STUDY OF THE CORROSION OF LOCOMOTIVE BOILER TUBES

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A study of the corrosion of
locomotive boiler tubes

A STUDY OF THE CORROSION OF LOCOMOTIVE BOILER TUBES.

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Preface.

The literature which treats of the corrosion of boiler tubes is scattered throughout a great number of books, and it is not readily available to all who are interested in this particular subject. For this reason, it has seemed desirable, to the author, to collect such useful information, as investigators have given us in the past, along with a few personal investigations and conclusions, and to bind them together in this volume.

It is hoped that the information contained in this book will be useful to the many who are interested in the practical side of the corrosion of boiler tubes, and who are unable to make extensive investigations for themselves.

C.C.Congdon.

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THEORIES.

Theoretically, pure water evaporated from a pure iron vessel will not cause corrosion of the vessel. In practice, however, these conditions are never realized, and it is the object of the author to show the conditions which influence corrosion, and the effects brought about by it. Where remedies or preventives have an important influence on the corrosion of boiler tubes, they will be indicated.

A study of the literature concerning the corrosion of boiler tubes and other iron and steel materials in service under similar circumstances, shows that the subject has not recieved the thorough, systematic, practical study that it deserves.

Considerable work has been done on pure iron, relative to its corrosion, and on other commercial iron and steels in tests suitable to show the susceptibility to corrosion as used in structural work subject to natural corroding influences. This side of the question has been

extensively investigated by Cushman (1), Friend (2), Heyn and Bauer (4) .

There have been several theories advanced concerning the cause or causes of corrosion, all of which have had their followers; yet there are only two which have recieved serious consideration in recent years, namely, the acid theory, and the electrolytic theory.

The acid theory, propounded by Calvert (5) in 1871, considers the presence of some acid essential to the process of corrosion. According to this, pure water and oxygen, alone, are not capable of producing corrosion. Since investigators have never been absolutely sure of the absence of all carbonic acid gas, in their researches, they have been unable to disprove the acid theory.

According to the electrolytic theory, it is not necessary to have an acid present to bring about corrosion or rusting. Water serves as the electrolyte between points of different

potentials. Small amounts of water are ionized according to the following equation;

$$H_2O \rightarrow H^{+} + {}^{-}OH .$$

The extent of the dissociation is limited. Work done by Alfred Holt Jr. shows that water is slightly dissociated at a temperature of 775 C. He was able to measure the molecular dissociation at this temperature. It is reasonable to suppose that iron will pass into solution in quantities of the same order of magnitude as the extent of the ionization of water. The hydrogen ions would then lose their charges of electricity to the iron ions and become atoms. The hydrogen atoms unite to form molecules, and thus become inactive.

It is certainly worthy of consideration to note that the iron may go into solution more extensively than its solution pressure would indicate, because of the currents set up between points of different potentials in the metal itself, as for instance, between the

ferrite and the enclosed slag, in the case of wrought iron, or between different potentials of particles of impurities as considered by themselves. The ionic hydrogen liberated is an extremely active agent.

In substantiation of the electrolytic nature of corrosion we have record of some very interesting experiments carried out by Dr. Cushman (6) . He prepared, what he called, a feroxyl reagent, by making a hot solution of gelatine and neutralizing it with one hundredth normal potassium hydroxide, using phenophthalein as an indicator. To the hot liquid he added a few drops of dilute potassium ferricyanide solution. The test pieces of iron and steel were put into the liquid, and upon cooling, it solidified around the articles. Electrolysis was soon indicated by the formation of a pink color at certain points, showing the presence of the hydroxyl ion, and by a blue coloration (ferrous ferricyanide) at points indicating positive poles,

where ferrous ions were liberated. This shows that iron tends to go into solution in the ionic condition. The iron gives up its positive charge and is rapidly oxidized to rust.

There has been considerable evidence brought forward by investigators, both for and against the electrolytic theory. The different materials used in the work, and the different ways of attacking the problem has, no doubt, given rise to much of the conflicting evidence. The experimental work done on the theory of corrosion has a great theoretical value, but the commercial iron contains so many impurities, and the conditions of laboratory experiment are so widely different from the actual working conditions, that comparisons seem to be of small value.

