and form metal chloride which in turn hydrolyses and produces free HCl.



HCl being a strong acid lowers the pH of the solution at the crevices and accelerates the attack. This type of attack is generally localized in nature and causes unnoticed failure of the material.

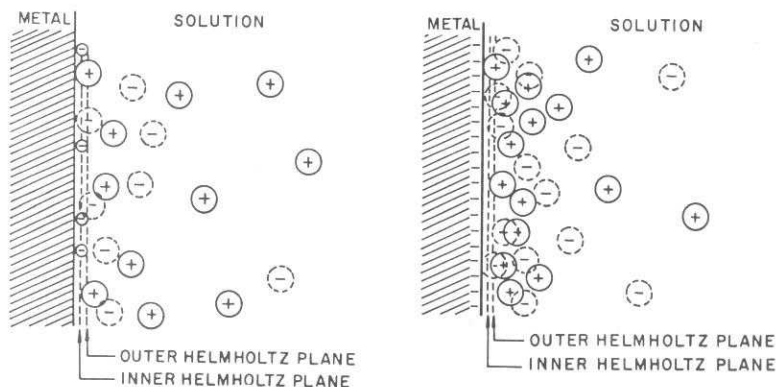


Fig. 1 : Schematic diagram of double layer

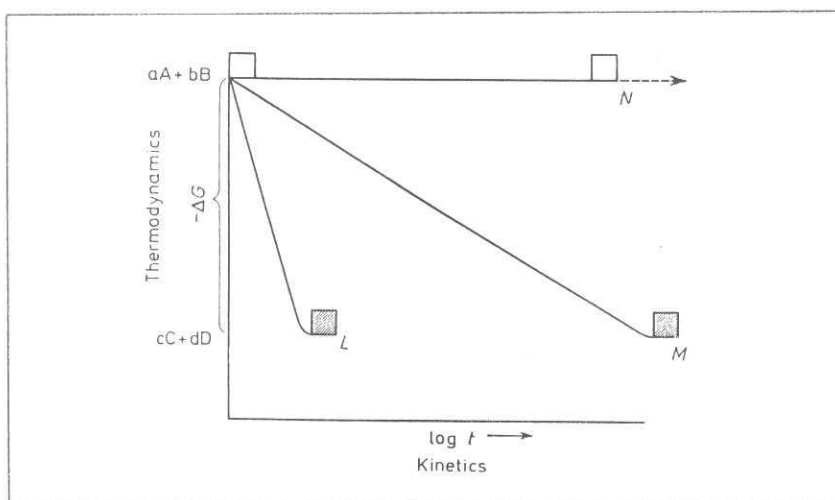


Fig. 6 : Block on inclined plane illustrating the relationship between the thermodynamic tendency ($-\Delta G$) of a corrosion reaction $aA + bB \rightarrow cC + dD$ and the rate of conversion of metal A to corrosion products C and D.

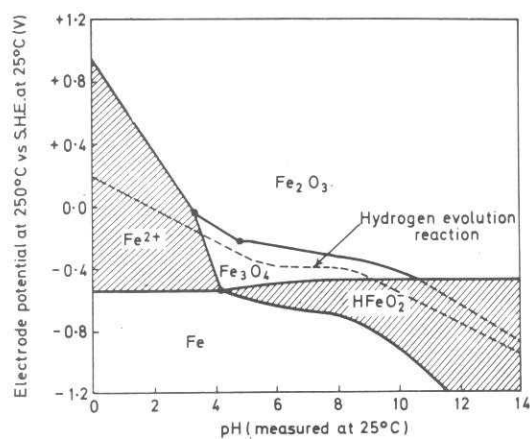


Fig. 7 : Potential-pH diagram for iron

Pitting Corrosion

A pit may be defined as a cavity or hole with the surface diameter about same as or less than the depth. Pitting is a form of extremely localized attack that results mainly due to the existence of large cathodic to anodic area ratio. It is very destructive form of corrosion and causes a catastrophic failure of the materials.

The basic mechanism of pitting is similar to that of the crevice corrosion. Pitting is autocatalytic in nature. Once a pit is formed it cathodically protects the other parts of the material.

