POWER AND DESALINATION CHEMISTRY

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Summary

This article covers aspects of commissioning, initial operation and general chemical management of power and desalination plants. Its main aim is to inform its readers on the various techniques that can be implemented to minimize corrosion and hence increase plant availability. It represents the author's 30 years' experience with the Central Electricity Generating Board in the UK together with his 10 year desalination experience as Director of Chemistry with the Water and Electricity Department in Abu Dhabi.

1. Introduction

The persistent, nagging, and wasteful process of corrosion has been "on going" since the beginning of time. Everyone has experienced some form of corrosion at some time during their stay on this planet.

Corrosion studies are basically "The study of the reactivity of materials in their surrounding environment" and prevention of corrosion is normally achieved by changing the material or changing the surroundings to which it is exposed.

Usually the choice of material is limited to its abundance, mechanical acceptability and cost and therefore most techniques used for corrosion prevention are limited to the study of the environmental conditions and making fundamental changes to minimize wastage.

Since the earliest days of steam power, boilers have suffered from corrosion problems. Perhaps this is not surprising. Made, for the most part of ordinary unprotected steel, boiler tubes spend their working lives exposed to hot water and steam on one side and to furnace flames on the other.

2. Boiler Corrosion

Boiler corrosion first appeared in the late 1930s in the USA attacking what were then the most modern of the steam-generating plants. Since then it has struck nearly every kind of boiler throughout the world. The apparent non-predictability of on-load corrosion was once the despair of boiler operators and for a long time seemed to defy rational explanation. Some plants would experience a devastating attack, while others of apparently similar chemical and engineering history remained unaffected. Boilers that had operated for years with no trouble would suddenly fail without warning. The frequency of outbreaks reached its peak in the early 1960s resulting in high financial losses in all the nationalized utilities, being a combination of repair costs and the costs incurred in having to operate less efficient units to maintain the system load requirements. It became obvious that the underlying corrosion mechanisms were more complex than originally thought and were likely to be a combination of many factors. Yet the essential nature of corrosion remained simple. Basically it is a process of oxidation, in which the metal attempts to return from its refined state to a state of combination with other elements, as in its original ore.

Nearly all metals of industrial importance are unstable in their normal environment. Mild steel and the other metals used in boilers are no exception. They are only able to retain their structural integrity during prolonged contact with hot water or steam only because the initial corrosion products deposit as a protective surface film, which effectively inhibits future attack.

Corrosion becomes a problem only when conditions are such that the protective film breaks down. This can happen if the boiler process produces very high local concentrations of contaminating acids or salts in the boiler water, or in the presence of excessive amounts of dissolved gases such as oxygen or carbon dioxide. In short, only when an environmental change has been created.

One important source of boiler-water contamination is the ingress of cooling water (usually seawater in desalination plants) during the periods when the systems are being operated with turbine and brine heater condenser cooling leaks.

Other significant sources of contamination are the release of corrosion products, such as iron or copper oxides from the feed water pipework, and the passage of ions from the water treatment plant or the mixed bed condensate purification plant. Salts are also deliberately added to the boiler water circuit as conditioning chemicals. For example, in most steam raising plants it is normal practice to add controlled amounts of sodium hydroxide or phosphates to counteract the possible effects of acidity, hence ensuring an alkaline boiler water at all times. Ironically, such additions can lead to their own problems.

What happens to the local solute concentrations under boiler conditions depends on the types and combinations of salts present, on the detailed distribution of heat and fluid flow, and on the chemical interactions that occur as the tube metal dissolves and its resultant oxides form.

In practice, minimum corrosion of steel occurs at a solution pH of 8.5 to 11.0 (Figure 1). This is the main objective of boiler and feed conditioning. It can be seen that deviation outside these pH values leads to rapid attack.

