

# Some Problems of Corrosion in Thermal Power Plants

by

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## INTRODUCTION

In thermal power plants the following types of corrosion are generally encountered :

- (i) Water/gas/acid corrosion.
- (ii) High temperature corrosion.
- (iii) Low temperature corrosion.
- (iv) Oil-ash corrosion.
- (v) Stress corrosion.
- (vi) Fatigue corrosion.

The present paper discusses a few important factors that are responsible for the destruction of ferrous metals by corrosion in thermal power plant. It is unfortunate that practically all metals under some environment or other are subjected to corrosion attack with the ultimate result in metal failures. It is estimated that the annual cost of corrosion in India approaches several crores of rupees. In the United States alone the annual figure is ten billion dollars and that of the world is at least double this figure. A small part of this figure can be attributed to corrosion found in power plants where the metal parts come in contact with water. With the growth of power plants in India one can therefore guess the increasing amount of metal loss under these circumstances. Therefore any useful means to combat corrosion in power plant will not only save money but prolong the life of costly equipment, help to continue trouble-free operation and many other inconveniences that may arise as a result of failures.

It is now well recognized that corrosion is largely electrochemical in nature. Voluminous literature exists dealing with various factors that are responsible for power plant corrosion, their fundamentals and specific instances. The present paper, will however, confine the topic to some of the areas where corrosion in power plants is likely to take place at normal operating temperatures, their causes as well as control measures to combat corrosion. Finally, the discussion will include a few illustrations of typical corrosion failures commonly encountered in power plants.

Water and steam side corrosion in power plants can be ascribed to the presence of the following in feed water :

- (a) Dissolved oxygen
- (b) Carbon-dioxide
- (c) Low pH of water
- (d) A combination of all three factors mentioned above.

Since in a boiler system there are various other areas, separate consideration should be given to understand the corrosion problem and evolve effective means for their control.

## **Causes of Corrosion**

The alkalinity of feed water must be raised so that the acidic nature is prevented. It is, however, possible for acidic conditions to be produced by hydrolysis of chlorides at a later stage. Magnesium chloride for example, is readily hydrolysed into magnesium hydroxide and hydrochloric acid. Similarly, magnesium sulphate and sodium chloride may cause acidity as a result of interaction with the production of sodium sulphate, magnesium hydroxide and hydrochloric acid. Carbon dioxide dissolved in water is acidic and accelerates the corrosion of boiler waters specially in presence of oxygen. Therefore, unless magnesium salts are removed completely or unless there is a sufficient reserve of alkalinity in the system to neutralize acids so produced, corrosion will occur. But if pH of feed water is greater than about 7.5 and the boiler water is maintained at a pH round about 11.0 corrosion can be prevented to a considerable extent.

### **Galvanic attack**

Electrochemical corrosion also occurs when two dissimilar elements are in contact in an aqueous solution. The potential of corroding cell depends on the position in which the elements are placed in the electrochemical series and upon the concentration of ions in solution.

### **Oxygen attack**

This is caused by differential aeration. The magnitude of the electromotive force developed between two areas of a metal exposed to different conditions of aeration is sufficient to cause localized attack of iron when placed in water containing zones of varying dissolved oxygen content. If a piece of scale, paint, dirt or even a bubble of gas adheres to the surface of iron or steel immersed in water containing traces of dissolved oxygen, differential aeration cell will be set up. Corrosion will start under this layer and a crust of ferrous hydroxide will form. If this crust so produced is not removed mechanically, the action will continue. In course of time, a hole will appear. Such conditions are very common in boiler to develop corrosion of this nature. During shut down of boiler this effect may be observed. The tubes retain water when boiler is drained as water accumulates in the middle and cannot be emptied by gravity. After the water is stagnant for a few days, corrosion will start at rough spots inside the tubes. A pale green crust of ferrous hydroxide will grow over the areas. As oxygen is absorbed at the surface of the water and gradually diffuses downwards, crusts penetrate inside the tubes. If this condition is allowed to persist, the crust gradually darkens in colour and finally transforms into red colour of ferric hydroxide.

In a thermal power plant, corrosion is most commonly encountered in the following areas :

- (a) Feed water circuits including piping, valves, pumps and heat transfer equipment.
- (b) Boiler internal surfaces and economizers.
- (c) Condensate return circuits.
- (d) Wet stages of turbines.
- (e) Cooling water systems.

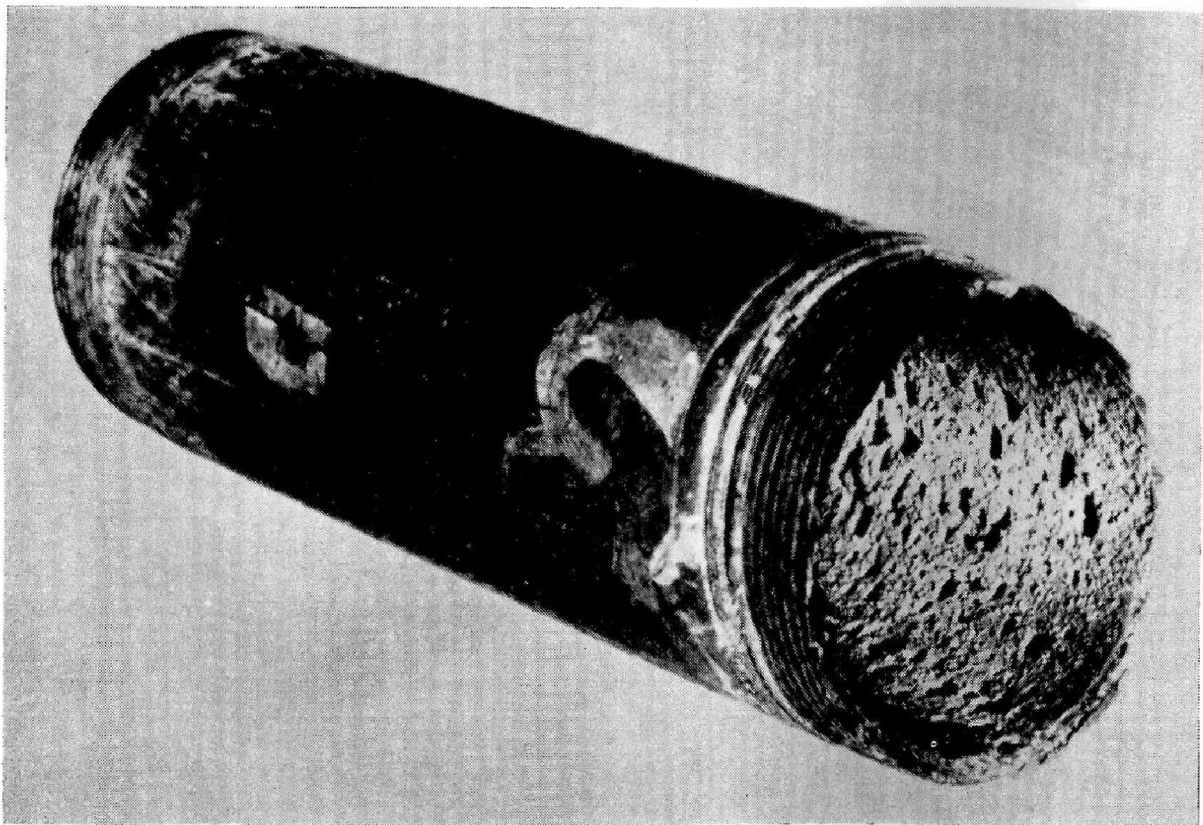
The corrosion aspect in these different areas will be discussed separately in subsequent pages.

## Feed water circuits

Feed water to a boiler may consist of 100% make-up or a combination of make-up and various amounts of condensate returns. Raw make-up water, either surface water or well water, may be saturated with dissolved oxygen. Surface waters particularly are normally saturated with oxygen because of direct contact with atmosphere; whereas deep well waters may be free from or contain only a very small amount of oxygen.

Return condensate may contain oxygen as a result of air leakage through pipe fittings, pumps, and valve glands.