Inter Granular Corrosion

Grain boundaries are anodic to the matrix. Localized attack at and adjacent to the grain boundaries with relatively little corrosion of grains is intergranular corrosion (IGC). IGC can be caused by the impurities at the grain boundaries, enrichment of the one of the alloying elements or depletion of one of these elements in the grain boundary areas. Depletion of Cr e.g., in the grain boundary regions results in IGC of stainless steels. IGC of welded structure of 304 SS is called weld decay.

Stress Assisted Cracking

It is a type of corrosion cracking where a conjoint action of corrodent and tensile stress takes place at the metal/ electrolyte interface. It is of two types :

- a) Stress corrosion cracking of a material takes place only in electrolytes who satisfy the conditions of its attack on the material as shown in Fig.5. As is evident from the figure, the cracking of materials can occur only in a specific potential zone of the system. In this zone, the passive film formed on the surface remains in a critical state of rupture and repair. This failure occurs transgranularly and or intergranularly.

Corrosion Fatigue

It results due to simultaneous action of cyclic stress and environment. Unlike S.C.C., corrosion fatigue can take place in all environments who can solvate the corrosion products.

Polarization of Corrosion

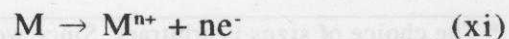
Reactions

E.M.F. Series :

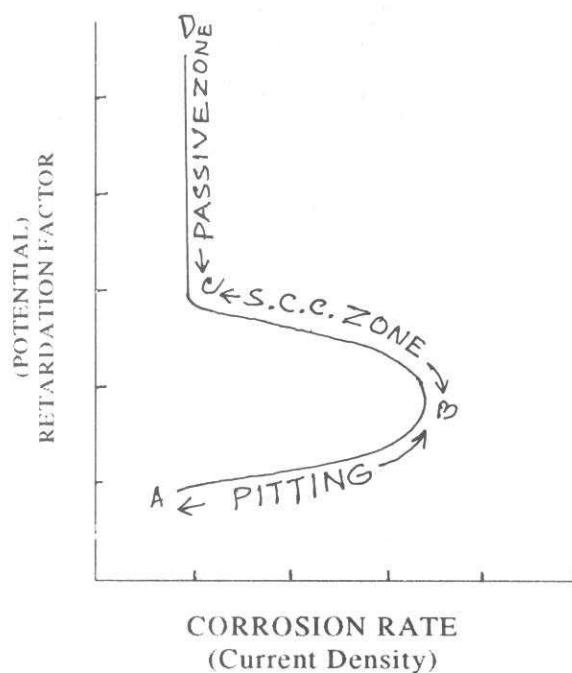
As described earlier, all the metals and alloy have a tendency to interact with its surrounding environments. The tendency of a metal/ alloy to interact with the environment can be expressed in terms of potential and free energy of change which are interrelated with the expression :

$$\Delta G = -n EF \quad (x)$$

where ΔG is the free energy change in a corrosion reaction :



E is the potential at which reaction



FOR FAILURE TO OCCUR

- o Corrosion rate should be between B & C
- o Stress should be above threshold

Fig. 5 : Criteria of failure by S.C.C.

Table -1
Electrode Potentials (25°C; Molar Solutions)

