THESIS.

Corrosion of Steam Boilers,

FOR THE

Degree of B. S. in School of Chemistry.

BY

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The question of corrosion in steam boilers is one that commands the attention, not only of the engineer who is directly concerned in correcting the evil, but the chemist as well, for it is now conceded that when water is heated under high pressure, chemical reactions take place within the boiler, the understanding of which requires some knowledge of chemistry.

To the engineer it is a standing source of anxiety, trouble and delay, to the steam user it means great expense, not only in actual cost of repairs but in loss of efficiency by having to reduce the pressure, after the boiler has been in use a short time, on account of the eating away of the pipes and connections, and even the flues and sides of the boiler. From the hour the boiler is set at work it is being acted upon by destroying forces and many of them are almost uncontrollable in their work of deterioration.
Both from within and from without there is constantly going on processes of destruction due to this cause which will sooner or later be the cause of having the boiler condemned and carried to the scrap-heap. These processes of rotting may be classified into two main divisions: External Corrosion and Internal Corrosion, with a score or more minor divisions to each, according to the following scheme.

Corrosion

<table>
<thead>
<tr>
<th>External</th>
<th>Due to Dry Rust.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Due to Leakage.</td>
</tr>
</tbody>
</table>

Internal

| Due to inequalities in Plate-metal of varying densities causing pitting due to decomposition of salts. |
| dry rust and scale |
| electrolytic action |
The causes of external corrosion may be put down primarily as due to leakage or dry rust. The leakage may be either steam or water, both have the same effect of wearing away and weakening the metal. When a leak is sprung in a boiler, most generally at the joints, due to imperfect riveting, the superheated steam by its continual passage through the, what may at first be an almost invisible crack, soon widens it into a hole of such proportions as to require a patch or if it be in several places may be of such magnitude as to require a new boiler. If the steam as it escapes from the feeding strikes across another part of the boiler it very soon shows its effect in a continually growing weak area, the iron being literally eaten away by a process of oxidation. If it is water which escapes from the opening, which may in this case be either in the boiler itself or from some overhead water pipe, the continual drip,
drift, drift of the water striking the iron very soon melts through from the same cause as before. This effect is much hastened if the water strikes a heated portion of the boiler, as heat very materially aids the oxidation.

In the rusting of iron and steel it is a well-known fact that when rust starts, no matter from what cause, it continues to grow both outward and downward. This rusting is due to a chemical reaction taking place between the metal and the water forming first the hydrate $\text{Fe} + 3\text{H}_2\text{O} = \text{Fe(OH)}_3 + 3\text{H}$. The hydroxide then breaks down when heated to the oxide or common rust.

$2\text{Fe(OH)}_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$.

This dry rusting of boilers is one of the common forms of corrosion and may be due either to moisture and the oxygen of the air or to gases from the fire box. Its effect may be partially overcome in many cases by frequent painting the boiler with a noncorrosive paint.
Internal corrosion is the malady from which most boilers suffer. This silent and ever-active evil presents itself in various forms; sometimes it happens that it is mainly the transverse seams, rivet heads and flange edges which are attacked, in other cases it is the longitudinal seams alone. The stays are often more violently corroded and more rapidly wasted away than the plates; a threaded stay will be attacked at the thread while the unbroken or unturned surface will escape. The body of the plate away from any disturbing influence is often attacked by furrowing and pitting and in consequence of this weakening has often to be condemned and removed, causing a heavy loss of material and very often a serious delay. Pitting is a very common result of corrosion. It is believed that it is due mainly to inequalities of the ingredients of the boiler plate. Very often in furnaces
While the mass is in the molten condition, certain elements of the charge segregate thus giving to the finished plate different qualities than the rest; these spots are usually more easily attacked by the corroding agents in the feed water and are dissolved out leaving pits. The pits are usually more common in boilers using a water which carries very little lime in solution. If this substance be plentiful the evaporation of the water leaves it deposited upon the sides of the boiler in the form of a hard scale thus preventing the water from attacking the boiler. But this deposition is of itself a serious problem to boiler management - an evil, when of any extent, equal to corrosion. Even when the water is heavily charged with lime, if the boiler be new, the pits will get the start of the incrustation to some extent. These pits take the form of conical or more frequently
spherical depressions which become filled with a yellowish brown deposit—mainly iron oxide. They are generally most numerous in the parts of the boiler where the circulation is bad. The yellow powder is due to what may be called rust. In all processes of rusting carbon dioxide and moisture play an important part, the iron uniting with the carbon dioxide and oxygen of the water to form ferrous carbonate while hydrogen is set free. The ferrous carbonate then takes up more oxygen and forms ferrous hydroxide. This is not affected by the CO₂ but when heated it loses its water and forms the oxide.

