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CORROSION OF CONDENSER TUBES.

In the first number of these Papers, issued in 1920, a brief account was given of the then existing knowledge regarding the corrosion of condenser tubes. This information was a summary of conclusions drawn from many years of practical observation of the behaviour of condenser tubes in Naval installations, together with the results obtained after 10 years' investigation of the subject by the Corrosion Research Committee of the Institute of Metals. The researches of the Committee referred to have continued unbroken since 1910 up to the present time, and, while a certain degree of success has been achieved, the lack of detailed knowledge regarding the factors which control the distribution and rate of corrosion has limited the practical utility of the results obtained by this prolonged investigation.

The subject of condenser tube corrosion includes a great variety of problems, connected both with the nature of the tube material itself and also with the condition in which the tubes are set to work. The latter category is evidently very wide, comprising as it does not only the chemical composition of the circulating water but also the temperature, aeration and distribution of the water, together with such questions as the settlement of solids and the electrical conditions which may obtain. The range of research is so vast that it has hitherto been possible to explore but limited portions of it, confined mainly to those aspects which seemed to cover the greatest number of practical cases of corrosion; other areas, which may, in fact, be all-important in individual cases, have been necessarily neglected. Even so, the amount of work that has been achieved has been monumental in its extent, while almost countless theories have been evolved to account for this or that observed fact. Add to this the research work which has been carried out in other countries in the same field, and it becomes an impracticable task to give any concise account of the various avenues that have been explored. The conclusions to be drawn from this great amount of apparently fruitless endeavour are that either the causes of tube failure are very varied and of large number or else that the underlying fundamental reason has yet to be discovered: probably both these statements are true.

The practical results that have been attained are that nearly all types of corrosion can be produced by laboratory methods and without imposing conditions of a severity that appears impossible in actual condensers. Hence it is possible to argue backwards as to the conditions which probably occurred in a particular tube. The process of attempting to find the causes of corrosion in actual condensers has been found impracticable in most cases owing to the fact that the conditions of working are so difficult to investigate. Remedies may be discovered to meet an individual case, but it is unlikely that these would prove to be the best means of dealing with any other case and might even leave the real cause of the trouble in that particular instance quite undiscovered.

The problem, viewed in its broadest aspect, is peculiar in that a large majority of condenser tubes do in fact give excellent service and that even in bad cases, where perhaps it is judged desirable to retube the whole condenser, the actual proportion of seriously affected tubes is but a small one. The Engineer, on the other hand, is faced with the possibility of complete breakdown of his plant through the failure of but one tube, and this aspect of the question is likely to be aggravated by the adoption of even higher steam pressures than those now current in the Naval service.

It was realised some four years ago that complete success was impossible while the investigators attempted to attack simultaneously two closely related but different problems. These were (1) the nature of the corrosion process itself and (2) the corrosion of a particular alloy under practical conditions. Arrangements were therefore made to separate the study of these two problems, very close co-operation being maintained between the two committees charged with the work, both being presided over by the same Chairman. Evidently complete success will not be achieved by the practical committee unless the more fundamental investigation is also successful.

The main part of this article deals briefly with the practical results that have been obtained, but it will doubtless be of interest to refer to the lines on which the committee dealing with the more scientific problem have proceeded during the four years which have now elapsed since its inception. The committee decided that in order to examine the existing theories of corrosion it was necessary to develop very accurate methods of quantitative measurement, and as a first step to work out a technique to enable such measurements to be made under well defined and controllable conditions. The development of this indispensable foundation for the proper scientific study of the subject has occupied three years, time which has been well spent, however, as it has provided the means for accumulating well established data and so removing that element of uncertainty which has hitherto characterised corrosion research. This technique is now being systematically applied to the known theories of corrosion and definite results will no doubt appear in due course.

The position as regards the practical aspect of condenser tube corrosion, at the time (1924) when the two committees referred to were formed, was that the results of many years' work were available and that the chief features of the usual types of condenser tube corrosion were apparently well understood. It had become increasingly evident that resistance to corrosion depends largely upon the properties of films which form upon the surface of the metal under corrosive conditions and exhibit varying degrees of resistance. These films, not necessarily visible, may be either porous or impervious and may be anodic or cathodic to the underlying metal. Porous films by shielding the metal from oxygen may promote local attack on the area so covered, while on the other hand a completely impervious scale can confer entire protection although, if it is cathodic to the metal surface itself, very severe corrosion of any bare patches will occur as these will be anodic to the scale. Such films or scales are generally composed of corrosion products, but may contain included matter from the circulating water.