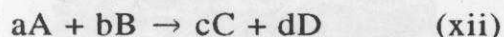
Anode half-cell reaction (the arrows are reversed for the cathode half-cell reaction)	Electrode potential used by physical chemists & corrosion engineers,* volts		Electrode potential used by electrochemists & corrosion engineers,* volts
Au $\rightarrow$ Au ³⁺ + 3e ⁻	+1.50	C a t h o d i c ↑	-1.50
2H ₂ O $\rightarrow$ O ₂ + 4H ⁺ + 4e ⁻	+1.23		-1.23
Pt $\rightarrow$ Pt ⁴⁺ + 4e ⁻	+1.20		-1.20
Ag $\rightarrow$ Ag ⁺ + e ⁻	+0.80		-0.80
Fe ²⁺ $\rightarrow$ Fe ³⁺ + Fe ⁻	+0.77		-0.77
4(OH) ⁻ $\rightarrow$ O ₂ ⁺ + 2H ₂ O + 4e ⁻	+0.40		-0.40
Cu $\rightarrow$ Cu ²⁺ + 2e ⁻	+0.34		-0.34
H ₂ $\rightarrow$ 2H ⁺ + 2e ⁻	0.00	Reference	0.00
Pb $\rightarrow$ Pb ²⁺ + 2e ⁻	-0.13	A n o d i c ↓	+0.13
Sn $\rightarrow$ Sn ²⁺ + 2e ⁻	-0.14		+0.14
Ni $\rightarrow$ Ni ²⁺ + 2e ⁻	-0.25		+0.25
Fe $\rightarrow$ Fe ²⁺ + 2e ⁻	-0.44		+0.44
Cr $\rightarrow$ Cr ²⁺ + 2e ⁻	-0.74		+0.74
Zn $\rightarrow$ Zn ²⁺ + 2e ⁻	-0.76		+0.76
Al $\rightarrow$ Al ³⁺ + 3e ⁻	-1.66		+1.66
Mg $\rightarrow$ Mg ²⁺ + 2e ⁻	-2.36		+2.36
Na $\rightarrow$ Na ⁺ + e ⁻	-2.71		+2.71
K $\rightarrow$ K ⁺ + e ⁻	-2.92		+2.92
Li $\rightarrow$ Li ⁺ + e ⁻	-2.96		+2.96

* The choice of signs is arbitrary. Since we are concerned with corrosion, we will use the middle column.

takes place and F is the Faraday. E values for different metals had been calculated taking thermodynamic values for their tendency to pass on in their own salt solutions (Molar solutions) at 25°C. The values are incorporated in Table - 1. This table is known as electromotive force (emf) series. Two signs of values are given here. However, in corrosion studies, the middle column is internationally accepted. The elements arranged at top of the table are least reactive where as bottom metals are considered as the most active. Hydrogen is considered as the reference.

Thermodynamics & Actual Kinetics

The potential values shown in Table 1 provide an indication about the tendency of a metal to interact with an environment. However, there are certain factors who stifle the reactions although they have a strong tendency (if judge on the basis of thermodynamical values) to interact with its surrounding environment. A schematic representation of this phenomenon is shown in Fig. 6. For a reaction :



to occur; $-\Delta G$ is the free energy change expected on the basis of thermodynamic calculations (stage x of Fig. 6). If certain external forces interfere with this reaction, the kinetics will be slowed down as shown in Y. If effects are still very strong interfering, the metal A will never pass in to its corrosion products C

and D and remain immune. These effects are known as polarization. Polarization can be broadly classified in three categories :

- * *Activation polarization* : this is caused owing to the energy associated with the electrode reactions.
- * *Concentration polarization* : caused by diffusion barrier of corrosion products and corrosive species from/to the corrosive interface.
- * *Resistance polarization* : caused due to the Ohmic drop at the interface such as passivity, coating etc.

An example of such polarization is corrosion of aluminium. Its standard electrode potential is -1.66 V which indicates a strong tendency to interact with its surroundings. In practice, however, aluminium corrodes very slowly compared to nobler metals. It is owing to the formation of an impervious oxide film (Al_2O_3) at the interface which isolates metal from the corrosive environments. This is an example of resistance polarization.

Corrosion Control

All the corrosion control practices are based on the principle of polarizations :

- * *Corrosion resistant alloys and surface alloying* : it is based on resistance and activation polarization.
- * *Paints, Coatings & Platings* : Resistance polarization

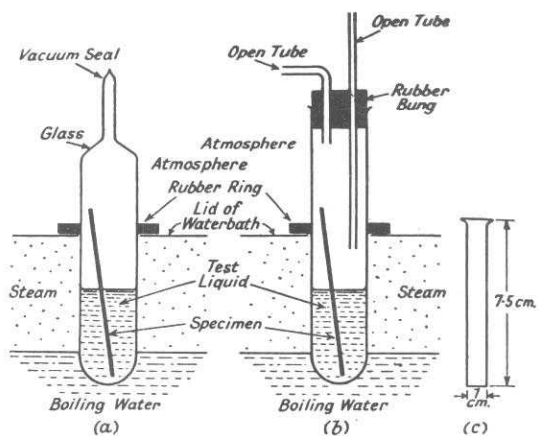


Fig. 8 : Apparatus for studying the behaviour of steel in boiling water under (a) anaerobic, (b) aerobic conditions, using specimen of form shown in (c) (A.J. Gould and U.R. Evans).