Dr. Cushman (7), in speaking of laboratory experiments and acceleration tests, made the following remarks:

"Owing to the nature of corrosion, it is

probably true that no perfectly reliable acceleration tests on corrosion resistance can be made. Corrosion, in the natural process of rust formation, that is to say, in a very slightly acid media, is a question of comparatively slow growth under special conditions, and any effort to hasten the action changes all of the conditions of equilibrium, producing an entirely different order of phenomena."

"Nevertheless, evidence has been brought out to show that stresses and strains, as a result of the cold rolling and imperfect annealing of steel, will affect not only the degree of solubility in acid, but also the tendency to maintain differences of surface potential affecting the rapidity of corrosion. In view of this fact, it is probable, that when its limitations are understood and its results properly interpreted, the acid test will be useful in the hands of competent investigators."

MECHANICAL TREATMENT OF TUBES.

In the mechanical working of boiler tube material, there is always variation from the conditions which would be most liable to bring about homogeneity of the material. If it is worked hot, that is, above its critical temperature, the crystalline structure disappears, and it is as near homogeneity as it can be, outside of the liquid state. If it is cooled from this state properly, a fine structure results; but if cooled improperly, the crystals will grow to a large size, and the tube will be weak.

In the case of lap welded and butt welded tubes, the metal is first rolled out into sheets of the desired gauge and cut to size in the flat. The edges are then beveled off, and the material is bent to shape by passing through three or four forms. It is next raised to the welding temperature and run rapidly through the welding rolls, where the edges are rolled into a strong weld. A welded tube, properly made, is generally more resistant to corrosion at the weld than at any other part of the tube.

This is, no doubt, due to the excellent, hard, fine grained surface formed by the mechanical treatment. In fact, the whole surface of the tube is more resistant to corrosion than the interior metal, because of the mechanical working it recieves. This statement is born out by the fact that points in a boiler, where workingmen have cut through the outer layer in carelessly handling their tools during cleaning or other operations, are much more rapidly corroded than immediately surrounding parts.

Some laboratory experiments carried out by the author gave evidence of the difference in the rate of corrosion of the material examined, at various distances into the metal from the outer surface. A piece of boiler tube material, which had some mill scale on it, was scratched by a sharp chisel. The scratches ranged in depth from the thickness of the mill scale to perhaps one thirty-second of an inch. The piece was then exposed to acid vapors and moist-

enedat intervals to hasten the corrosion. After three or four days it was found that the sides of the scratches having the greater depth were the more heavily corroded. The portion covered by scale did not seem to be affected at all. The evidence showed that the effect of rolling on the structure of the material, so far as corrosion was concerned, extends to only a small depth.

In certain operations where the tubes are cold drawn, or too suddenly cooled, etc., internal strains are set up in the material, depending in extent upon the rough handling recieved. Investigators have found that there are differences of potential between the strained and unstrained parts of the iron and steel which cause galvanic action.

Photomicrographs show the boundaries, where the crystal surfaces slide past one another during straining. The edges of the crystals are very susceptible to corrosion, a statement

that is born out by the action of etching chemicals, such as free acids and chlorides, in attacking the crystals at the edges.

After the welding or drawing out of the boiler tubes, they should be above their critical temperature, momentarily, to allow the crystalline structure to disappear. This relieves the internal strains in the material. If the tubes are then cooled at the proper rate, the internal strains will not reappear.

Mill scale is the name given to the black magnetic oxide formed on the metal during the period in which it recieves its mechanical treatment at the mill.