Experiments which were performed with iron filings exposed to action of sea water, it was found that hydrogen gas was liberated and FeCO₃ formed. A second dry fraction took place later, the carbonate changing to the hydroxide and finally to the oxide—Fe₂O₃.
Sometimes the water supply is of such a quality as not to cause corrosion if used in its natural state, but in its passage from the tank to the steam chest it passed through oily valves. Particles of oil are taken up and being decomposed by the superheated steam form an active corrosive agent. As often especially in factories where stationary boilers are used, the driftings and waste waters are collected and returned to the boiler. These are always oily and play havoc within the boiler. When corrosion is due to such a cause it is found that the greatest damage is done at the water level. It is supposed that the destructive substances are held in the scum which floats on the surface and clings to the sides of the boiler. If the scum be the corrosive agent, anything taken into the boiler capable of forming a scum tends to increase the corrosive action of the ingred
sinks into the feed water. The scum in boilers is similar to the curd which forms on hard water when soap is used. It consists mainly of salts of lime, magnesia and fatty or oily acids—the latter derived from the lubricants.

The scum forms a porous scale when it hardens and is like an insoluble soap, beneath it corrosion takes place in a very irregular manner. Dry rusting is one of the commoner phases it takes the action and progress being very similar to the same process on the exterior of the boiler. Its effect is best overcome by frequent cleaning.

Corrosion has long been known to take place in boilers using very soft water. By puri is meant, water containing too small a quantity of lime or magnesia to form a protective scale, and fines from such salts which decompose on heating to form acids.
Usually called corrosive, such as hydrochloric and sulphuric acids.

Even dry air and pure water deprived of air have separately no corrosive action, but air or oxygen dissolved in water oxidizes iron rapidly. Besides from air corrosion is due to carbon dioxide contained in the water and also to free hydrochloric or sulphuric acids.

To correct these latter, sodium carbonate has been used as it in part neutralizes the acids. It becomes objectionable however if too much be used—the only safe method is to first have a chemical analysis made of the water and then add the proper amounts of soda. When water containing calcium sulphate is treated with sodium carbonate, the first effect is to form calcium carbonate; this forms an insoluble scale under ordinary conditions, but if any fatty acid is present the two react, the acid is neutralized and the scale dissolved.
When the corrosion is due to acid in the water it is usually brought about by some salt in the water being decomposed under the high heat and pressure, to which it is subjected in the boiler, and liberating the acid. Of all salts carried in solution by water the one most easily decomposed is magnesium chloride. This substance decomposes to a certain extent when a solution is boiled in the open air, when boiled under pressure the action is much more effective. Other experiments carried on at the same time with other salt solutions showed that magnesium sulphate, calcium chloride and sulphate and sodium chloride and sulphate are all decomposed in varying amounts depending on the strength of solution and time heated.

In these experiments the different salts in varying amounts were dissolved in pure distilled water and boiled with iron filings, first under atmospheric pressure...
then in a specially prepared boiler where a pressure of ten
kilograms per square centimeter (about 150 lbs. per sq. in.) could
be obtained. This gives the normal conditions in a boiler.
The boiling was continued for four hours and about 25
grams of steel filings were used in each case. The iron
dissolved by the action was oxidized by adding a few
drogs of HNO₃ and then precipitated from the boiling
solution with NH₄OH. The precipitate was then gently
ignited, weighed, and calculated to metallic state.

First series of experiments—Boiling in open flasks.
In these experiments solutions of MgCl₂, CaCl₂, and
KCl were made up to such a strength that one liter
contained 2.83 grams of the salt or about 25 grams per gal.

Experiment 1:

500 c.c. solution of MgCl₂ containing 25 grams per gal.
25 grams of filings were boiled four hours.
.022 grams equals weight of iron dissolved.
experiment II.
500 c.c. solution of CaCl₂ containing 25 grains per gal.
25 grams of filings - time of boiling four hours.
Trace of iron dissolved.

experiment III.
500 c.c. solution of NaCl containing 25 grains per gal.
25 grams filings - time of boiling four hours.
No iron dissolved.

experiment IV.
To see if water alone had any effect.
500 c.c. pure distilled water
25 grams filings - time same.
Just trace of iron was found to be dissolved.