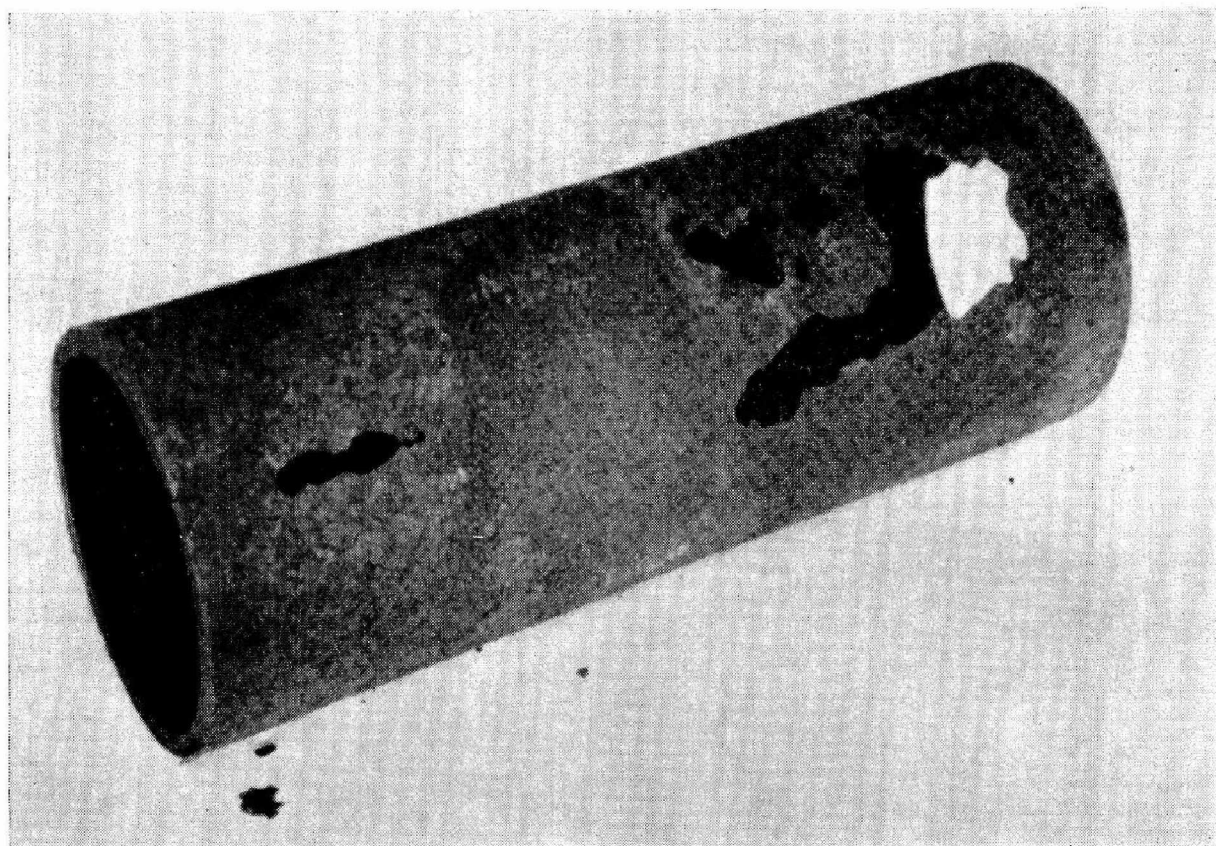
Since the temperature of the raw make-up water introduced into feed water system is generally quite low, corrosion of piping, valves, water softeners, etc., due to the presence of oxygen in the cold water is not too serious even though the solubility of oxygen is highest at low temperature. However, as the temperature of water increases in passing through the heat exchangers, pumps or in mixing with hot condensate returns, the corrosive action of oxygen is greatly accelerated. This type of corrosion arises from the presence of oxygen resulting pitting of metal surfaces (Fig. 1).



*Fig. 1. Pitting corrosion caused by oxygen in feed water system*

Generally, the rate of reaction is approximately doubled for each 18° F increase in temperature. Simultaneously, there is another factor that works in opposite manner by which the solubility of oxygen is decreased with increase in temperature. Experience has shown that the speed of corrosive action is greatest at a temperature of approximately 160 to 180° F beyond which an increase in temperature tends to decelerate the corrosion rate<sup>2</sup>.

Surface water and well water may also contain free carbon dioxide which is corrosive. If it is present in water along with oxygen, the combined effect proves to be more corrosive. Corrosion as a result of carbon dioxide can be seen by general thinning and grooving of pipe walls or metal surfaces (fig. 2)<sup>2</sup>.



*Fig. 2. Corrosion in presence of carbon dioxide gas resulting thinning of pipe walls and to cause holes*

In a surface condensing plant where the feed water is relatively pure, the pH of water may be low and iron and steel pipe will be attacked even at low temperature giving rise to ferrous hydroxide. This attack will continue till ferrous hydroxide, being alkaline, raises the pH to approximately 8.3 when no more iron will go into solution. Any oxygen present will oxidize ferrous ion to ferric ion to form insoluble precipitate of ferric hydroxide. Carbon dioxide present in water lowers the pH and dissolves the iron. The ferric hydroxide will adhere to pipings and will be carried into boiler to coat the boiler tubes to cause localized attack and tube burn out.

A combination of corrosion and erosion presents a further problem in the case of pumps, valves, and pipe fittings where a sudden change in direction results in high velocity of water stream to clean any iron deposit that might form on the surface. The base metal is exposed to further attack of corrosion and erosion.

The corrosive influence of boiler feed water as a result of the presence of dissolved oxygen and carbon dioxide may be eliminated through mechanical deaeration of feed water which will reduce the oxygen content to less than 0.005 ml per litre and free carbon dioxide to zero. In practise, engineers

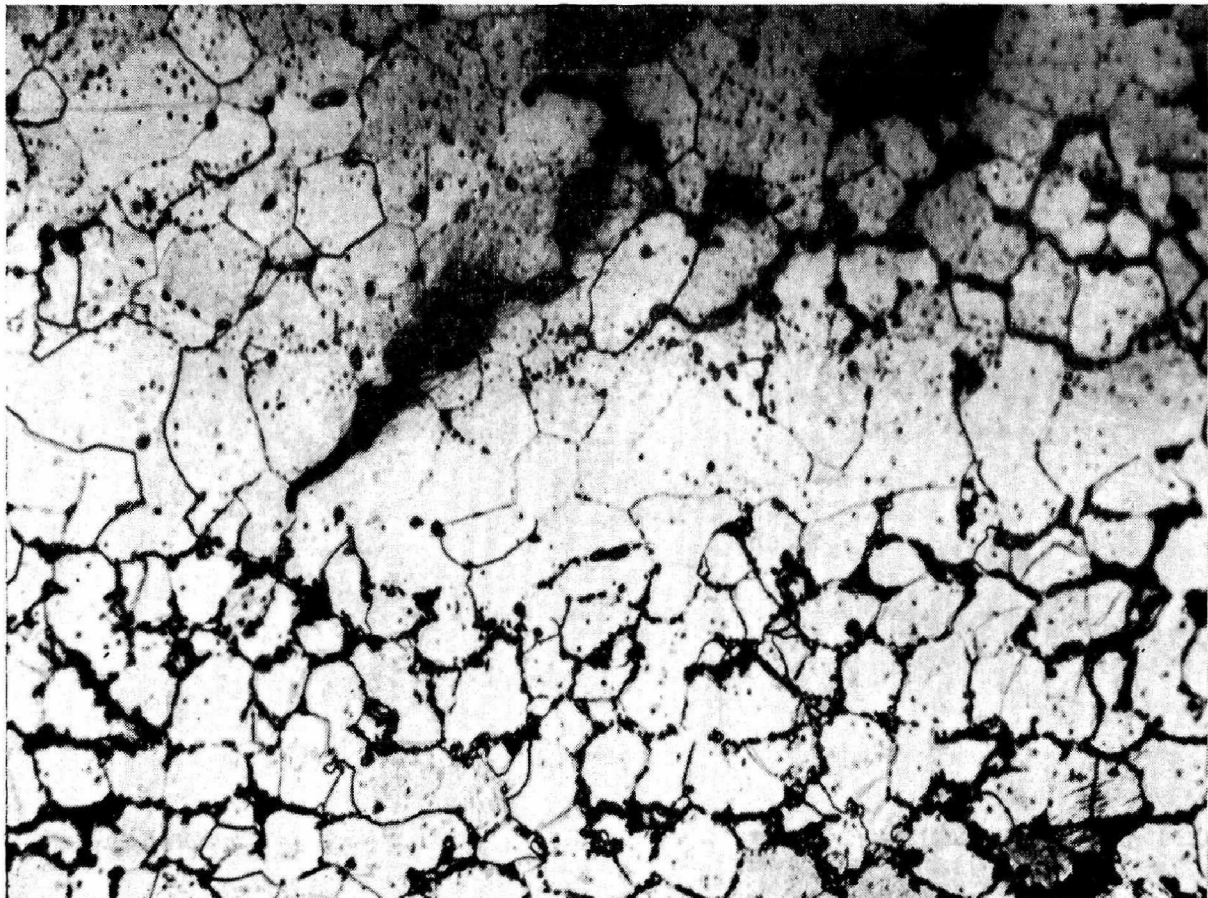


frequently prefer to follow mechanical deaeration with chemical oxygen scavenger for removing the last traces of oxygen.