All metals are electropositive to their oxides. This means that mill scale present on the boiler tubes is an agent which aids corrosion. As a matter of fact, if the scale is tightly adherent to the metal, it forms a good protective layer; but if it loose and cracked, the corrosive action is much greater than if none

were there at all. On the inside of fire tubes, mill scale acts as a protective coating insofar as it prevents the deposit of soot from coming into contact with the metal. The soot is generally saturated with distillation products of unburned fuel, and the acids formed by the burning of sulphur, etc.,

The mill scale is often removed at the mill by pickling the tubes in sulphuric acid. When the scale is dissolved off, the tubes are washed and the acid neutralized in lime water. Investigations (8) have shown that the acid effects are not entirely removed by neutralizing in lime water. After this treatment the tubes should be baked for several hours at from 400 to 450 Fahrenheit. The baking drives out the occluded hydrogen which has been absorbed during the pickling process. The hydrogen is present apparently alloyed with the iron or steel. The metal is hardened to a considerable extent by the hydrogen, and it is readily oxidized while

in this condition. Tubes baked in this manner are much benefitted. The galvanic action due to the scale is removed by pickling, and also any defective spots in the material are exposed to the view of the inspector.

IMPURITIES IN METAL.

A metal that contains impurities is greatly affected in its rate of corrosion by the impurities in it.

If carbon is present in the material as a constituent of pearlite, it tends to prevent corrosion. The pearlite is harder than the ferrite and is less rapidly attacked by the ordinary corroding agents. As more and more of the pearlite is exposed during corrosion, its protective influence increases.

Sulphur is generally conceeded to be an accelerator of corrosion. It is probably present in the material as sulphides, of which the most prominent is manganese sulphide. As the sulphide is exposed to the corrosive action at the surface, it is oxidized to sulphuric acid. The action of free acids will be stated later.

Phosphorus and silicon tend to prevent corrosion. Sang suggests that this resistant effect may be due to their hardening powers.

The action may be similar to that of combined carbon. The effect is only noticable when the material is homogeneous. The fact that common cast iron is often more resistant to corrosion than some of the better grades of iron and steel may be due to its higher phosphorus content.

When manganese is present in iron and steel in the form of sulphide it tends to aid in the process of corrosion. It is more rapidly corroded than the iron, and it forms centers for corrosion in the latter metal. Manganese is also an important factor in relation to the amount of gases that the metal will occlude.

IMPURITIES IN WATER.

Oxygen is one of the very common dissolved constituents of ordinary feed water. Its presence promotes corrosion by disturbing the equilibrium established between ferrous hydroxide and water, by oxidizing the ferrous hydroxide formed to ferric hydroxide, according to the following equation:

$$4\ Fe(OH)_2 + O_2 + H_2O \rightarrow 4\ Fe(OH)_3$$

It may also promote corrosion by forming water with the hydrogen as the latter is set free on the metallic surface.

Rain water and water taken from some mountain lakes have a very low solid content, yet they are often very corrosive because of the large amount of dissolved gases in them. The solubility coefficient of oxygen, at the boiling point is zero, showing that there is no dissolved oxygen in the water at that temperature, yet in the steam space above the water it is easy to find oxygen at all times owing to the fact that it is always being put

into the boiler along with fresh feed water.

Carbon dioxide may be present either as the dissolved gas or in the form of bicarbonates of calcium and magnesium. It is freed in the latter case, when the water is heated. The bicarbonates are decomposed with the liberation of carbonic acid gas and the precipitation of the normal salt, according to the following equation:

$$Ca(HCO_3)_2 + \Delta^\circ \rightarrow CaCO_3 + H_2O + CO_2.$$

Some river waters contain free acids, such as sulphuric and hydrochloric acids, due to factory waste or other polution of the stream. Waters having an acid reaction are very corrosive to iron and steel and must be neutralized before feeding into a boiler.

Along with the gases which we commonly find dissolved in the water are such dissolved solids as calcium bicarbonate, magnesium bicarbonate, and often sodium, potassium, and magnesium chlorides. Magnesium sulphate is

occasionally found in water.

It has long been known that chlorides promote corrosion, and that magnesium, potassium, and sodium chlorides are unusually active agents in this respect. Sodium and potassium chlorides are found more commonly in water used for feed purposes than magnesium chloride. These salts, as well as some of the other salts found in water, act as electrolytes, and assist materially in the process of corrosion. They conduct the current between points of different potential, such as exist between a foreign substance in the boiler, like scale, and the tubes and shell of the boiler. This action would occur more where the scale is rough, thick, and loosely adherent, than where it has a close contact with the boiler metal.