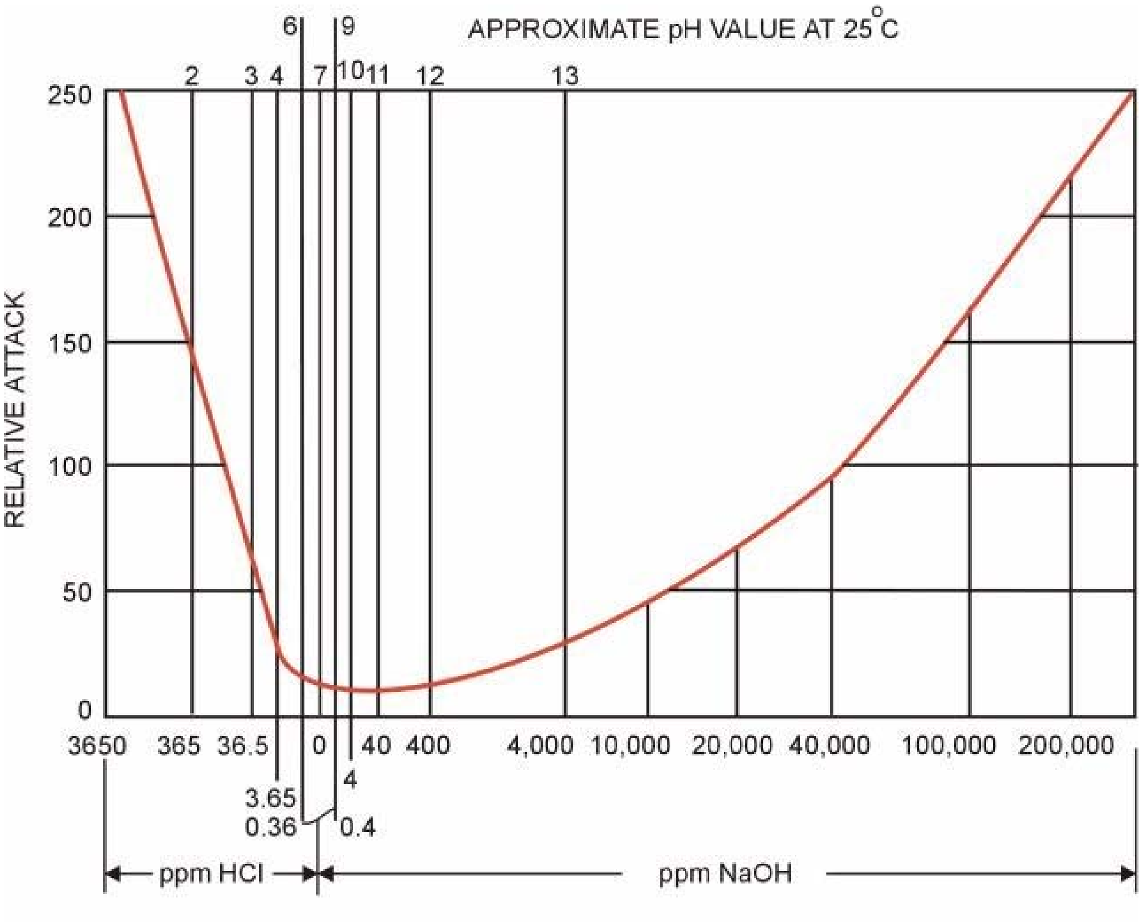


Figure 1. Attack on Mild steel by Acid and Alkali at 310°C.

2.1. Protective Oxides and Corrosion

Pourbaix and his co-workers (1962) studied film growth on iron surfaces for Fe/H_2O reactions at high temperatures. The Pourbaix diagrams are isothermal phase diagrams which represent metal-iron-oxide equilibria plotted with potential and pH as coordinates. These diagrams show that under normal deoxygenated boiler operating conditions, at 300-350°C, that magnetite is produced as a stable oxide film which is protective, and prevents further corrosion. The overall iron/water/magnetite reaction is:

$$\underset{\text{Iron}}{3Fe} + \underset{\text{Water/Steam}}{4H_2O} \rightarrow \underset{\text{Magnetite}}{Fe_3O_4} + \underset{\text{Hydrogen}}{4H_2} \qquad (1)$$

The corrosion rate is limited by the rates at which the reactant (water) can reach the metal surface and the reaction products can leave.