### **Boiler internal surfaces including economizers**

Any corrosion that occurs in a boiler can usually be traced for the presence of dissolved oxygen in feed water. In general, carbon dioxide is not a contributing factor as long as the desired alkalinity and pH of boiler water is maintained. Oxygen must be dissolved in the boiler heater before it can attack ferrous metal surfaces. Normally, the dissolved gases present in the feed water entering a boiler drum are immediately released to the steam due to the substantial increase in temperature. However, a sudden increase in feed water demand and high boiler circulation carries the cooler water entering into the downcomer boiler tubes before the oxygen has had a chance to be released thus causing corrosion below the water line and at the tube entrances. Sometimes corrosion with a boiler can be attributed to the iron oxides contained in the feed water. If these oxides are not removed by blow down and are allowed to form deposits in the areas of less rapid circulation, a hard dense adherent, scale can form to cause overheating of the metal and further production of iron oxide.

Intercrystalline cracking or caustic embrittlement may accompany this overheating of the tube metal by allowing high concentrations of caustic soda to form at these overheated spots to cause attack along the grain boundaries of the metal. Also caustic soda may concentrate in other hide-out spots in the boiler, such as the end of boiler tubes where the tubes are rolled into boiler drum or caustic



*Fig. 3. Intercrystalline cracking due to caustic concentration in boiler water*

can precipitate out of the solution at such points where the formation of steam is too rapid for replacement by water circulation and the tubes become dry. Intercrystalline cracking may also occur at the points of high caustic concentration if the boiler metal is stressed and if the boiler water possesses embrittlement characteristics. This type of attack was more pronounced in case of revetted boiler seams (Fig. 3). The use of welded seams has, however, minimized this condition.

Earlier investigations towards prevention of caustic embrittlement favoured the maintaining of certain sulphate-carbonate ratios as suggested by ASME. However, relatively recent work indicates that these ratios do not necessarily prevent such attack. Another method is to maintain certain ratio of sodium nitrate to sodium hydroxide. The most recent method for plants where feed water is mostly condensate, is the coordinated pH-phosphate method where tri-sodium phosphate is fed to the boiler water to maintain the desired pH and to eliminate free sodium hydroxide in water. Whether a boiler water has embrittlement characteristic can be determined by embrittlement detector which has been developed by the Bureau of Mines of United States.

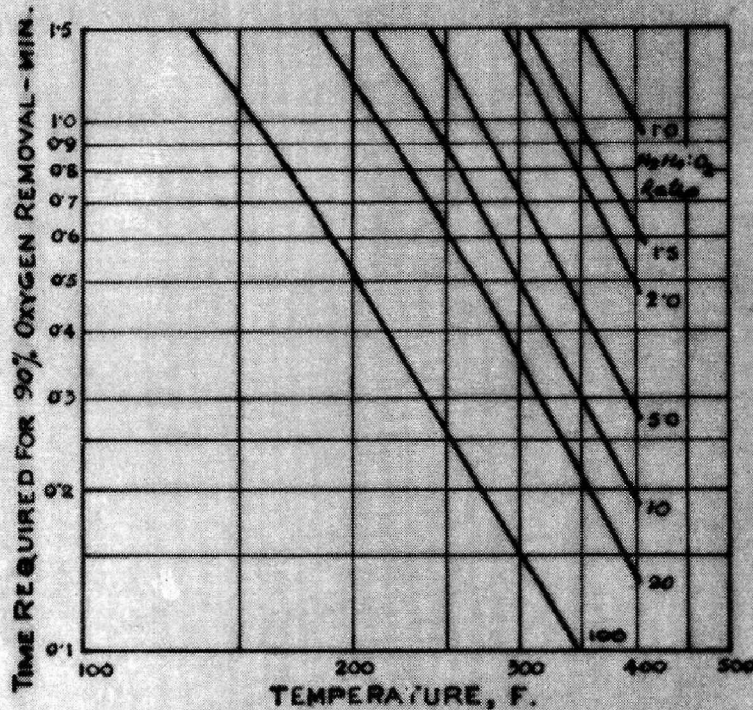
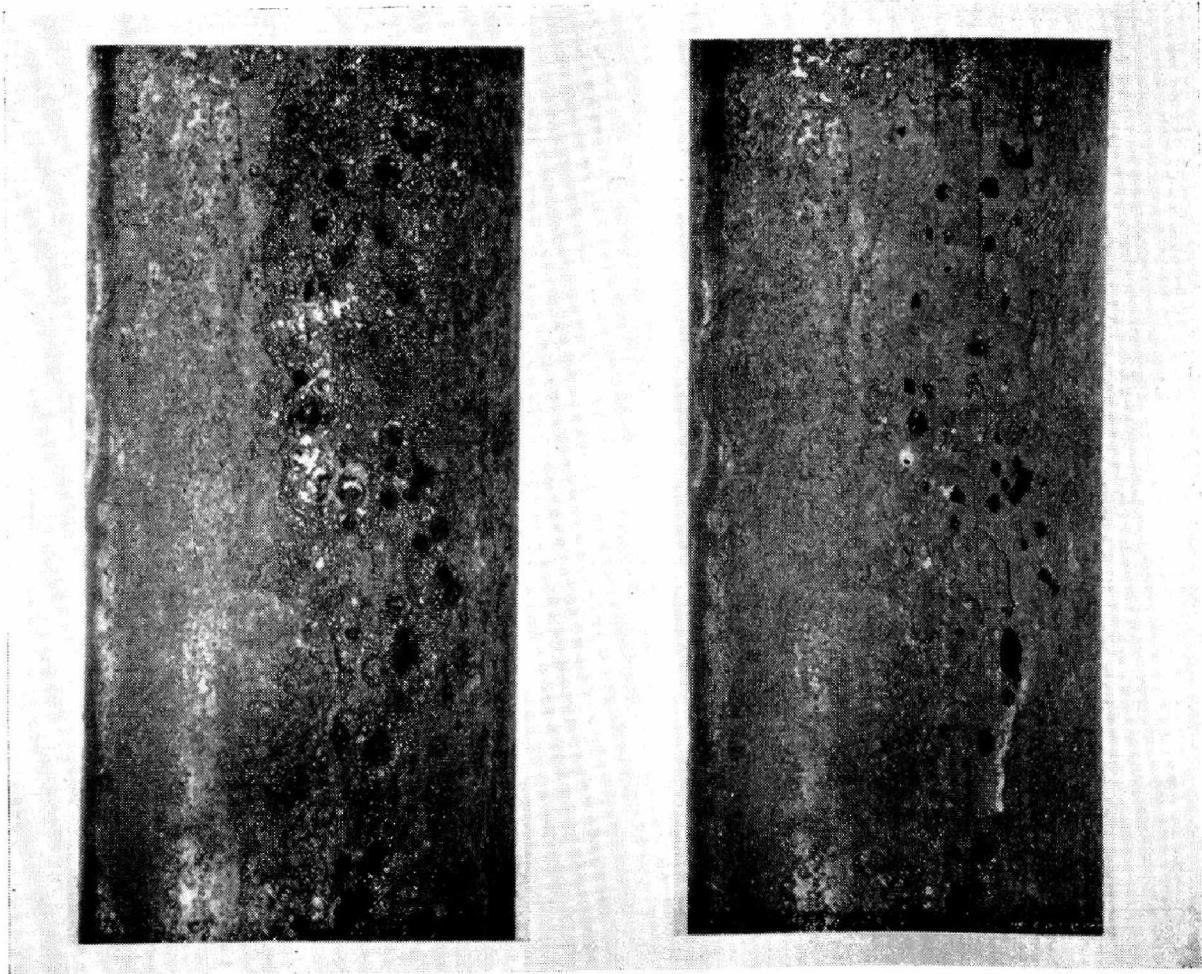


FIG. 4. HYDRAZINE - TIME - TEMPERATURE RELATIONSHIP FOR 90% OXYGEN REMOVAL AT pH = 9.5.