Because of these impurities found in feed water, there has been a great amount of study concerning the most efficient and proper ways to remove them or to inhibit their action. There have been many companies estab-

lished which make the subject of water purification their sole business. Many of the railroads, which have only poor waters available along their routes, have established water softening plants along their lines, in order to treat the water in such a way as to inhibit the corrosive and scale forming action as much as possible.

Sodium carbonate and lime are extensively used in the softening processes. They have a greater effect on the reduction of the amount of scale than on the inhibition of corrosion. Their big effect in this latter instance is due to the removal of the excess carbonic acid gas present in the calcium and magnesium bicarbonates. The following equation is typical of the reaction:

$$Ca(HCO_3)_2 + CaO \rightarrow 2CaCO_3 + H_2O$$

The calcium and magnesium present are precipitated in the form of their normal carbonates.

Barium hydroxide is an effective pre-

ventive of corrosion when used to purify water that contains magnesium chloride. At the boiling point of water, the following reaction takes place,

$$MgCl_2 + Ba(OH)_2 \rightarrow Mg(OH)2 + BaCl_2.$$

The magnesium hydroxide precipitates and the barium chloride which is formed will react with any calcium sulphate present with the precipitation of barium sulphate and the formation of calcium chloride. The calcium chloride formed is not a corroding agent. The precipitated material may be blown off at desirable intervals to prevent the formation of scale.

EFFECT OF OIL IN FEED WATER.

The presence of oil in feed water is undesirable. Fatty oils which have been used in the lubrication of working parts, and which find their way into the boilers, work much harm on the tubes and plates. It has been found that they break up into an acid and a base at the high temperature of the boiler. The base, which is generally glycerol, has no bad effect. In fact, glycerol is said to have a beneficial effect in tending to keep the calcium salts in solution. In this case, however, it is not present in large enough quantities to do any good. In a few instances it has been added for this purpose, but for special experiments only. The organic acid generated has a direct action on the metal.

Fatty oils may be removed from boilers by saponifying them with caustic alkali. The soaps formed are soluble, and they will react with any calcium salts in solution, forming insoluble soaps, which sink to the bottom to form a soft sludge. This may be removed by

blowing off.

The presence of the hydrocarbon oils or the so-called mineral oils in boilers, is generally detrimental because it forms a thin layer over the tubes, which, on account of its poor conductance, permits overheating of the tubes and plates, with consequent burning. A layer of oil only one one-thousandth of an inch thick reduces the heat transference greatly. Iron and steel tubes which have been overheated in this manner, lose considerable of their resistance toward corrosion.

In certain instances, boilers have been painted internally with mineral oils mixed with graphite, to inhibit corrosion, but whether it was detrimental to the boiler through causing overheating and bulging of the plates, or not, has not been stated.

PITTING AND GROOVING.

Pits generally take the form of small round or conical holes in the metal. They are filled with a deposit of light colored oxides. Sometimes organic matter is found in pits covered with a thin shell of calcium or other carbonate. The oxides are often hydrated, and are easily removed from the exposed pits. The pits do not have to extend entirely through the metal to cause failure, for when the thickness of the metal is reduced to a certain minimum value, the tube will rupture from the steam pressure.

A thin layer of calcium carbonate deposited in the boiler tends to prevent pitting general corrosion.

Basing deductions on the electrolytic theory of corrosion, we have a possible explanation of the cause of pitting, once corrosion has started. The solution pressure of the material from which the tubes are made is different in different spots, owing to the inherent heterogeneity of mild steel and wrought

iron. This means that the tubes, which are electropositive to the scale, are going to dissolve more rapidly in some spots than in others. This action produces the uneven surface, which is said to be pitted.

Tubes and plates are sometimes found to be grooved in the process of corrosion. The grooves take irregular shapes and may be due to the process of corrosion following the line of least resistance, caused by internal strains in the material.