In neutral and slightly alkaline solutions, magnetite is only slightly soluble and it deposits as a coherent, tenacious surface film which greatly impedes the reaction. The reaction rate diminishes with time as the oxide thickness grows. Even after years of exposure, the layer is no more than a few microns thick.

This is the condition that the chemists and engineers are trying to achieve through boiler water conditioning.

In more alkaline or more acidic solutions, magnetite becomes increasingly soluble and precipitates in a different physical form. It has a much more porous structure and any soluble species in the water can now diffuse relatively rapidly through the film and the corrosion rate becomes faster.

When the solution becomes very acid or alkaline, the precipitated magnetite can no longer restrict access of solution to the metal surface. Corrosion then proceeds rapidly and the magnetite layer becomes many millimeters thick over a relatively short period.

The oxide formed in strong acid solution (<pH3) is coarse magnetite, very porous, thick and laminated. It offers no protection to the underlying steel and in fact traps the corrosive environment causing the corrosion process to propagate further. In strong alkaline environments (>pH11) hematite becomes the stable oxide phase which deposits as coarse unprotective crystals.

The nature of the oxide formed at a corrosion site can be used to diagnose the environment causing corrosion. In addition to the above corrosion problems heavy magnetite deposits, being poor conductors of heat, can lead to overheating failures especially if the steel structure has been weakened due to creep damage.

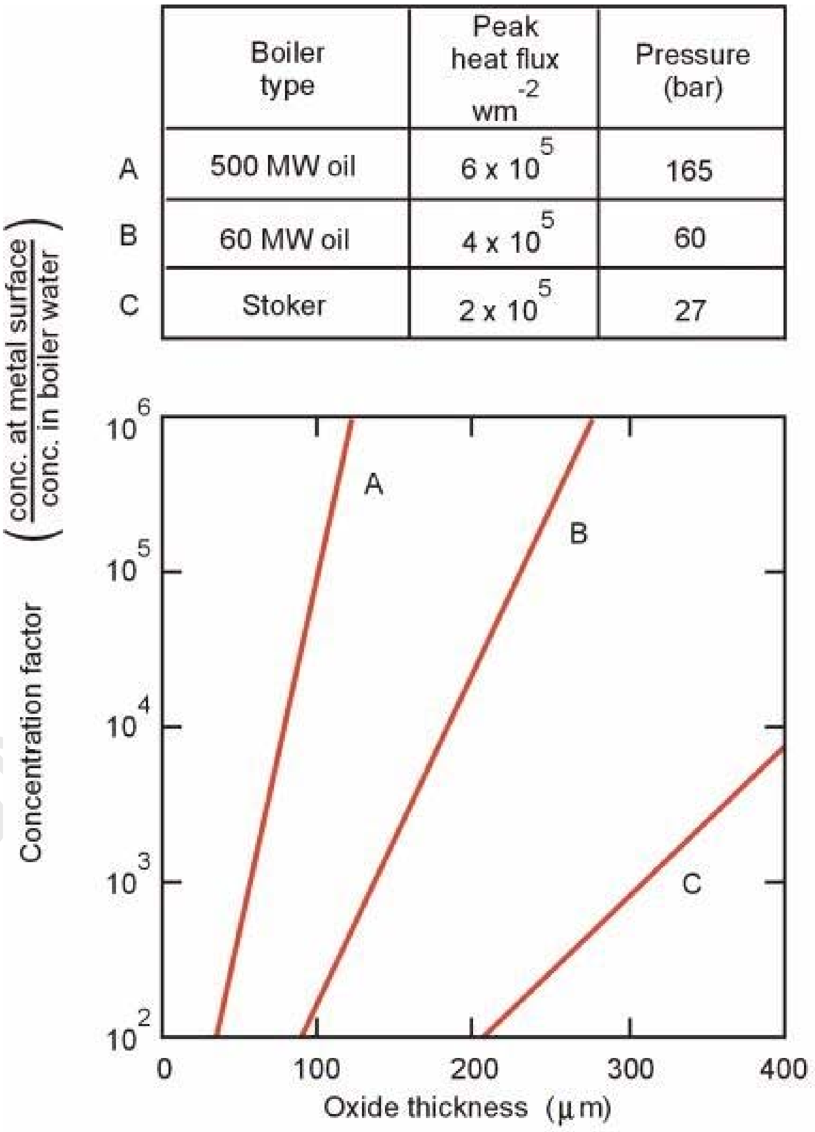
The free hydrogen generated by the corrosion reactions is a further potential hazard. Diffusing very rapidly into the steel it can cause metallurgical damage by reacting with alloying elements. In mild steel, hydrogen reacts with iron carbides to form methane. Since methane diffuses much less easily through the metal than hydrogen, it builds up to high pressures, which fissure and embrittle the steel well ahead of the advancing corrosion front.