Many high pressure boilers incorporate economizers through which the boiler feed water passes before entering the boiler drums. This is an economic measure whereby the temperature of feed water is increased by taking heat from the hot combustion gases passing to stock, thus reducing the feed costs. Economizers necessarily have steel tubes because of high boiler pressure. If, therefore, the feed water contains oxygen or carbon dioxide corrosion of steel tubes will occur as the temperature of feed water is elevated in passing through the economizer (Fig. 5).



*Fig. 5. Failure of economiser tubes in a high pressure boiler due to high concentration of oxygen in feed water*

### **Condensate return circuits**

Condensate return line corrosion may be caused by the presence of dissolved oxygen or carbon dioxide in the condensate or a combination of both. An efficient mechanical deaeration heater placed in the feed water system will remove oxygen and carbon dioxide before it enters the boiler. In the boiler, however, bicarbonate or carbonate alkalinity present in the water will decompose to introduce carbon dioxide to steam. It has been demonstrated that the high temperature conditions within a boiler cause complete decomposition of bicarbonate alkalinity. For each 100 ppm of bicarbonates in the boiler feed water, 79 ppm of carbon dioxide will be given off with the steam. For each 100 ppm of normal carbonates, approximately 35 ppm carbon dioxide will be evolved. At points where the steam is condensed in the return system, the carbon dioxide will be redissolved to form carbonic acid and corrosion takes place in the return lines<sup>2</sup>.

The feeding of ammonia or ammonia compounds to the system is practised in many plants for neutralizing the carbon dioxide and raising the pH of the condensate<sup>3</sup>. The high boiler temperatures decompose these compounds to release ammonia gas to the steam. As the steam condenses, the ammonia is redissolved in the condensate and reacts with  $\text{CO}_2$  to form highly soluble carbonate compounds thus raising the pH. Control of ammonia into the system is rather difficult due to its high volatility. High



concentrations of ammonia will attack copper and zinc-bearing metals. Neutralizing amines<sup>4</sup> have been used in many plants in the past few years as a substitute of ammonia for the prevention of condensate return line corrosion. Organic amines, e.g., cyclohexylamines, benzylamines or morpholine are alkaline in nature. These are quite soluble in water and will readily volatilize with the boiler steam. On redissolving with condensate, the amine combines with any carbon dioxide present to form an amine carbonate or bicarbonate. This neutralizes the carbon dioxide and raises the pH to prevent corrosion of the return system. Although amine treatment is more expensive than ammonia treatment, the use of neutralizing amines provides easier control of condensate pH, and also the danger of attack on copper or zinc alloys is eliminated.

Filming amines to protect return lines against corrosion is more recent practice. Instead of reacting with carbon dioxide in the steam this type of filming amine forms a non-wettable film on metal surface. It thus acts as a protective barrier between the metal and the condensate. Usually this type of filming amine is fed into the main steam line where it is diffused and carried along with the steam to form a film on all of the contracting surface. Usually 15 to 30 ppm of filming amine is necessary to cover all metal surfaces and is said to be independent of the carbon dioxide present in the condensate. This type of treatment is reported to be cheaper than neutralizing amine treatment.

### **Wet stages of turbine**

In a power plant steam passes through various stages of the turbine and is finally condensed on the turbine surface. This condensate is then pumped back to the boiler through several stages of closed heaters with usually a deaerating heater. The boiler feed water consists almost entirely of condensate with only 1% to 2% make-up water, being added to the system to take care of losses due to leakage. The make-up water is either demineralized water or vapour from evaporators.

Due to high purity of feed water, the alkalinity is essentially zero and therefore, there is no break down of alkalinity in the boiler to give off carbon dioxide with the steam. However, the relatively pure water has low pH value to cause iron to go into solution with the result that feed water lines will be attacked unless pH value of the condensate is elevated. The high purity water necessitates the complete removal of oxygen from the system so as to prevent corrosion. Therefore, the deaerating heater in the cycle must be a good and efficient operating unit to give zero oxygen content in the deaeration water. Many plants, as an additional precaution, employ a chemical reducing agent such as sodium sulphate to remove minute traces of oxygen in feed water. However, sodium sulphite decomposes in high pressure boilers to give off sulphur dioxide to the steam which redissolves as the steam condenses to form sulphuric acid. Thus pH of the condensate is reduced to cause corrosion of the turbine wet stages and condensate lines. In order to neutralize the effect of sulphur dioxide in the condensate and to maintain pH of the condensate at the optimum level, many power stations feed ammonia or ammonia compounds into boiler water. The ammonia gas that passes off with the steam recondenses in the condensate and raises pH. However, ammonia will not redissolve in the condensate as rapidly as sulphur dioxide with the result that serious corrosion occurs in the turbine stages immediately following the first condensation of steam even though sufficient ammonia is present in the steam to maintain the desired pH value at the condensate pump discharge.

Amine type chemicals, to substitute for ammonia, have been tried successfully in some plants where ammonia could not give full protection against corrosion throughout turbine and condensate return system. Similarly, morpholine that has a high vapour pressure was found to bring down carbon dioxide to zero and the iron content was found to have reduced to consistently to 0.1 ppm or less.



In high pressure boiler sodium sulphite being an ineffective oxygen scavenger, hydrazine holds particular promise.<sup>5</sup> Hydrazine is used in the hydrate form and there has been considerable use of this product.

### **Cooling water systems**

In any cooling water system, corrosion or erosion of metal parts and excessive deposits of scale which might decrease the heat transfer rate of the cooling surfaces must be prevented. In most cases any scaling of heat transfer surfaces is caused by the precipitation of calcium carbonate resulting from calcium bicarbonate naturally present in the cooling water breaking down under rising temperatures. For this reason, scale formation is most prominent in the hotter sections of the heat transfer equipment. Sometimes, when the scale formation is heavy in these hot sections, there is no scaling at the cooling water inlet with clean, bare metal exposed to corrosion.

In order to prevent excessive scale in a system and at the same time to avoid corrosion a practice sometimes used if control conditions are suitable and temperature differentials are small. This is called 'controlled scale' treatment, by which a thin film of calcium carbonate is allowed to form throughout the system. This ultimately protects the metal surface from the corrosion without affecting the heat transfer rate.

Sometimes corrosion spots in boilers are attacked by hydrogen in power boilers. Hydrogen damage is found only in the steel underlying an area where visible corrosion has occurred in service. Hydrogen thus produces damage to steel parts in boilers. Since this is not directly associated with corrosion we are not going to discuss the subject here.

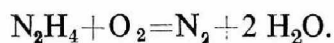
### **Use of Chemicals to remove Oxygen**

As already stated chemical oxygen removers are frequently used to supplement mechanical deaeration in order to reduce the dissolved oxygen to zero. Sodium sulphate is often used for this purpose, particularly in boilers working at pressures below 2000 lbs/sq. in. However, sodium sulphite increases dissolved solid content in the boiler water and may require increased blow down rates. Further, there is some evidence of sulphite breakdown at high pressures with the formation of sulphur dioxide and hydrogen sulphide. These acidic gases diffuse into the steam and may cause corrosion at the point of initial condensation in the turbine and heaters. Consequently, sulphite should not be used in excess at high boiler pressures. This means maintaining the sulphite concentration in the boiler only slightly above the level required to react with the quantity of oxygen entering the boiler, with low and medium pressure boilers an excess of 20 to 50 ppm can be used safely.

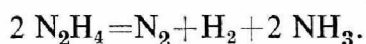
Hydrazine is rapidly replacing sodium sulphite as an oxygen remover. The principle advantages of hydrazine over sodium sulphite are :

1. It is volatile and its reaction products with oxygen are also volatile. Therefore, hydrazine does not increase the dissolved solid content of the water.
2. By thermal decomposition only the neutral gas, hydrogen and the alkaline gas, ammonia, are formed.