These experiments show that when salt solutions are heated in contact with iron that the salts are decomposed liberating free acid which attacks the metal dissolving it. The amount found in solution gives the ex-
tent of decomposition. It shows that MgCl₂ is the most easily decomposed, hence natural waters carrying this salt in solution will be corrosive. CaCl₂ is also decomposed but to a much lesser extent while NaCl is not affected at all.

Second series of experiments. (Boiling under pressure.)

Experiment I.
500 cc solution of MgCl₂ containing 10 grains per gal.
25 grams of filings. Time four hours.
.018 grams of iron dissolved.

Experiment II.
500 cc solution of CaCl₂ containing 10 grains per gal.
25 grams of filings. Time four hours.
No iron dissolved.

Experiment III.
500 cc solution of NaCl containing 10 grains per gal.
25 grams filings - No iron dissolved.
Experiment II.

500 cc solution of MgCl₂ containing 20 grams per gal.
25 grams steel filings. Time four hours.
0.28 grams iron dissolved.

Experiment II.

500 cc solution of CaCl₂ containing 20 grams per gal.
25 grams filings. Time four hours.
0.1 gram iron dissolved.

Experiment III.

500 cc solution of NaCl containing 20 grams per gal.
25 grams filings. Time four hours.
Trace of iron dissolved.

Experiment III.

500 cc solution of MgCl₂ containing 30 grams per gal.
25 grams filings. Time four hours.
0.34 grams iron dissolved.
Experiment VIII.
500 cc solution of CaCl₂ containing 30 grains per gal.
25 grams filings. Time four hours.
.019 gram iron dissolved.

Experiment IX.
500 cc solution of NaCl containing 30 grains per gal.
25 grams filings. Time four hours.
.006 grams iron dissolved.

Experiment X.
500 cc solution of MgCl₂ containing 25 grains per gal.
25 grams filings. Time four hours.
.01 gram iron dissolved.

Experiment XI.
500 cc solution of CaCl₂ containing 25 grains per gal.
25 grams filings. Time four hours.
.006 grams iron dissolved.
Experiment XII.
500 cc solution of MgSO₄ solution 50 grains per gal.
25 grams filings. Time four hours.
0.16 gram iron dissolved.

Experiment XIII.
500 cc solution of CaSO₄ containing 50 grains per gal.
25 grams filings. Time four hours.
0.19 gram iron dissolved.

Third Series of Experiments.
To test the theory of corrosion due to carbon dioxide in the water. Some experiments were conducted using solutions of magnesium bicarbonate prepared by treating MgCl₂ with an excess of Na₂HCO₃ forming (Mg₂(OH)₂(CO₃). This breakdown on heating forming normal carbonate and CO₂.

The solutions were made up to a strength of 25 grains per gal and were saturated with CO₂ before boiling. Experiments were conducted under basic conditions as before.
Experiment I.
500 cc solution of magnesium bicarbonate - 25 grains per gal.
25 grams filings. Time four hours.
0.08 gram iron dissolved

Experiment II.
500 cc solution of magnesium bicarbonate - 50 grains per gal.
35 grams filings. Time four hours.
0.12 gram iron dissolved.

All these experiments were duplicated with results same in each case. A summary of results in form of a table is given in the sequel.

Besides the theory of oxidation caused by gases held in solution, and the decomposition of salt into free acid, there is another theory as to corrosion, namely that of an electrolytic action. The superheated water in contact with the metal of the boiler acts like the liquid in a battery with the result that the iron is dissolved.
To overcome this it has been suggested that zinc, connected with the iron, be suspended in the boiler. The zinc now acts like the positive pole of a battery with the result that it is eaten away while the iron remains unattacked. In a paper read before a Meeting of British Institute of Marine Engineers it was stated that the proper amount of zinc required to a square foot of boiler surface was considered to be about four pounds. It was also stated that the zinc should be placed in the steam as well as in the water space. The zinc when so used wastes away forming a white powder which is found incrustated upon the sides of the boiler. This is a very common method for preventing corrosion, especially in marine boilers.