These views may eventually prove to be incorrect, but are useful for many practical purposes as they give an apparently true picture of what happens in most cases of corrosion. It is thus possible to regard the well-known types of condenser tube corrosion as resulting either from changes in the naturally-forming protective film or from various kinds of film breakdown.

The Research work of the committee has been mainly directed during the past 4 years to only one type of corrosion, namely that produced by the impingement of rapidly moving sea water, particularly in cases where free air is present or where intermittent cavitation occurs: this form of action is now known as "*Impingement attack*." This type of attack is of course not the only kind of condenser tube corrosion, but it appears to be the most important.

The work to be described in this article substantially confirms the existence of protective films and many of their effects upon condenser tube corrosion are now less obscure, while apparatus has been devised which enables rapid tests to be made of proposed new materials for condenser tubes.

Impingement attack of condenser tubes.

Earlier work had shown more or less conclusively that at the water speeds used in condenser work the material of the tubes was not mechanically eroded by the liquid. On the other hand serious destructive action does occur in rapidly moving sea water. The probable existence of a protective film had been shown by the fact that, while clean specimens of an alloy suffered attack, other specimens, which had been immersed for a few days in slowly moving sea water, resisted. It was inferred that this latter treatment developed a protective film; if attack subsequently reappeared, then evidently the film had broken down.

The foregoing points made it appear probable that the effect of impingement was to attack a film on the surface of the tube and, by laying bare the material underneath, permit corrosion to commence. The subsequent corrosion products might then easily be washed out of the resulting pits, which would thus appear to be formed by erosion rather than by corrosion.

Measurement of Protective Film.—It was known that a specimen of metal when covered with a coating of its corrosive products was at a different electric potential to the same metal without the film, although of course the absolute voltage differences are very small. An apparatus was devised, however, employing a three electrode valve, whereby measurements of such potentials could be made.

Tests were carried out using small discs cut from condenser tubes; these were mounted in a special apparatus arranged to give the desired degree of impingement attack. It was soon found when clean materials of the nature of Admiralty condenser tube metal were tested in a jet of air-free sea water, that the film potential gradually increased with time till it reached a maximum figure which was maintained unless the tube was scratched by mechanical means or air was admitted with the jet. In either of these cases the potential immediately fell off, this being ascribed to breakdown of the film.

It has been observed, however, that in many, if not in most, materials the potential may regain its normal value fairly rapidly, pointing to the possibility that the film has healing powers which permit it to reform if conditions are favourable. Thus, if the violence of the corrosive conditions is reduced by cutting off the air supply, the potential at once starts to change. Many potential-time curves of this type were taken and have confirmed in a satisfactory manner much of the earlier work, but results were obtained in a few hours as compared with the prolonged periods that have hitherto been necessary.

The situation which now exists is that by means of this apparatus it is possible to indicate when a change occurs in the supposed film. It has been demonstrated also that attack of the material is accompanied by a change in the film potential, which fact may therefore be reasonably used as a rapid indicator of the commencement or change of attack.

Jet Test.—Another piece of apparatus, known as the jet test, was devised with the object of investigating the factors which control impingement attack. The apparatus merely comprises a suitable centrifugal pump arranged to deliver a jet of water against a specimen, the potential of whose surface film can at the same time be measured. Controlled quantities of air can be admitted, while the size of the bubbles, the velocity of the water and similar factors are also capable of alteration.

Causes of Impingement Attack.—It has been concluded, as the result of a long series of experiments, that the main factor in producing attack of this type in Admiralty alloy tubes is the presence of air bubbles in the moving water. A high water speed through the tubes will of course tend to increase impingement attack, but it is now certain that velocity is not the principal controlling factor. Air free sea water even when moving at fairly high velocities appears to have little or no effect, while the addition of only about 1 per cent. (by volume) of air in the form of bubbles is sufficient to give a violent form of attack. The discovery has been made that the size of the bubbles is evidently a controlling influence, the attack being greatly diminished as the size of the bubbles is reduced. The minimum size of bubble necessary to establish attack has not, however, yet been determined, nor is this a point of great importance.