Catastrophic fracture can follow, even though only a small part of the metal thickness has actually been corroded away. This type of attack is known as hydrogen embrittlement. It is characterized by large pieces of metal being blown out of what appears to be a thick walled tube. Low-alloy steels, which contain relatively stable chromium carbides, are much less vulnerable to this kind of failure. Hydrogen embrittlement is normally associated with acid conditions in the boiler. Caustic corrosion rarely induces hydrogen damage and the actual rate of corrosion is usually less than for acid chloride corrosion.

2.2. Achieving Concentrated and Aggressive Environments

Even during severe turbine condenser leaks, the bulk boiler water chemistry does not deviate significantly from fairly pure water. A few mg kg^{-1} of chloride cannot cause rapid corrosion of mild steel even at 350°C. Generally, values in excess of 500 mg kg^{-1} are required to promote significant corrosion rates. Some concentration mechanism therefore must be present. The most common resulting from boiling taking place in the restricted capillaries/pores of the porous oxides. This concentrates the boiler water and limits diffusion of the concentrates back into the bulk water. High concentration factors (local concentration divided by bulk concentration), up to 10^4-10^5 can be achieved, the value depending on oxide thickness, porosity, heat flow and partition coefficient of the dissolved species. A more detailed account is given in the paper by Mann (1975).

High heat flux boilers quickly develop high concentration factors and therefore aggressive environments, resulting in failure when peak oxide thickness are in excess of 100 μm, whereas low heat flux boilers can operate with thick oxides and poor chemistry without generating local corrosive environments. As heat flux generally correlates with the pressure class of the boiler, it can be seen that target values recommended for chloride and other aggressive species decrease with increasing boiler operating pressures (Figure 2).



	Boiler type	Peak heat flux wm^{-2}	Pressure (bar)
A	500 MW oil	6×10^5	165
B	60 MW oil	4×10^5	60
C	Stoker	2×10^5	27

Figure 2. Concentration factor - oxide thickness.

Boiler tube crevices and weld protrusions also limit the back diffusion of boiling solutes resulting in aggressive environments. A large proportion of tube failures occur in welded areas and it is for this reason that, during any repairs, the length of the insert should be such that the new welds are made outside the high heat transfer areas.

Concentration of solids can also result where dry-out patches form on the tube surface. For example the combination of high heat flux and low mass flows on near horizontal furnace floor tubes on some high pressure boilers can lead to separation of the solid at the crown of the tube. Dry-out in these regions produces high metal temperatures which could support strong caustic solutions and subsequent tube failure.

The various concentration mechanisms can also alter the character of the impurities in the water locally. As concentration proceeds, some basic species may precipitate leaving the liquid phase to become acidic. For example, hydrolyzable metal chlorides such as $MgCl_2$, hydrolyze and precipitates the sparingly soluble hydroxide:

$$\underset{\text{Magnesium Chloride}}{MgCl_2} + \underset{\text{Water}}{2H_2O} = \underset{\text{Magnesium Hydroxide}}{Mg(OH)_2 \downarrow} + \underset{\text{Hydrochloric Acid}}{2HCl} \qquad (2)$$

Seawater, a common coolant used in boiler and desalination plants contains a relatively high level of magnesium chloride. Any condenser leak would result in the seawater coolant entering the feed system which would lead to the boiler water becoming acidic. During these periods it is common practice to add caustic soda to the boiler and maintain a NaOH/NaCl ratio of 1.5.