The reaction of hydrazine and oxygen is as follows :



Hydrazine decomposes at temperature above 400°F and the following reaction takes place:



Because of its volatility and the decomposition at elevated temperatures, only a small residual, of the order of a few parts per million, can be maintained in the water of a medium pressure boiler. It is, therefore, apparent that this will provide protection against only small quantities of oxygen entering the boiler. Therefore, the oxygen must be removed from the feed water as completely as possible and the hydrazine should be added in sufficient concentration. The reaction between hydrazine and oxygen is a function of time, temperature and concentration. This relationship is shown in fig. 4. These conditions must be observed to prevent corrosion or to reduce corrosion in boiler operating at low or medium pressures.

### **Conditions for control**

It can be generalized from the above observations that three conditions are necessary for corrosion control in boilers. They are :

1. The alkalinity reserve of the boiler water should be sufficiently high to neutralize any acidity introduced into or formed in the water.

The pH of the solution should not be less than 11 at working temperature, which means maintaining a caustic soda concentration of at least 2 parts per 10,000 when sodium carbonate or trisodium phosphate is also present or at least 5 parts per 100,000 in the absence of other strongly basic salts.

2. The dissolved oxygen and carbon dioxide dissolved in the feed water should be reduced to low value. The dissolved oxygen content should be less than 0.01 ml per litre for boilers operating at pressures between 400 and 800 lb/sq. in. The deaerating equipment with low pressure boilers is normally not so good, but a dissolved oxygen content greater than 0.1 ml per litre is definitely harmful and severe corrosion troubles are bound to occur in some parts of the plant if this limit is exceeded. Sodium sulphite or hydrazine should be added to feed water in quantity sufficient to react with any oxygen not removed by the deaerators.
3. Tubes and drums should be well cleaned at every opportunity to remove loosely held scale, rust or dirt. When boilers are shut down for overhaul, every effort should be made to empty completely the drums and all tubes. In case of shut down for any length of time, it is an advantage to place trays of quicklime or calcium chloride in the drums. If the boilers are not to be emptied they should be filled as full as possible with deaerated water, containing caustic soda and hydrazine and all vents closed.

### **Equipment required for corrosion control**

In order to minimize corrosion of feed water lines and equipments, boiler internal surfaces and condensate return lines, it is essential that proper water treating equipment may be employed to accomplish the following :

1. Reduction of dissolved oxygen in the boiler feed water to the lowest possible limits.
2. Reduction of carbon dioxide present in the boiler feed water as free CO<sub>2</sub> and in the form of bicarbonate and carbonate alkalinity.

In practically all plants, complete elimination of dissolved oxygen and free carbon dioxide is mandatory. However, the degree to which it is necessary to reduce the carbon dioxide present as bicarbonate or carbonate alkalinity depends upon the plant requirements as related to boiler pressure, quantity of condensate reforms, steam usage, etc. Many industrial units are now available for water treatment and corrosion control.

#### **Treatment & control of feed boiler water<sup>a</sup>**

Natural water is not normally suitable for boiler use unless it is treated, since untreated water may cause corrosion in boiler parts and other associated troubles. Water of various sources and localities has different compositions and hence it is difficult to prescribe any standard form of water treatment. However, natural water can be classified into two main types :

1. Water with low hardness or soft water containing calcium and magnesium salts in amounts to about 150 ppm.
2. Hard water containing salts in quantities upto 500 ppm or more.

Soft water can normally be made satisfactory after internal treatment. But specific treatment can only be found out after examination of the supply water for a given installation. In case of internal trouble, addition of chemicals reacts with water entering boiler resulting precipitation of hardness salts as sludge which is removed during blow down. A properly balanced treatment is necessary to convert all hardness salts into soft and easy flowing sludge to protect boiler against corrosion.

Hard water presents difficulties in the water treatment process. Suspended sludge may promote the cause of corrosion and other difficulties. Choice of treatment again depends on the raw water supply.

For internal treatment the following chemicals or mixtures are normally used.

#### **Sodium Phosphate**

This precipitates calcium and magnesium salts as soft calcium and magnesium phosphate.

#### **Sodium Aluminate**

This is used as a coagulent.

#### **Tannins**

They render the precipitates free-flowing by surface action; absorb oxygen from boiling water and act as protection against corrosion.

## **Starch**

It is used sometimes as an alternative to tannins or with tannins. It absorbs traces of oil that may get into boiler water.

## **Sodium Sulphite**

It reacts with dissolved oxygen present in water forming sodium sulphate.

## **Alkali**

Normally caustic soda is used. It improves alkalinity to boiler water.

## **Sodium Sulphate**

This is used when water is deficient in this compound. A minimum ratio of 2.5 for sodium sulphate/phosphate is recommended for the protection against caustic cracking.

## **Control treatment of water**

Feed water must always be alkaline with pH value between 8.5 and 9.5 preferably as high as 11.0.

The quantity of chemicals to be added may be determined by the following tests :

## **Hardness**

The hardness should always be zero. It is also an indication of scale forming tendency in boiler.

## **Phosphate**

The residual quantity of phosphate normally should be not less than 50 and not more than 100 ppm. It is expressed as trisodium phosphate. It is the most important test to maintain zero hardness in water.

## **Alkalinity**

The total alkalinity expressed as calcium carbonate should not be less than 15 or 20% of the total dissolved solids.

In hot water heating systems and where condensed steam is returned to the boiler feed, it is advantageous to use hydrazine as an alkalinity control since it also removes dissolved oxygen.

## **Total dissolved solids**

Total dissolved solids present in boiler water plus due to the addition of chemicals for treatment should not exceed 2000 to 4000 ppm. Since there are several influencing factors, only experience can indicate the optimum condition.



## **Sodium Sulphate/Caustic Soda ratio**

Where there is no rivetted joint, it is not very essential to maintain this ratio but in rivetted boiler the recommended ratio is 2.5. It is also a protective against intergranular corrosion of tube plates or stressed areas in boiler.

## **Ideal boiler**

Quicklime treatment is often resorted to as a protection against corrosion when boiler is idle for a few days. Alternatively, if a boiler is to be made ready for immediate use, it should be emptied and cleaned and then filled completely with feed water sufficiently made alkaline by the addition of caustic soda to which sodium sulphite has been added to the extent of 100-150 ppm as an oxygen absorber. The water should be tested for caustic soda and sodium sulphite residual from time to time.

## **Conclusion**

Instances of corrosion in water environment in thermal power plants have been described. Basic theories underlying this corrosion phenomenon have been briefly discussed. The factors responsible for the failures of metals as a result of corrosion in thermal power plants have been pointed out. Different methods commonly adopted to combat corrosion in thermal power plant have been indicated.

Current experience shows that corrosion in thermal power plants leads to a considerable degree of metal loss. This affects boiler operation increasing plant shut downs. Water chemistry holds a responsible role in corrosion in thermal power plants. It is therefore felt that arrangement should be made so that power house people can have laboratory service for routine check of water under qualified chemists.

The operating personnel of power houses should have specified knowledge of modern remedial measures to combat corrosion in power plants.

For future guidance of operating personnel as well as for control measure it would be helpful if the causes of corrosion failures are systematically investigated and a record is maintained.

Power houses should have necessary equipments for corrosion control.

