

CORROSION IN BOILERS AND WATER CIRCULATION SYSTEMS WITH SPECIAL REFERENCE TO MARINE INSTALLATIONS

By

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Several different types of corrosion may be found to occur in boilers, especially marine boilers, in addition to ordinary fatigue effects. There may be a more or less uniform and widespread attack upon all the metal surfaces of the boiler ; secondly, various forms of pitting are met with ; caustic embrittlement, or caustic cracking, may occur ; and lastly there will almost certainly be external corrosion on the fire side of the generating system. Of these, pitting is probably the commonest internal form of corrosion.

General internal wastage will take place rapidly in a boiler, even in the absence of oxygen, whenever the pH of the water is allowed to fall below 6.0. The corrosion which occurs under these circumstances is of the hydrogen-evolution type. The necessary degree of acidity can result from the use of acid feed water, but needless to say a great deal of the water in an active boiler is returned condensate. In many turbine systems as much as 97% of the feed comes from the condensers; and in any event, distilled water is normally used on board ship for make-up purpose. Condensate is always acid due to the presence of carbon dioxide, derived from salts such as calcium bicarbonate which may be present in raw feed water, or from the hydrolysis of sodium carbonate used in treating the water. Carbon dioxide usually makes no contribution to the corrosion of generating surfaces but sometimes causes trouble in turbines, condenser tubes, and steam pipes. In closed steam heating systems, excessive amounts of carbon dioxide cause extensive corrosion, iron being dissolved as bicarbonate which is returned to the boiler, the carbon dioxide being reformed. Magnesium chloride, if present, will decompose under the conditions which prevail in an active boiler to yield hydrochloric acid directly. Another possibility is that if alum has been used as a coagulant in the treatment of the feed water sulphuric acid may be produced in the boiler unless sufficient alkali is present.

Preventive measures are simple and consist in maintaining a certain degree of alkalinity in the boiler water. The attack upon iron is at a minimum at about pH 11.5. This does not, of course, protect an installation at points above the water line.

If dissimilar metals are in contact anywhere in the boiler system the possibility of electrochemical attack on the anodic member of the pair at once arises. Steel is anodic to brass, copper, and gun-metal, stainless steel and graphite. Since the total area of steel is usually greater than that of any fittings made of other metal which is likely to be present, the attack on the former, regarded as an average, may not amount to much ; but a rather more severe attack may take place in the immediate vicinity of the zone of contact between the dissimilar metals. Under alkaline conditions, however, the polarisation of the steel anode is increased by the formation of protective films on the surface of the metal, and this is effective in reducing the amount of attack.

Zinc protectors are sometimes used in marine boilers. These are simply blocks of zinc, placed in electrical contact with the steel-work of the boiler so as to form a galvanic couple. The idea is that since zinc is anodic to steel any corrosion which ensues will take place entirely on the zinc, leaving the steel unaffected. However of protection is to be provided over the entire surface of the boiler the zinc protectors must be distributed regularly within it since the effect which each produces falls off with distance. A practical difficulty is that the attack upon the zinc is focussed upon the point of contact between it and the steel, which may lead to the physical detachment of the zinc, or alternatively there may be an accumulation of corrosion products around the

joint such that further electrochemical action is to some extent stifled. Zinc may be relied upon to undergo sacrificial corrosion when coupled to iron in a corrosive medium under cold conditions but it is by no means clear what the effect of high temperatures and pressures will be upon the course of the electrochemical reaction; it has been claimed by some writers that the main function of the zinc is to remove oxygen chemically rather than to act galvanically, whilst others have stated that under certain conditions zinc behaves cathodically, not anodically, towards steel.

The type of pitting that occurs in boilers is found to vary considerably according to circumstances, and it is usual to distinguish three different kinds—"air bubble" pitting, "scab" pitting, and "soft scab" pitting.