A very important paper published by Sir Charles Parsons (and referred to elsewhere in this series of Papers) brought to light another possible cause of impingement attack. He showed that the vortices, long known to occur in the water boxes of condensers, might cause the formation of cavities in the stream of water entering the tubes. Collapse of these cavities can give rise to very high pressures with a most destructive effect upon the tube material. It is, however, at present open to doubt whether cavitation of this type may not produce a severe attack by removal of the protective film on the tubes rather than by mechanical failure of the material itself, and such a suggestion agrees well with the previous evidence as regards the effect of air bubbles. In either case the observed attack appears to be identical and the surface of the metal shows no microscopic or other differences. It is improbable that the type of action associated with cavitation in condenser tubes can be *solely* due to mechanical erosion of the metal as no evidence is yet available of impingement attack having been observed in *non-corrosive* water. On the other hand the pressures that can be generated by collapsing cavities have been shown to be more than adequate to cause failure of the material and are independent of the nature of the fluid.

The action which occurs when the attack is due to air bubble impingement is, however, difficult to understand, as there appears little reason why the mere breaking up of air bubbles against a surface should be able to remove films which are frequently somewhat resistant to abrasion. The factor of bubble size may, however, be illuminating. It may, on the other hand, be important to note that cavitation causes air to come out of the water, thus leading to the formation of bubbles, which may give rise to impingement attack.

There is ample evidence to show, however, that the tubes of a condenser can be rapidly attacked by the occurrence of air bubbles in the circulating water or by the formation of vortices, the precise nature of the action in either case being at present obscure.

FOOTNOTE.—*It has been suggested that possibly the so-called "erosive" action on propeller blades may in like manner be due to the destruction of surface films upon the material and the subsequent rapid corrosion of the bare metal. It appears at least probable that this may be a frequent cause of the action, the "water hammer" of Mr. Cook (Papers No. 4, page 50) being not necessarily sufficiently powerful to damage the materal itself, although possibly adequate to destroy the protective film.*

Properties of Films as regards Impingement Attack.—It has now been demonstrated that the natural protective films do not always break down even under severe attack. Thus in the case of copper the action of moving sea water alone is sufficient to cause failure of the film, but in 70 : 30 brass the occurrence of either cavitation or of air bubbles of sufficient size has been shown to be necessary to cause failure. A few alloys appear to be substantially immune from breakdown and their development appears a hopeful line of advance.

The film on an alloy is often sensitive to the presence of extraneous substances either adherent to the tube or present in the water : thus CO_2 may have an injurious effect on the film in some cases. The electrical potential of the film relative to the underlying material is often of importance, since if cathodic to the latter very severe corrosion may occur should the film be injured.

The resistance of tubes to attack may often depend upon a delicate balance between formation and removal of the film, a temporary reduction in the rate of attack sometimes permitting the film to reform and to become strong enough to resist further violent impingement for considerable periods. This effect is particularly important in 70 : 30 brass and Admiralty alloy tubes, and it accounts for the special liability of such tubes to impingement attack when new and also explains why they may often give good results in practice.

It has been hoped that means might be found to form protective films on the new tubes, thus providing effective protection : the conditions favourable for film formation are, however, insufficiently understood to enable this to be effected at the present time.

Control of Impingement Attack.—It has been shown that, quite apart from the cavitational effects of Sir Charles Parsons, rotational motion of the water in the inlet water box may give rise to severe corrosion. This is probably due to the fact that air bubbles tend to collect at centres of rotation, and so a quantity of air that would be harmless, when generally distributed throughout the water, becomes capable of destructive action when concentrated in this manner. Evidently then from all points of view it is desirable not only to restrict the quantity of air entering with the sea water but also to damp out all rotational movement in the water boxes. The former of these factors is but little susceptible to control, any deaerating devices being out of the question owing to the large quantities of water that pass through the condenser. The circulating water is, of course, saturated with air, and this in itself is capable of giving rise to attack if conditions, of the type referred to above, are favourable for local concentration of the air to occur. It is, however, possible to avoid placing bilge pump and other discharge orifices in the neighbourhood of the circulating inlets, so lessening the possibility of abnormal quantities of air being drawn into these orifices: the position of the bilge keels may be important in this respect.