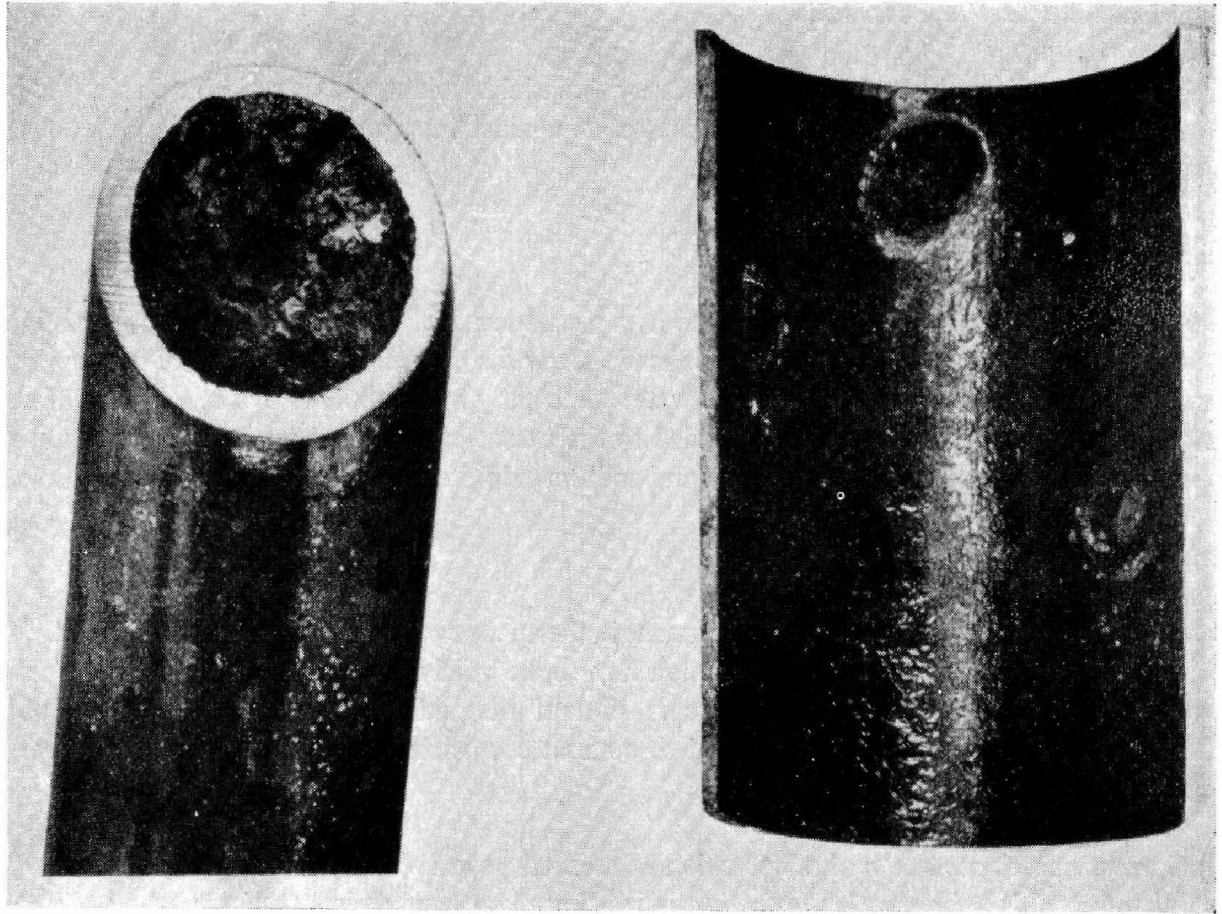
## **ACKNOWLEDGEMENT**

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## **SOME CASE HISTORIES**

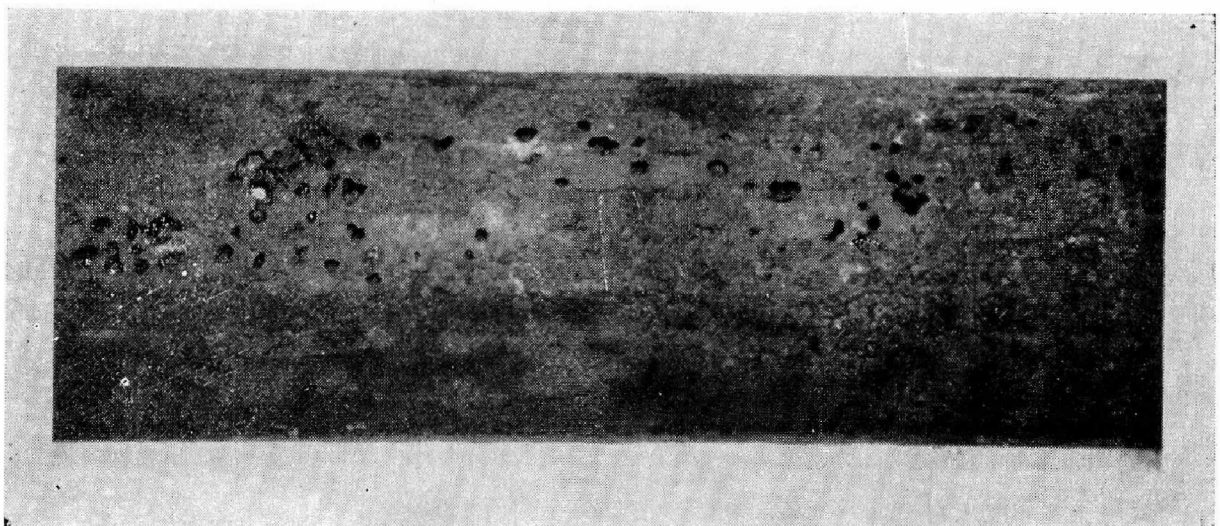
### **Case No. 1**

Superheater tubes of a boiler showed a heavy deposit of salts carried over in the steam due to excessive concentrations in the boiler water (fig. 6).



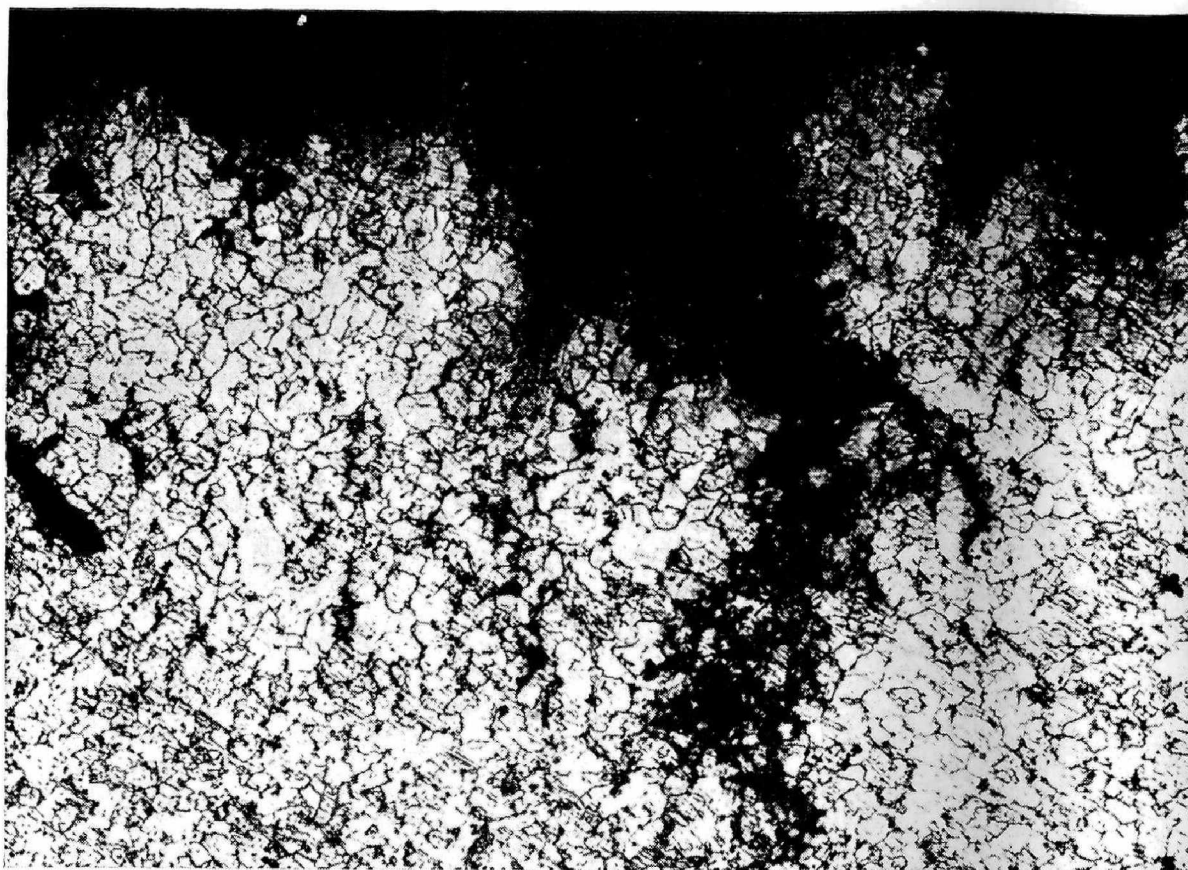
*Fig. 6. Corrosion spots in a feed water pipe underneath crust*

Corroded tube due to heavy deposit. The investigation revealed that there was no control over the total quantity of dissolved and suspended solids. Corrosion started beneath the crust (fig. 7).