Air bubble pitting is caused by local differential aeration effects, the action being initiated at points where bubbles of air or oxygen are able to adhere to the surface of the metal. Naturally there is little opportunity for bubbles to form and remain in contact with the metal when the boiler is steaming, owing to the violent agitation which occurs, but they can collect together and form pockets in the tops of steam and water drums and around the heads of nuts and boiler fittings. Once the bubble has formed and is in stable contact with metal the conditions necessary for corrosion to occur by the differential aeration mechanism are immediately established; the metal against which the bubble rests is relatively well-aerated in comparison to the surrounding areas and consequently is able to behave cathodically with respect to them. Corrosion at once takes place on those areas. The iron which dissolves away in the ferrous state from these corroding zones diffuses outwards and where it meets the alkali liberated by the cathodic reaction ferrous hydroxide is formed. When this reaches the circumference of the bubble the air within oxidises it to ferric hydroxide, which is much less soluble than ferrous hydroxide, and ultimately, a film is produced over the bubble. This film permits the passage of ions but restricts the access of further supplies of oxygen from other bubbles which may form later. When the oxygen in the original bubble has become exhausted in feeding the cathodic reaction and in oxidising iron to the ferric condition the situation with regard to the availability of oxygen has changed entirely; the area which was formerly cathodic because it was relatively well-supplied with oxygen has now become deficient in oxygen and it behaves anodically instead of cathodically in consequence. All subsequent corrosion—which will continue indefinitely so long as the difference in oxygenation persists and the corrosion products do not stifle further action—is thus focussed on one small area beneath the site of the original bubble, leading to very deep pitting. The various stages of the process are shewn diagrammatically in figures 1 and 2. Differences in oxygen concentration at various points due to the irregular deposition of sludge or the existence of crevices or fissures, or within joints, also contribute to localised corrosion.

The typical appearance of an air bubble pit is a hemispherical depression covered with a loose mass of corrosion products which are red on the outer layers but black within, due to the presence of magnetite, which is formed under the prevailing conditions of oxygen-shortage.

In order to prevent the occurrence of this type of pitting it is necessary to remove oxygen from the boiler feed water or to destroy it chemically, especially in idle boilers. Quite apart from the question of pitting, oxygen plays a major part in promoting boiler corrosion generally, and its elimination is an important aspect of efficient boiler maintenance. The higher the pressure rating of the boiler the more important it is to keep the oxygen concentration low—not merely to reduce the possibility of air bubble pitting alone, but to reduce the other forms of pitting referred to later. The oxygen concentration in boilers which operate at 300 lbs. working pressure should not exceed 0.02 mls. per litre, and for working pressures above 450 lbs. it should be under 0.01 mls. per litre. In the case of boilers working at pressures below 300 lbs., 0.05 mls. per litre is regarded as acceptable. Both mechanical and electrical methods of removing oxygen from feed water are available. An example of the latter is the passage of a small current between carbon electrodes in the feed water, the potential being maintained at a level insufficient to decompose the water; this, if combined with ordinary vacuum deaeration, reduces the concentration of oxygen to negligible proportions. Often, however, chemical methods are used to eliminate the last traces of oxygen, especially if the boiler is left idle but full of water. Another remedial measure is the systematic cleaning out of pits during boiler overhaul.

The so-called scab pitting is probably the most common form met in practice, and is found in both highly forced and non-highly forced boilers. It takes the form of localised deep pits covered by a hard layer of magnetite. Once initiated, this form of attack cannot be arrested easily, and it often continues until the metal is perforated. Scab pitting usually occurs in the hotter regions of the generating surface, where heat transference is greatest. The precise explanation of the phenomenon is not known, but it appears to be associated, at any rate in the case of marine boilers, with contamination of the feed with sea water. It seems likely, therefore, that the first step in the process is damage to the protective film on the metal at localised points; the damaged areas will thereafter behave anodically relative to the undamaged regions around them. The subsequent attack on the anodic metal will be not unlike that described in the case of bubble pitting, except that a much harder scab is formed in consequence of the much higher temperatures involved.

The only way of arresting further action once a scab has started to form is the complete mechanical removal of the hard magnetite scale that has formed, and the re-formation of a protective oxide film on the cleaned surface. The principal preventive measure is the maintenance of the correct degree of alkalinity in the boiler.

The third kind of pitting, known as soft scab pitting, is rather similar to ordinary scab pitting, but the scab is softer and the corrosion products contain a much higher proportion of ferric oxide as distinct from magnetite. The pits are broad and shallow rather than narrow and deep. The initiating factor is the presence of salts lodged on the metal of the superheater or other affected areas after priming of the boiler has occurred. When the boiler is shut down condensation will place and if salts have been left behind the result will be the formation of drops of fairly concentrated solutions on the walls of the tubes. Corrosion will then take place by the normal differential aeration mechanism.