Christie states (9) that one of the worst things that can happen to a boiler is to have it fired at irregular intervals, hot for a time, and then cold. This condition is found to exist in locomotive boilers, where the fires are not kept up over night in engines making day runs. The injury he suggests is no doubt due to the stresses set up through the expansion and contraction of the metal, and the unusual susceptibility of strained metal to corrosion.

Corrosion often occurs to a considerable extent in boilers which are not in use for a long period of time. This action has been reterded in different ways.

In American navy practice, the boilers are cleaned and painted internally with a mineral oil. When the period of non usage is short or only for a few days, the boilers are filled with fresh water.

When boilers not in use are filled with fresh water, and the water made strongly alkaline with sodium carbonate or other strong alkali, the rusting action is almost completely inhibited.

Evidence shows that idle boilers deteriorate largely through pitting.

OBSERVATIONS.

Specimens taken from a locomotive boiler, which was used on one of the railroads in regular runs, showed very little pitting, and a remarkably even corrosion. This was no doubt due to the fact that the feed water used had been properly treated before injection into the boiler, and to the fact that the tubes were made from good material. Patches of mill scale were still on the tubes. The scale was firmly and closely attached to the metal. The metal was mild steel which had been lap welded.

Some specimens obtained from a boiler used on another railroad were also lap welded mild steel material. They showed much more corrosion than the tubes mentioned in the last paragraph. Some of the pits in the material were as much as three sixty-fourths of an inch in depth, and they were most evident along the weld. The rust was loosely adherent to the tube.

Pieces of boiler tube metal were freed from mill scale, after which a surface was ground flat. Dilute nitric acid was poured on

the surface, and after a few seconds, was washed off. On one specimen a fan-like design was etched, plainly visible to the eye without a glass. On another specimen a design was etched which had the appearance of a natural wood grain. These tests show that the material is not entirely homogeneous, and that some parts of it are more resistant to attack than others.

Steel boiler tubes are coming into favor extensively now. Twenty years ago it was considered that wrought iron was less susceptible to corrosion than mild steel. If this was the fact, it was no doubt due to the slow and careful working that wrought iron recieved, in comparison to steel. The steel made twenty years ago did not have the homogeneity that steel made now has. Steel gives a much more uniform product than wrought iron, and it is very reliable.

An average analysis of lap welded steel

tubes furnished by the National Tube Co. for some government experimental work (10) follows:

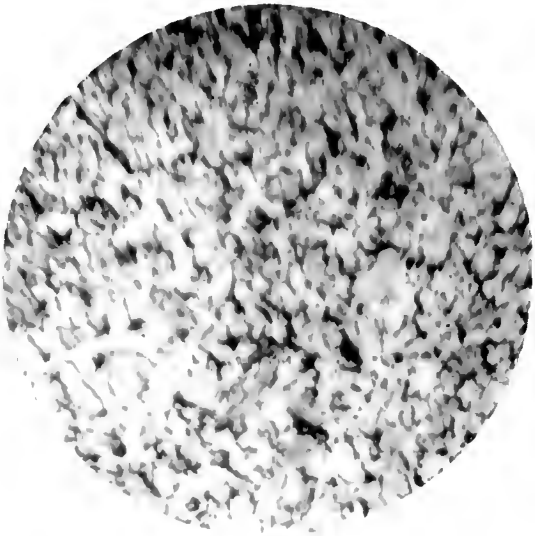
Carbon	00.08	percent.
Phosphorus	00.116	"
Sulphur	00.08	"
Manganese	00.32	"
Silicon	00.006	"
Iron (by dif.)	99.398	"

An average analysis of lap welded wrought iron tubes, as obtained from the above reference (10) follows:

Carbon	trace	
Phosphorus	00.038	percent.
Sulphur	00.008	"
Manganese	00.05	"
Silicon	00.02	"
Iron (diff.)	99.884	"