*Fig. 7. Pitting corrosion on boiler tube due to oxygen concentration in feed water*

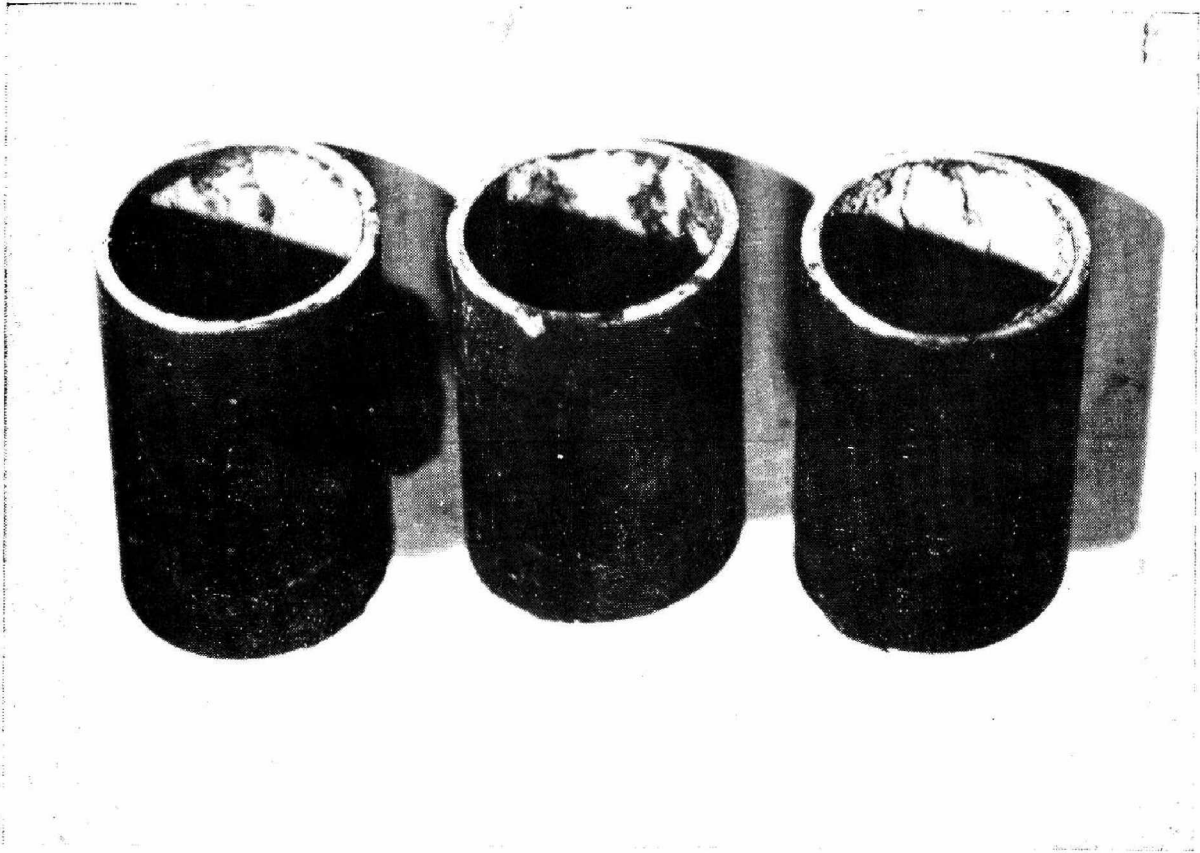
Microstructure of the corroded tube. Microstructure shows the presence of intercrystalline grainboundary corrosion (fig. 8).



*Fig. 8. Microstructure showing intercrystalline grainboundary corrosion*

## Case No. 2

Scale adhering to the surface of the tube and which was not removed, resulted corrosion under the scale in presence of water containing dissolved oxygen and set up differential aeration. Fig. 9 shows corrosion attack inside the tube.



*Fig. 9. Corrosion of tube as a result of adhering scale*



*Fig. 10. Localized corrosion attack due to high concentration of dissolved oxygen*



### Case No. 3

Failure of a tube in an industrial boiler. The investigation revealed lack of standardized method of feed water supply. As a result of high concentration of dissolved oxygen differential aeration was set up in the tube metal to cause localized attack when the oxygen was absorbed on the surface and diffused downwards resulting corrosion. Fig. 10 shows corrosion products inside the tube.

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## DISCUSSION

MR. D. P. R. CASAD (N. E. L. P., Nagpur)

I would like to ask about the norms to be followed by the industries in order to minimise the corrosion of boiler as the small industries and power plants are not well equipped to have a good treatment plant and have to use whatever water they get. When we get clear pure water our problem is reduced. Would you suggest how to reduce scale formation and corrosion with regard to boilers when the water quality is not too good.

MR. S. N. MUKHERJI (Acc-Vickers-Babcock Ltd., Durgapur)

As already described corrosion is basically dependent on the interaction between the metals and the chemicals present in the environment and must therefore hold certain rules. If the environment is corrosive, it is not possible to stop corrosion without taking adequate preventive measures. You must first analyse and note the characteristics of the water for oxygen content, total dissolved solids, alkalinity, etc., and then find out the best and the most economical method for conditioning of water. Without water treatment you cannot have any control and one day your tube will burst out.

MR. S. G. KRISHNAN (NOCIL, Thana)

It is a very difficult situation to make a general statement on what sort of critical test one should carry out on steam generation as a whole, because the most important consideration is 'what is the end use of the steam.' So, as a practical industrial engineer, I would suggest number of steps for good quality control of water. In general the feed water quality in the drum is practically related to steam pressure and also to the end-use of the steam because corrosion not only occurs within the feed water system but also occurs within the heater and economisers. To counteract this phenomenon some checks are necessary. First, you test your feed water quality. In our country, as well as abroad, there is a tremendous variation in the feed water quality from season to season. If your demineralised plant is expected to get an average of 50 ppm solid in some seasons like summer in monsoon the dissolved solid may go as high as 500 ppm and your demineralised water does not perform up to expectation.

Secondly, check on the actual and designed quality of the de-aerated water and recycled condensate, pH of the water and the more critical parameters like iron, copper, organics, etc., of the water. If we are able to maintain these critical parameters with minor deviations upto the prescribed limits, it is not difficult to minimise corrosion in most of the cases with conventional treatments. In the modern high pressure technology, as we are used to in the petrochemical complexes, where we generate steam at pressures of 60-100 atmospheres, we have to pay tremendous amount of respect to all these parameters.

Going to the steam side, the quality of the steam used for end purpose depends very much on the feed water quality. There is a relationship between solid content of the steam

and solid content of the boiler. One of the best methods to measure what sort of steam you are producing would be to condense the steam and to measure its conductivity and pH. The other important criteria for high pressure turbine operations that we normally recommend is a very close track on the chloride content. We have found that continuous entry of chlorides even at the minutest level has resulted in some sort of corrosion phenomenon resulting in loss in many of the installations. The other important observation in the feed water system is velocity consideration which has already been emphasised.

MR. T. S. BHAKUNI (IDPL, Rishikesh)

In our plants we have 3 boilers where we are facing trouble in the economiser tubes made of steel. The temperature is 100-90°C. Only the end portions are eaten away. I would like to know whether this is due to stress corrosion or any other type of corrosion?

MR. P. K. GHOSAL (DVC, Chandrapura)

The normal practice is to give a stress relieving treatment and stress analysis on the tube is a very critical test specified in the boiler regulations. To my knowledge such tests can be carried out at the Central Mechanical Engineering Research Institute, Durgapur. I think the example that has been described here might be a case of stress corrosion.

MR. T. S. BHAKUNI (IDPL, Rishikesh)

We have got 3 boilers. This particular type of phenomenon has occurred only in case of one boiler and not in the remaining two. The tubes have also been procured from the same company. Of course, one tube is bent.

DR. A. K. LAHIRI (Corrosion Advisory Bureau, Jamshedpur)

From the particulars given by Mr. Bhakuni it is difficult to guess whether this is a case of stress corrosion or something else. As the attack is more near the bend, erosion may also have some part to play. What is required is a detailed examination of the practices that are being followed in the particular boiler unit and the examination of the damaged tubes. Such investigations are being carried out in the National Metallurgical Laboratory and the Bureau can help in getting the samples examined.