Munn: On-Load Waterside Corrosion in Power Boilers

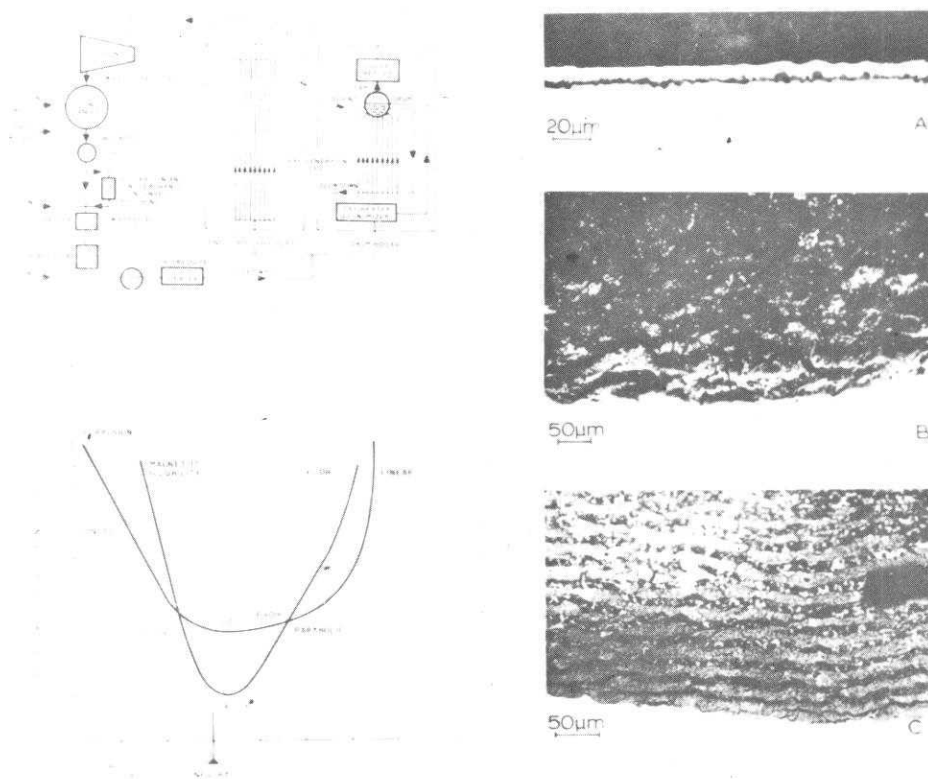


Fig. 10 : Corrosion of mild steel and solubility of magnetite at 300°C, showing corrosion rate laws (a) one year in pure water : average corrosion rate $10^3 \mu\text{mph}$ (b) 1000 h in 40% NaOH solution : corrosion rate : $1.9 \mu\text{mph}$ (c) 200 h in 0.1 mol dm³ HCl solution : corrosion rate $1.2 \mu\text{mph}$

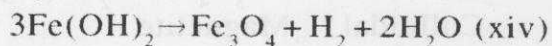
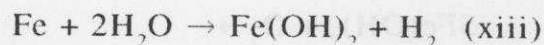
- * *Cathodic Protection* : Activation polarization.
- * *Anodic Protection* : Resistance polarization
- * *Inhibitors, Passivators* : Activation, resistance and concentration polarization.

Boilers Corrosion Water side

The water side corrosion problems of boilers are associated with the quality of water fed in to boilers. The inner surface of a boiler is protected due to the formation of an adherent and impervious magnetite film at the metal/water interface. If formation of this film on the surface is ideal one (having least defects, uniform, thin and adherent), the problem of corrosion is controlled automatically. However, owing to the faulty method of water treatments, the film formation is not appropriate and on set of corrosion reactions takes place.

Ideal Situations for the Formation of Magnetite

A closer look to the potential-pH diagram for iron (Fig.7) clearly shows that the magnetite layer is formed in a pH range of 7-10. The pH of boilers water, however, should be maintained close to neutral range to avoid other type of complications such as caustic cracking. The formation of magnetite is temperature dependent and above 200°C, the conversion of Fe(OH)_2 (which is the initial corrosion product of iron and water) to Fe_2O_3 is spontaneous :

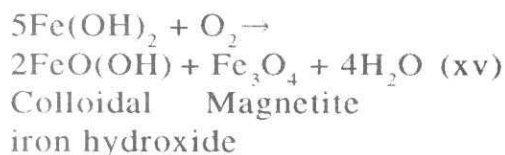


The above reactions are known as schikorr reaction.