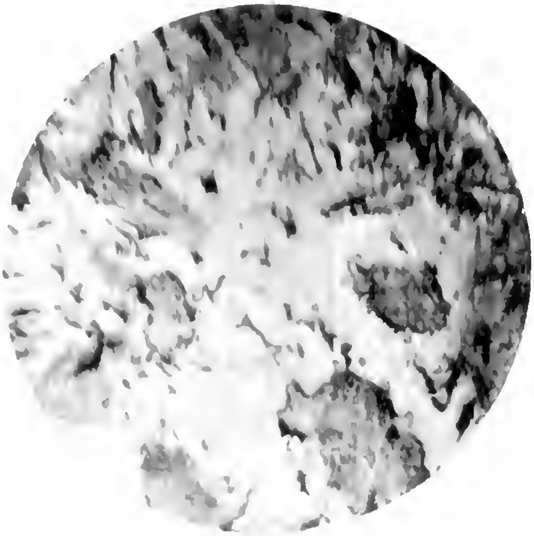
Some specimens were polished and etched with nitric acid according to the method suggested by Sauveur (11) to show the ultimate structure of the material. The following

photomicrographs were obtained from the specimens examined.

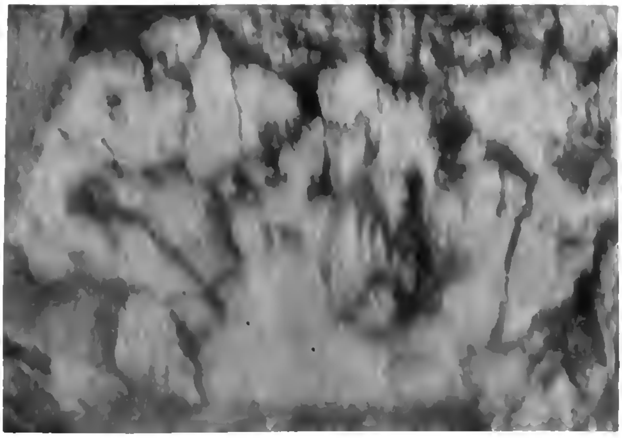


The above is a transverse section of a mild steel tube magnified 240 diameters. It shows clearly the ferrite grains.

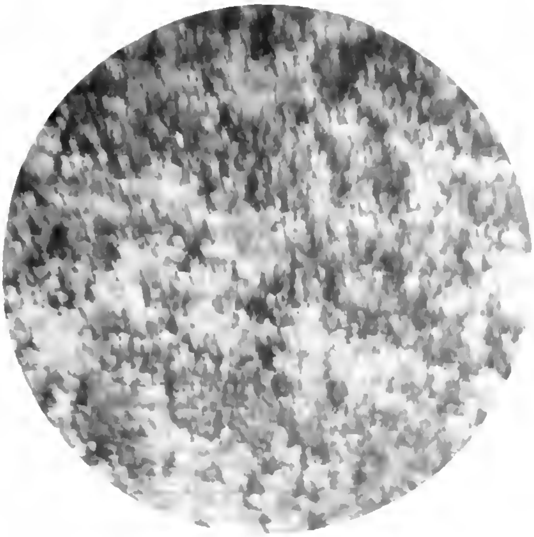
From longitudinal section of mild steel tube. Magnification 240 diameters.



Magnification: 240 dia. A spot of segregated impurities brought to surface by working.



Magnification: 300 diameters. An oblique section of the metal. Light colored masses of ferrite clearly defined.



Magnification: 240 diameters. A polished surface which had been corroded by acid gases.

SUMMARY.

In summarizing from the preceeding study, we find that corrosion is an electrolytic process. Its rate of action depends on the many conditions arising from impure metals being used in the construction of the tubes, and from the impurities found in the feed water.

In order to inhibit corrosion as much as possible, every effort should be made to get more pure and homogeneous tubes, or tubes of alloys which are rust resisting , and to see that they are worked up properly mechanically, and finished free from strain. The feed water used for steaming purposes should be freed from solid and gaseous impurities as much as possible by the proper softening process, either a chemical or heat pretreatment, before injection into the boiler.

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