Suggestions have been made that rotation of the circulating water might be prevented by providing grids in the water-boxes, but such a method is objectionable not only on the score of weight but also because access to the tube nest would be rendered more difficult, while the resistance to flow of the water would be unavoidably increased unless the fittings were of very large size. Grids would also be liable to become choked by weeds, etc. Good results have, however, been obtained in individual cases by methods of this type, and it may well be of value to fit local grids in conditions where attacks are consistently experienced in particular parts of the tube nest.

Various devices, such as ferrules with stream lined or rounded entry, have been suggested in the past with a view to reducing the disturbances to the flow of water at entry to the tubes, but these are, in general, longer than normal fittings, and usually lead to the provision of deeper and therefore heavier condenser covers in order that the ferrules may be manipulated. Much may be done in the design stage, however, to ensure that the leads of circulating pipes are as straight as possible, devoid of pockets where air may collect, and that the direction of discharge into the water box is such as to obviate rotational flow.

The other obvious method of attacking the problem is to discover materials which develop highly resistant films or in which the healing power of the film is very marked. The jet test referred to appears to offer valuable possibilities in this connection, as it should enable the relative values of different materials to be rapidly determined, the most promising being subsequently tried out under controlled conditions in an experimental condenser.

Several materials have already been proved in this manner with very hopeful results as regards their resistance to impingement attack. It remains to be seen how tubes of these alloys will stand up to service conditions, observing that, although they may satisfactorily withstand impingement attack, failure may occur from other causes which are not readily determinable in an actual condenser.

Other types of attack.

Corrosion of condenser tubes is generally thought to be fundamentally an electro-chemical process, though it is by no means certain whether the differences of potential are set up by chemical changes or whether the latter action results from the differences of potential. The ultimate decision of this question may be long delayed and in any case does not appear to be a point of great practical importance: what does matter to the engineer is that both of these phenomena accompany corrosion and that therefore anything giving rise to such effects is to be suspected.

The usual forms of attack other than impingement are—

1. *Settlement of Solids*, such as cinders, pieces of wood, etc. in the tubes. These substances are liable to set up attack on the metal beneath them, but do not all appear to be equally efficacious : thus cinders and iron fragments nearly always seem to cause corrosion, while fish and weeds are frequently found in the tubes unaccompanied by any observable effect on the metal.

The general effect of these obstructions appears to be to keep oxygen away from a portion of the tube, which part then becomes anodic to the remaining surfaces where exposure to the fully aerated water is experienced. This may be called "*Deposit Attack.*" There are, however, other effects that have been noted in such cases, namely, (*a*) if the obstruction is too small to appreciably affect the water flow, an attack may be started on the up-stream side, the thin layer of water in viscous flow on the wall of the tube being broken up and impingement attack started; (*b*) if the flow of the water is considerably obstructed an impingement attack commences on the down-stream side. Either of these latter types should be resisted by tube materials which will withstand laboratory impingement attack. It is to be specially noted, however, that films which are impervious to impingement attack will not always resist deposit attack : in other words, a variation in the oxygen concentration may cause attack almost as readily as if the scale or film were not there.

The obvious remedy for attacks of this nature is to clear out the tubes periodically by means of rods, in the manner referred to in the Engineering Manual.

2. *Reactions* occurring between the metallic constituents and/or the corrosion products of the metals composing the tube alloy. The action known as "dezincification" is the most common example of this type of corrosion in brass tubes. This is due to the fact that brass can react with copper chloride solutions (resulting from oxidation of the copper), the whole of the brass being frequently replaced by re-deposited copper. The most important factor determining this action is the rate of oxygen supply, and thus any factor which tends to keep the dissolved copper in contact with the tube surface and oxygen away from it may result in dezincification. Slimy deposits of mud, certain types of scale, minute pores in the metal, etc., are all therefore predisposing causes, while the effects of temperature and water speed are both important. It has also been noticed that the constituents of the alloy have some bearing in this regard, and evidence is not wanting to show that very small proportions of arsenic may exercise a marked effect in preventing dezincification.

It may be remarked that tubes which ultimately fail by dezincing frequently have extremely long lives, and it has been suggested that the development of arsenic free tubes may be of value in this regard, more especially as there appears to be a tendency for the formation of a very tenacious and practically impervious scale, containing no copper compounds, to form on such tubes.