Dissolved oxygen can also influence on the local environment, producing highly acidic conditions from neutral or slightly alkaline bulk waters and is a major contributor to chloride corrosion. Its role is to speed up the slow background dissolution of iron within pits or porous oxide by means of the providing the balancing cathodic reaction.

$$1/2O_2 + 2e + H_2O + H_2O \Rightarrow 2OH^- \text{ ... cathodic reaction} \qquad (3)$$

$$Fe \Rightarrow Fe^{2+} + 2e \text{ ... anodic reaction} \qquad (4)$$

The hydroxide ions are formed outside the pit and the ferrous ions within it. The increased rate of ferrous ion formation then provides a hydrolyzable base for any chloride ions within the pit and so forms a low pH environment.

$$\underset{\text{Ferrous Chloride}}{FeCl_2} + \underset{\text{Water}}{2H_2O} \Rightarrow \underset{\text{Ferrous Hydroxide}}{Fe(OH)_2} + \underset{\text{Hydrochloric Acid}}{2HCl} \qquad (5)$$

3. Chemical Conditioning to Avoid Corrosion

3.1. Boiler Water Conditioning

It is now generally accepted that low level caustic soda treatment (2-3 mg kg^{-1}) should be used to treat boilers operating at pressures in excess of 120 bar. This ensures that alkaline conditions are maintained at all times providing the NaOH/NaCl remains at 1.5. The upper limit of 3 mg kg^{-1} for the boiler water is set to ensure that the steam sodium limits of 5-10 $\mu g\ kg^{-1}$ are not exceeded. Applying the ratio restricts the boiler chloride value to a maximum of 2 mg kg^{-1}. However occasional problems have been experienced with high heat flux boilers (>600 kWm^{-2}). Even at values as low as 2-3 mg kg^{-1} NaOH would lead eventually to caustic corrosion through either dry out or any other mechanisms of attaining very high concentration factors. These high heat flux units are normally operated with 0.5 mg kg^{-1} to reduce the risk of caustic soda corrosion. Some high-pressure (165 bar) boilers are unable to operate on caustic soda dosing as occasionally these boilers concentrate the alkali which leads to caustic soda attack of the boiler tubes and excessive carry over of sodium into the steam resulting in attack of the superheater and reheater sections of the boiler. Such boilers are normally operated on ammonia and hydrazine conditioning. This being known as volatile alkali treatment (VAT). Unfortunately ammonia is too weak a base to provide any protection against significant chloride ingress. In consequence a chloride limits of only 0.2 mg kg^{-1} is applied when operating under these conditions. This value is largely derived from experience and known to be safe, but recent work has shown that chloride values up to 1-2 mg kg^{-1} can be tolerated for short periods of time. Usually when boilers are operated on volatile alkali treatment (VAT) they are dosed with small amounts of caustic soda during periods of chloride ingress to ensure the recommended NaOH/NaCl ratio is maintained.

Lower pressure boilers (100 bar) may operate on trisodium phosphate chemistry which acts in a similar manner to sodium hydroxide providing the necessary pH. In addition the phosphate reserve can precipitate any calcium and magnesium brought about by any seawater ingress. However, if high phosphate concentration factors are achieved, some of the phosphate will precipitate and separate into one or more phases. At temperatures greater than 280°C liquid acid phosphates, Na_2HPO_4 or NaH_2PO_4 can occur which is corrosive towards mild steel. Consequently phosphate treatment should not be used at pressure in excess of 100 bar unless heat fluxes (and therefore concentration factors) are low.

3.2. Feed System Conditioning

Feed systems are normally provided with in-line deaerators which reduces the oxygen to below 0.005 mg kg^{-1}. Under these conditions it is only necessary to add hydrazine as an oxygen scavenger and adjust the feed pH to approximately 9.0 by addition of ammonia. Indications are that the feed magnetite stability increases with increase ammonia concentrations. However 1.0 mg kg^{-1} is regarded as the maximum allowable ammonia value to avoid corrosion of the copper and copper alloy components present in the feed system and in the distillers.

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