It should be mentioned that copper is often found included among the corrosion products present in pits, frequently in metallic form, but sometimes as the oxide. Since copper is strongly cathodic to iron, it would be expected that its presence would greatly assist in the anodic corrosion of the underlying steel. The evidence upon the point is, however, rather conflicting. Cases are known where the corrosion does not seem to have proceeded very far although metallic copper was present. Moreover, copper fittings in boiler systems are sometimes found to have suffered very serious wastage, suggesting that in the presence of alkaline water at high temperatures copper may behave anodically instead of cathodically towards steel. On the other hand, cases where steel in the neighbourhood of copper or copper alloy fittings has suffered severe corrosion are also known. It may well be that the course of the reaction in any given instance depends greatly on the nature and thickness of the coating on the metal, though on the other hand it is true that we do not possess complete information regarding electrochemical reaction under boiler conditions.

A rather different type of corrosion results from the mechanical removal or disruption of protective films at points where metal is under varying stress; this is the so-called "necking" or "grooving" which takes place mainly on smoke tubes, stay rods, etc., at points where they pass into the end-plates of cylindrical boilers, and round the fillets of flanges and sometimes even on the edges of seams. The rods or tubes become ringed round, near the end-plate, with pits which sometimes join upto form a groove, whence the name. There is a considerable loss of mechanical strength in consequence. The apparent cause lies in the fact that the normal expansion and contraction of the rod under thermal stress is affected at the points where it joins the end-plate so that abnormal strains are set up, resulting in damage to the protective film on the surface of the metal. Here again, the maintenance of the correct degree of alkalinity in the boiler will favour the renewal of the protective film, should it become damaged, thus keeping the attack down to a minimum.

Instances of corrosion fatigue may also be met with in boilers, especially in the fire-row tubes. If the circulation of water through the tubes is irregular, it is likely that the metal will be subjected to alternating heating and cooling cycles, with corresponding phases of expansion and concentration which when reinforced by corrosive action may result in early failure. Should any part of the tube system become temporarily deprived of water distoration of the tubes concern-

ed is likely to result, and this will leave internal stresses in the metal which will still further affect—in an adverse manner—the fatigue and corrosion-fatigue resistance of the metal. Uneven expansion of the boiler may have much the same result.

The external symptoms of corrosion fatigue in the tubes is usually a network of fine cracks. Metallographic examination will reveal that these are mainly transcrystalline in nature.

Preventative measures include of course, the avoidance of corrosive conditions in the boiler by appropriate water-treatment, but an essential precaution is careful design of the system in the first place so that faulty circulation or water starvation do not occur.

Another consequence of bad circulation is the possibility that direct oxidation of the metal may occur at points which undergo local overheating. This sometimes occurs in fire row tubes and in superheaters, especially in the more highly forced systems. The well-known interaction between steam and iron, yielding hydrogen and Fe_3O_4 , takes place readily at 550°C .

The results of such action manifest themselves superficially in the form of a hard layer of magnetite, often dark-grey in colour. The solid product of the above reaction is more voluminous than the iron from which it was formed, and its other physical properties, such as expansibility, are also different from that of the unaffected metal, so that under working conditions the layer of magnetite may flake away, exposing the metal beneath. Moreover, the electrochemical behaviour of the oxidised areas are markedly different from that of the unoxidised regions (the former tend to act cathodically under these conditions) so that ordinary corrosion trouble may ensue over and above the wastage of metal due to direct oxidation—which is not, of course, a form of corrosion as usually understood in the strict sense. Where the hard layer has flaked away, the bared area will behave anodically, and unless the conditions in the boiler are such that the protective film can reform rapidly, a considerable amount of corrosion will be concentrated on these areas.

A further consequence of the formation of magnetite scale (or, indeed, of any other type of scale) is that the transfer of heat through the metal is adversely affected leading to still more severe local overheating and distortion of the metal. Ultimately a stage may be reached when the metal begins to yield under the working pressure of the boiler, and bulging, followed by splitting, may result. The drastic cooling of the metal which follows a burst due to the rush of steam and water through the gap causes effective quenching so that on subsequent examination the broken portions will often reveal a hard martensitic structure.

Caustic embrittlement, though not very common in naval boilers, sometimes occurs in other types, and when it does take place serious failure of the metal is the result. It takes the form of cracks or fissures in the metal, mainly below the water-line, and in joints, seams or crevices into which boiler water may penetrate and ultimately become highly concentrated; and often becomes visible as cracks radiating out from joints and rivet heads. The latter are sometimes so greatly weakened that they fall off under a slight blow. Caustic embrittlement—caustic cracking is a better term to use can take place in the absence of alternating stresses, though naturally if such exist they will greatly accelerate the rate of failure; internal or residual stresses, however, do quite definitely assist the production of cracks. The fissures produced are generally intergranular in nature, and are sometimes associated with deposits of magnetite at the surface of the metal.