3. *Flaws in the Tube Material.* — The opinion has been expressed, as the result of much experimental evidence, that the ordinary surface defects, such as are hardly ever absent from the commercial tube, are seldom responsible for corrosion. Tubes containing literally hundreds of surface defects have behaved well in condensers, and local corrosion has often started at positions quite independent of flaws. If such defects really initiate corrosion it is difficult to see how tubes containing them can have any useful life.

Evidently, however, the above does not apply to deep surface defects, which may set up local changes in the oxygen concentration, thus giving rise to electro-chemical effects.

4. *Electrical Factors.*—The rapid destruction of condenser tubes is often ascribed to stray electric currents, but there is no definite evidence of such action. Stray currents are only likely in any case to cause corrosion at one end or other of the tube, an insulated end, where the current may be forced to pass through the water in order to reach the tube plate. The gromets can hardly insulate all the tubes in a condenser and some must actually touch the plate at some point; such tubes would carry the stray currents, short circuiting the insulated ones. In any case if evidence ever shows that this is a real trouble, it can be avoided by the use of metallic packing. In a ship, however, the paths that are open to the passage of stray currents are so numerous that it must be very exceptional indeed for such effects to cause corrosion in condensers; the case may be different in shore power stations.

Protection of Condenser Tubes.

(a) *Electrolytic Methods*, such as Cumberland, Harris-Anderson and Gush systems.

These methods are too well known to require description, and have been somewhat extensively adopted; faith in their efficiency seems to be steadily diminishing. The processes appear to work well in cases where it is possible to distribute the protecting current uniformly over the surfaces to be protected. This is in general impracticable, while the possibility of the current being inadvertently reversed is a practical disadvantage of such systems.

It is interesting to note the suggestion that the so-called electrolytic protection really depends on the formation of a protective scale on the surfaces. If this is true, the processes are unlikely to be reliable till more is known regarding the formation of such scales.

(b) *Tube Cleaning.*—The cleaning of tubes to remove deposits, &c., is evidently necessary, but it is obvious that the methods employed may be actually harmful if they are sufficiently violent to remove the protective films naturally formed on the tube surfaces. It is fortunate that such films are in general fairly resistant to abrasion, but the possibility must be borne in mind when attempts are made to remove hard scales of the type which interfere appreciably with heat transmission.

(c) *Formation of Protective Scales or Coatings on the Tubes.*—Experimental work both in the laboratory and in actual condensers is in progress in this connection but no conclusions can yet be stated. It is evident, however, from the fact that films on the tube surfaces appear to enter so largely into the question of corrosion, that methods of protection of this type offer some hope of success.

The coating of tubes with various metallic layers has been tried, but reports on their efficacy are very varied. Much obviously depends not only on the nature of the coating but also upon the continuity of its surface, this latter being particularly important when the metal of the tube is anodic to that of the coating.

The use of tinned tubes was abandoned for main condensers by the Admiralty many years ago as the result of extended experience, while on the other hand observations have shown that such tubes may give good behaviour in some cases, especially in estuarine waters. The matter appears to be determined to some extent by the nature of the scale formed on the surface. Experiments are now being undertaken with tubes covered with a coating of chromium by a modern electrolytic process which should give the desired degree of homogenity to the coating.

(d) *The Discovery of Special Tube Materials* which develop highly resistant surface films on exposure to corrosive waters, or in which the naturally forming film has such extensive properties of healing under attack, that the latter has little chance of making headway.

Summing up, it appears from the most modern information that most forms of condenser tube corrosion are intimately connected in some way with the condition and resistance of films formed upon their surfaces. Methods have been devised whereby the condition of these films can be examined while the material is exposed to corrosive influences, and these methods should be of great value in developing suitable materials for resisting attack.

If materials can be developed which will withstand both impingement and deposit attacks there appears to be much reason to expect that the problem of condenser tube corrosion for all usual marine installations will be effectively solved.

The mechanism of impingement attack is now largely exposed, and means, which may be difficult fully to put into practice, have been suggested for reducing the violence of such action in actual condensers.

The general scientific aspect of corrosion, as occurring in all engineering material, is being separately investigated, and there is evidence to show that the film action, forming so large a part of the subject matter of this paper, may be a common feature of all types of corrosion.

Tubes of the following materials are among those now under trial for Naval services, the first mentioned having shown signs on laboratory tests of being especially resistant to impingement attack :—

Aluminium-Brass, Cupro-Nickel, Monel metal, Stainless Steel and Chromium-coated tubes.