Factors Affecting the Magnetite Formation

Oxygen Concentration : It is a well established fact that presence of oxygen in boilers water destabilizes the magnetite layer and causes pitting type of attack. It was shown by Gould and Evans in 1947 that when two steels specimen are exposed in boiling water (one sealed in a glass chamber having water but no further supply of oxygen and the other in water having constant supply of oxygen) and taken out after 76 days, the specimen exposed in water having no oxygen supply formed tenacious magnetite layer where as on the other specimen which has continuous supply of oxygen suffered with attack and corrosion product was magnetite and rust (Fig. 8). It was recommended by them in fifties that to protect boilers from corrosion attack, the oxygen content of the feed water of boiler should be minimum. it can now be explained that why the presence of oxygen causes pitting of boilers.

At elevated temperature, an instantaneous formation of magnetite takes place from ferrous hydroxide as indicated in equation (xiv) provided no oxygen is present. If however, oxygen is present in the water at boiler condition, instead of reaction (xiii), the reaction :



takes place. The magnetite and colloidal iron hydroxide formation does not take place at the attack side of the boiler and therefore, a loose and non-protective layer is formed on the surface.

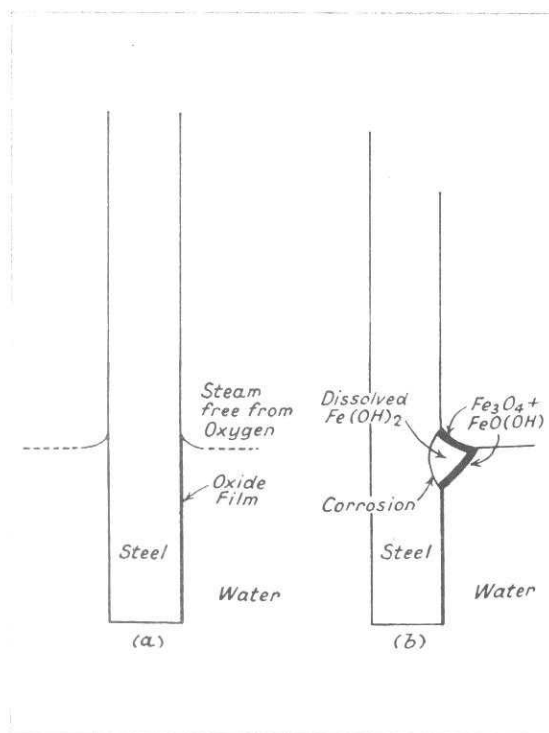
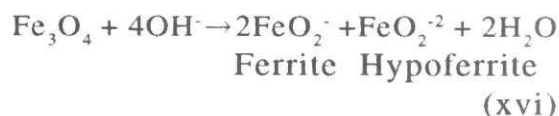


Fig.9: Schematic Presentation of Formation of Loosely bound Magnetite and Colloidal Ferrous Hydroxide on Boiler Surface

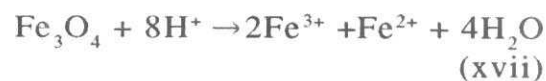
pH of Water

pH of water greatly affects the stability of magnetite. Fig.10 shows the magnetite layers formed on mild steel in aqueous solutions (pure water, sodium hydroxide solution are dilute HCl) at 300°C. In pure water it is most tenacious and

flawless compared to that formed in higher and lower pH solutions. Bringing the pH of the water slightly toward alkaline range is always advantageous especially if oxygen is not completely removed from water. Due to the excess of OH^- in the solution, solubility of oxide of iron is reduced owing to the common ion effect. Thus at an appropriate level of alkalinity no ferrous hydroxide is available in the liquid to precipitate a colloidal iron hydroxide and magnetite at a distance from the attack. However, the pH of boiler water, under no circumstances should increase more than 9.5. If it is above this, the reaction :



Commences and the protective property of magnetite is lost. If pH of water is less than 7, the reaction :



takes place and destroys the protective property of the magnetite layer.