A high concentration of alkali at localised points is the prerequisite condition for caustic cracking. It must not be forgotten that whilst caustic alkalinity equivalent to pH 11.5 has a protective value, higher concentrations are dangerous. Hot strong sodium hydroxide dissolves iron readily as sodium ferroate. Alkali is necessary for the correct conditioning of boiler water, usually being added in the form of sodium carbonate, which loses carbon dioxide under operating conditions and produces caustic soda. If the water has been treated by base exchange processes, sodium bicarbonate is likely to be present in the feed, and this too will obviously produce caustic alkalinity also when it reaches the boiler. There is thus every reason to suppose that the concentration of boiler water in secluded places such as joints and under deposits of scale, etc., may lead

to the production of highly alkaline conditions. Whether the concentrations which result will be such as to cause actual cracking or not depends on a number of other circumstances. A particular combination of high temperature, internal stress and high alkalinity is required before this can happen. In boilers which work on evaporated feed and thus do not require heavy dosage of alkali to produce the correct conditioning the occurrence of caustic cracking is very infrequent. But the possibility of local over-heating of the metal with distortion and the creation of internal stresses always exists, so that to a certain extent the occurrence of this type of failure is unpredictable. As usual, careful boiler design and efficient maintenance and operation will reduce the chance of failure. The addition of a certain proportion of sodium sulphate to the water tends to reduce the chances of cracking. It is understood that in American locomotive boilers the practice of maintaining a concentration of sodium nitrate equivalent to 20—30% of the caustic alkali has been found beneficial.

It is known that iron in a dilute solution of caustic soda is cathodic to iron in stronger solutions, though there is some evidence that after a certain period a reversal of polarity takes place, presumably because of the formation of protective films on the original anode. This would account for the initiation of intergranular attack. Should the metal be under stress, either external or residual, it might well happen that the fissure first produced continually opens out, thus exposing fresh anodic surfaces and maintaining the flow of corrosion current. As already mentioned, the presence of stress in the metal appears to be necessary for cracking—it is often found, when it does occur, on severely cold-worked metal, for example—so that the picture given is consistent with known facts.

It has been suggested by some writers that hydrogen embrittlement of the metal may also take place at points adjacent to those where the direct interaction between iron and hot concentrated caustic alkali is proceeding. This certainly appears to be a possibility, though the extent of the contribution that it makes to the ultimate failure of the metal is difficult to estimate.

There is also a danger of direct attack upon steel by strong solutions of caustic alkali at "hot spots" on the steam generating surfaces as the result of what is known as "steam blanketing", that is, the production of a continuous film of steam between the metal and the boiler-water. When this occurs, the concentration of alkali may rise considerably above the safe value. Whilst such increases are admittedly only localised and temporary, nevertheless the nett effect over a period will be to produce appreciable damage to the metal.

Severe external corrosion is found frequently in boilers, especially marine boilers, and more particularly at points where the superheater tubes enter the header and where water tubes enter the drums. Deposits of soot and dust and carbonaceous matter collect at these points, which cannot easily be cleaned. If the fuel oil used for firing the boilers contains sea-water, and such contamination is not infrequent, the deposits on the tubes may be bonded with fused sodium sulphate to such an extent that the passages between the tubes become blocked. The main trouble from the viewpoint of corrosion is the fact that these deposits often contain sulphuric acid—cases where as much as 2% of the free acid has been present are not unknown. The origin of the sulphuric acid is not far to seek; fuel oil may contain as much as 3% of sulphur, which is oxidised up when the fuel is burnt. When the furnace is closed down, those deposits which contain free acid absorb moisture and corrosion proceeds apace in the diluted acid; it is halted once again when the furnace is relit. Remedial measures include cleaning the furnace carefully, and removing all deposits as far as possible, and excluding moisture when the installation is left idle. In some cases mechanical removal of the deposits is necessary, in other cases there may be much water-soluble material present so that hosing down—with proper precautions to prevent the spread of corrosion, and damage to other metal surfaces—greatly assists cleaning. The use of surface active agents to facilitate the dislodgment of the deposits is becoming common.

Obviously, when a furnace installation is being designed, due attention should be paid to providing for the cleaning processes which will certainly be necessary when the boiler is in operation, and to the avoidance of inaccessible places when corrosive deposits can collect and from which it is difficult to remove them.