PROF. S. J. ARCEIVALA (CPHERI, Nagpur)

One of the speakers pointed out very rightly that chlorides have to be watched. I would like to know where steam turbines are not used and if it is a simple question of boilers, what are the limits for chlorides for boilers of different pressures? I would also like to know if the members have any experience on corrosion inhibitors for cleaning the boilers.

MR. S. N. MUKHERJI (Acc-Vickers-Babcock Ltd., Durgapur)

Acid cleaning, though very efficient, is dangerous because until and unless acid is well removed and neutralised it will lead to further corrosion. There are number of inhibitors available and persons experienced in the line should be consulted before use.

MR. C. T. GEORGE (Cochin Refineries Ltd., Cochin)

Mr. Mukherji has mentioned that sulphite content is between 100-150 ppm. But our experience shows that we can go down to 10-15 ppm and over a period of 4-5 years' operation we have not noticed any sort of corrosion so far.

As regards chloride content, in our plant we use water of about 80 ppm.

I would like to know some details regarding protection in steam condensate of pH 5 or 5.6.

MR. S. N. MUKHERJI (Acc-Vickers-Babcock Ltd., Durgapur)

Cochin refineries appear to be fortunate with their raw water supply.

MR. L. M. AGARWAL (Sudbury Laboratory of India, Calcutta)

I would like to know what is the economic and practical means of dosing small quantity of inhibitor continuously in the boiler feed line and whether such small dosing pumps are available in India?

MR. S. C. KRISHNAN (NOCIL, Thana)

Experience has shown that if you build up chloride concentration in your system you get corrosion in your tubes. You can counteract it of course by increased alkalinity. But this is not the solution. Our experience shows that if we can minimise chloride concentration in the boiler, not only our turbine performance is better but also the corrosion problems within the boilers are minimised. If you take 15 kg or 20 kg steam, you hardly get any problem. The system should maintain a certain solid level. But if you carefully observe the build up of chloride concentration in your system I am definite that with a little more careful analysis you will be able to draw the conclusion that certain levels of chloride at prescribed alkalinity levels have disastrous effects.

Filming amines are being extensively used in number of petrochemical complexes. The condensate has pH of 4.9 to 6.5 and conductivity of 1 to 6, partially because of electrolytes and partially because of dissolved gases. After 3 or 4 years of operation, substantial quantities of corrosion have been observed in the recycled condensate systems. On introducing filming amines in the recycled condensate system, our conclusion has been that they can do good. Of course, the performance of these amines is still being studied.

We have also had a bit of experience with sodium sulphite. As I have already mentioned there is a direct relation between the total solids content in steam and the steam generation. We have been adding sodium sulphite even though the effluent from deaerator has less than 0.5 ppb of dissolved gases and we do not have any problem as far as corrosion is concerned. But there is some build up of solids which is not always avoidable. We are seriously considering whether we should go for some sort of organic scavenger and unless we do some bench scale study we could say nothing more.

Much has been said about the use of ammonia in recycled condensate system. Installa-



tions in our turbine facilities have condensers which are normally cooled by brackish water. I would like to know what is the optimum level of ammonia which can be tolerated. We want to know if we introduce ammonia, whether this will have any effect on our copper and brass equipment.

MR. S. N. MUKHERJI (Acc-Vickers-Bobcock Ltd., Durgapur)

Regarding the question of Mr. Agarwal, I would request him to contact Ion Exchange (India) Ltd., who have developed dosing system for conditioning cooling water for demineralised system.

MR. A. G. NENE (Shriram Chemical Industries, Kota)

At Shriram Chemical Industries we have got boiler working at a pressure 105 kg/sq. cm. We add ammonia to the condensate for the pH correction before it is fed to the boiler. The ammonia is limited to less than 1 ppm and for the last 3 years the condition of condenser tubes has been found to be perfect.

MR. A. H. MAZUMDAR, (Synthetic & Chemicals Ltd., Bombay)

We have two boilers of 360 lbs/hr (each 180 lbs/hr) capacity. As per the design, we are supposed to send the steam back to boiler feed water system. But we found that conductivity of the condensate was very high and there was corrosion. For some times we had to throw all the recycling condensate water but since we started using filming amines, the corrosion rate has sharply declined.

We have still some problem with copper and brass. We have copper and brass tube condensers and we have a common cooling water system. We have refrigeration facility in one of the plants and in that we use condensers made of copper alloy. It so happened that the ammonia started leaking in the condenser cooling water system and the ammonia content of the cooling water went up to 2-5 ppm. Dosing with chlorine to bring down free ammonia was not the solution. The copper condenser started leaking and only stoppage of ammonia leak solved the problem. In this connection actual tests were carried out and it revealed that even if 0.5 ppm ammonia is kept for 2 years, all our copper tubes will dissolve. We now keep a constant check on ammonia to bring it down to a level of 0.1 or 0.2 ppm.

DR. A. K. LAHIRI (Corrosion Advisory Bureau, Jamshedpur)

I would like to clarify some important points about the effect of ammonia on the copper and its alloys. Ammonia though alkaline in nature attacks copper due to soluble ammonium complexes which copper forms with ammonia. Depending on the concentration and pH of ammonia solution various complexes  $\text{Cu}(\text{NH}_3)_n$  ions are formed, where n may vary between 2 to 5 with increase in pH. Copper will readily get dissolved in ammonia. In the use of copper and its alloys in any environment containing ammonia, we face two problems: attack by ammonia which is of general nature and stress corrosion cracking which is more important from the practical point of view. Now pure copper is not susceptible to stress corrosion cracking but specially copper-zinc alloys containing 20-30% of zinc, which are commonly used for tube material, are highly susceptible to stress corrosion cracking. One of the methods by which incidence of failure

can be considerably reduced is the selection of alloys. 90 Cu 10 Ni or 70 Cu 30 Ni alloys are not susceptible and can be safely used. Similarly Cu-Al or Cu-Zn-1-2%Sn or Cu-Zn-1-2%Si alloys are more resistant to cracking than ordinary brass.

MR. A. R. LIMAYE (Bharat Heavy Electricals Ltd., Hyderabad)

In the producer-gas plant of our factory, phenol is produced which is discharged in the water stream after dilution. I would like to know the method to reduce the phenol content of the effluent and also the concentration of phenol which is permissible and not injurious.

PROF. S. J. ARCEIVALA (CPHERI, Nagpur)

We are now going to waste treatment. Phenol is supposed to pollute water quite a lot and the ISI has got standard for discharge of phenol in stream. You have to bring it down to at least 1 ppm. Phenol has to be removed. Of course, there are methods of treatment which cannot be discussed in this house.

MR. A. G. NENE (Shriram Chemical Industries, Kota)

In our boilers pH is adjusted only by addition of trisodium phosphate. We are also not using any sodium sulphite and as oxygen scavenger hydrazine is added. Ammonia doses are controlled depending upon the pH and the conductivity of the steam.

MR. S. G. KRISHNAN (NOCIL, Thana)

Phenols can be very well removed by ion exchange. It is a simple process to work out.

MR. R. N. BANERJI (DVC, Chandrapur)

Our experience has been that corrosion of copper alloy heat exchanger can be controlled by proper control of ammonia, CO<sub>2</sub> and oxygen in feed water. Our boiler runs at a pressure of around 135 kg/cm.<sup>2</sup> where the CO<sub>2</sub> content in the demineralised water is reduced to get water conductivity of less than 2.2 at the pH of 7. Our initial attempt was to reduce the amount of CO<sub>2</sub> and oxygen. We checked our condensers. Unfortunately, the oxygen content in the condensate was more than 30 ppb and corrosion was quite high. We reduced the oxygen content to 14 ppb. With reduction in the total input of oxygen and CO<sub>2</sub> and increase in the hydrazine content of the boiler water we started feeding measured doses of ammonia which reduced the copper pick up from 25 to 15 and then to 5.

MR. K. R. BULUSU (CPHERI)

It is extremely difficult to reduce phenols below 0.1 mg/l with ion-exchange process. With highly basic ion-exchanger produced by the Ion-Exchange Company of U.K., we have not been able to reduce the concentration of phenols below 1 mg/l. The only method available is by adsorption using activated carbon.