Presence of Copper

The possibilities of entering the metals cation in boiler water always exist due to different reasons. Amongst the various cations, the presence of copper cation is extremely detrimental towards the stability of magnetite on boiler surface. It has been established that copper catalyses the schikorr

reaction of magnetite formation. The portion where copper deposits (on steel surface), attains a higher degree of magnetite formation. The other portion remains covered with thinner magnetite layer. This results in pitting of boilers.

Addition of Inhibitors

An ideal inhibitor should not interfere with the formation of magnetite rather they should stabilize it. Some oxygen scavengers are used to remove oxygen from the boiler water. Hydrazine and sodium sulphite are the main scavengers that are currently in use in modern boilers.

Addition of Polymers

A modern practice of stabilizing magnetite is use of polymeric materials in boiler water. These polymers not only passivate the boiler metal surface but also form complexes of hardness and enhance the solubility of hardness. Although the mechanism of action of polymeric materials on enhancing the magnetite formation (passivation of steel) is not very much understood, yet it is suggested that electron rich monomer units activate the process of film formation as they catalyse the adsorption of $\text{Fe}(\text{OH})_2$ on the boiler surface as shown in reactions (xiii) and (xiv).

Corrosion Failure Problems Associated with Boilers

Scale Breakage: Breakage of magnetite film occurs if boiler operating

at high temperature is suddenly cooled. This occurs due to the stresses set up by differences in thermal expansion. The cracked part becomes anodic and rest portion acts as cathode. A cell of high cathode to anode area ratio is formed leading to highly localized attack on the surface.

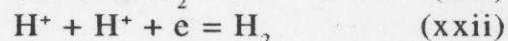
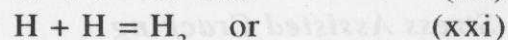
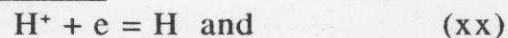
Control : Avoid sudden change in temperature of boiler water.

Hydrogen Degeneration of Steel: the schikorr reaction (xiii) and (xiv) can be written in steps as follows :

Anodic



Cathodic



Due to certain impurities present in water, the reaction (xxi) or (xxii) i.e., recombination of atomic hydrogen at the metal surface to escape as hydrogen molecule becomes too slow. These impurities which are called poisons, enhance the accumulation of atomic hydrogen on the steel surface. Hydrogen has a tendency to diffuse inside the body of the steel and causes a number of problems. Some times it is observed that pearlite converts into ferrite (iron), apparently through removal of carbon by hydrogen. The converted mass becomes porous due to the difference in densities of Fe and Fe_3C (7.86 and 7.40 respectively). A gram molecule of Fe_3C should

occupy about 24 cc., where as 3Fe is expected to occupy 21cc only. If water can penetrate in the part where pearlite originally existed, the ferrite will immediately convert in to magnetite (oxide). Thus whole decarburized zone is expected to be converted into oxide, provided original pearlite regions are continuous or sufficiently close to gether.

Control : To control decasburization of steels, it is essential that the feed water should be free of heavy metal cations such as As^{3+} , Cu^{2+} , $\text{Fe}^{3+}/\text{Fe}^{2+}$ and chloride ions who function as hydrogen promoters. Some specific alloys can be used instead of low alloy steels ($1\text{Cr}1/2$ Mo, & $21/2$ Cr $1/2$ Mo) to precent this type of failure. This aspect will be discussed by the other speakers.

Stress Assisted Cracking

Stress assisted cracking, especially stress corrosion cracking is observed to be a major cause of corrosion failure of boilers. As discussed earlier, the criteria for the failure of materials due to S.C.C., is that a specific environment must be available at the corroding interface. The specific environment in case of boilers is created by the deposition of scale on the surface. Due to the impurities in water, porous scale is

formed and in these pores, the fluids of high pH accumulate. This cause caustic cracking which is either intergranular or transgranular depending upon the construction of materials. It is important to mention here that intergranular cracking of certain materials can take place even without the application of stress. It is frequently observed in case of iron based materials in contact of an electrolyte of high pH. The iron forms soluble ferrite and hypoferrite at the grain boundaries (equation xvi). Grains are always anodic to bulk material and are quickly attacked by alkali especially under boilers conditions.

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