The corrosion of condenser tubes presents serious dangers, particularly in ships where sea-water is used as the cooling agent. Even a small leak is important, it will have consequences which extend far beyond the damage to the tube itself since chlorides may in this way gain access to the boiler.

Brass was formerly much used for these tubes. 70—30 brass is better than the 60—40 type from the standpoint of corrosion since attack upon the beta phase of the latter may cause the alpha grains to become detached, so that a relatively small amount of actual corrosion may produce a disproportionate amount of damage. The avoidance of internal stress in the metal is also important, since, under the influence of corrosion, it may lead to the longitudinal splitting of the tubes. Annealing at 280—300°C is effective in relieving these forces.

In general, however, localised rather than general attack is more frequently met with in practice, especially on tubes made from cupronickel or aluminium brass, which are nowadays widely used for this purpose. There are two main forms of corrosion to be considered deposit attack and impingement attack.

The former is due to the accumulation of extraneous material on the walls of the tube; mud, sand, sea-shells, small sea-weeds and even small dead fish, may be found lodged on the cooling surfaces. When this occurs, the attack can proceed in two ways; either there may be corrosion due to differential aeration effects, the covered area being anodic and undergoing concentrated damage; or the decomposition products of the organic matter may act directly on the metal. The damage sometimes takes the form of dezincification which, once started, will continue long after the tubes have been cleaned and the obstructions removed. Needless to say, the lodgement of foreign bodies often occurs at points in the system where the rate of movement of the water is slow, conditions which are known to favour dezincification.

Deposit attack may also be started off by patches of oil left on the tubes when they are first fitted. The use of oil soaked packing material has also been suspected of initiating this kind of trouble.

Where the rate of water movement is high,—in the case of modern marine condensers it may well be over 15ft. per second excessive turbulence may take place, leading directly to impingement attack to which copper-zinc alloys are rather prone. This type of corrosion is always associated with turbulent flow, and the effect is much assisted by the presence of air bubbles entrained in the moving liquid. It occurs mainly at the inlet end of the system.

The corrosion pits produced by impingement attack are clean and free from corrosion products, and have a characteristic horseshoe shape, the arms of the horse-shoe pointing towards the direction of flow.

The rate of movement of a corrosive liquid over a piece of metal is known to affect the speed of corrosion; the faster the movement the greater the attack. In the absence of oxygen the areas of metal exposed to the higher rate of motion tend to behave anodically; but in the case of iron, when oxygen is present, the differential aeration effect comes into play, rendering those regions cathodic. Copper behaves differently; even in the presence of oxygen, copper is anodic under high rates of transfer of solution owing to the preferential removal of copper ions.

The action of entrained bubbles appears to be to remove the corrosion products formed, the products adhering to the bubbles and being carried away by them, thus continually exposing fresh surfaces of metal and reducing the amount of protective stinging which can occur. Possibly, however, vortex effects are also involved in this the surface deposits being removed as a result of differential pressures. If actual vacuum bubble cavitation occurs, matters may become still worse.

If conditions in the condenser cooling system are stagnant at any point, or if the movement of water is very slow, air bubbles may be able to attach themselves to the surface of the

metal, and in such situations ordinary corrosion of the differential aeration type may proceed. The presence of the bubble will interfere with heat transfer so that the attack may be very rapid, in consequence of local over-heating. Similarly, corrosion may be initiated near the water line in condensers which are not working.

The design of the cooling system has an obvious bearing on the amount of impingement attack which may be experienced; the aim should be to secure an even flow of liquid throughout, and the avoidance of both turbulence and static pockets.

Wet steam is also capable of producing a form of impingement attack which may lead to trouble in brass valve seats and the like. The removal of moisture by suitable traps and the fairing off of the design will assist in preventing this.

In conclusion, it may be mentioned that there are several lines of approach to the problem of reducing corrosion in boiler systems. One obvious possibility is the development of metals and alloys which will be resistant to all forms of attack. This is, however, an ideal solution which is not likely to be realised in the immediate future. In a country such as India, whose industrialisation is still incomplete, we would be particularly unwise to rely on such a remedy for our troubles, although of course we should obviously do all we can to seek it. In the meantime the best possible use must be made of materials that are available, and attention to questions of design—as pointed out frequently in this paper—and the efficient operation and maintenance of installations will do much to reduce the failure of metals in service.