Another method used is the painting the sides of the boiler with a mixture of cylinder oil and graphite. In a test which was made with this preventative it was
found, after the boiler had been cleaned, that no further fitting had taken place after six months time. This remedy also allows the scale to be easily detached.

Neither of these methods are strictly chemical. This name may be applied to such methods in which the water, after it has been subjected to a chemical analysis, has been treated so as to neutralize any free acid.

Before a water can be successfully treated for corrosion it is necessary that a chemical examination be made of it so as to know just what it is that causes the trouble and how much of it there is in the water. When this is known it is a comparatively easy matter to overcome the evil both with the correct substance and the proper amount. This blindly following a rule of thumb, which corporations use because it is cheap, and assigning the same causes to corrosion and treating all waters alike after causes more trouble after the
would be remedied has been applied than what the original water ever could do. A great many times, no remedy proposed which no doubt would correct the evil were the cause understood but from misapplication or in wrong amounts, does not give satisfaction and is discarded as useless.

In this work the first thing aimed at and one of the most important to be accomplished, was the working out and testing of a rapid and satisfactory method for analyzng food waters. Several methods were worked out and tried but the one which gave the greatest satisfaction was according to the following scheme:

1. The bottle containing the sample to be analyzed must have no sediment on the bottom—have what floating matter there is in the water equally distributed throughout by thoroughly shaking. Use 100 c.c. for an analysis evaporating to dryness in a water bath in a weighed platinum
dish. Dry for an hour in an air oven at about 150° and weigh. Then constant, the difference is the amount of total solids. To determine the organic matter, hold the dish in the small naked flame of a Bunsen burner, being careful not to heat the contents too high as to drive off any CO₂, cool and weigh. Separate the soluble from the insoluble by treating the residue with hot water, using 25 cc lots, and filtering on a hardened filter paper, leaving as much of the residue as possible in the dish. The filtrate contains the alkali, MgSO₄, MgCl₂, part of Ca SO₄, Ca Cl₂. While in the dish is the insoluble calcium carbonate, calcium sulphate, magnesium carbonate, iron and alumina oxides and silica. Wash what remains on the filter back into the dish, evaporate to dryness, dry for an hour at 150° and weigh. This gives the insoluble residue and the difference the soluble part. This is done
merely to check the final results. Treat the contents of the dish with dilute HCl, evaporate to dryness and boil for half an hour at 120°. Treat with hot water, filter and weigh the insoluble part as silica. To the filtrate add a drop of HNO₃ to oxidize any ferrous salts to ferric, neutralize with excess of NH₄OH which precipitates the iron and alumina as hydroxide. Filter while hot, burn and weigh as the oxides. The balance of the filtrate still contains the calcium and magnesia. Add NH₄Cl and NH₄OH, to keep magnesia in solution, and precipitate the calcium with NH₄C₂O₄. Filter and burn to the oxide. To the cold filtrate add NH₄PO₄ and allow to stand overnight, to precipitate magnesia. The sum total of these substances when calculated to the composition in which they are found in the water should agree with weight of FeCl₃. Boil the original filtrate and add a solution of
Ba(OH)₂, keeping the beaker covered with a watch glass, to prevent the Ba(OH)₂ from forming a carbonate with the CO₂ from the air, filter that in a covered funnel. The precipitate contains BaSO₄, BaCl₂ and Mg(OH)₂. Wash into a beaker and digest with HCl, to dissolve everything but the BaSO₄, filter and weigh. To the filtrate add H₂SO₄ to get rid of excess of Barium, filter. The filtrate may be evaporated to dryness and weighed direct as MgSO₄ or may be treated with NaH₂PO₄ and magnesium estimated as Mg₃(PO₄)₂. The filtrate from the first precipitation contains Ba(OH)₂, CaCl₂ and the alkalies. Add H₂SO₄ to throw out Barium, filter and to filtrate add NH₄OH until neutral then (NH₄)₂CO₃ to throw out the CaCO₃. Filter and burn as CaO. Evaporate this filtrate to dryness, heat, to drive off any ammonia salts and weigh the residue as the alkalies as sulphate.

An outline of this method is given on next page and following is the analysis of some feed waters with a brief discussion of their relative qualities as feed waters.
<table>
<thead>
<tr>
<th>Water</th>
<th>Total Solids</th>
<th>Active SiO₂</th>
<th>Fe₂O₃</th>
<th>CaCO₃</th>
<th>MgCO₃</th>
<th>CaSO₄</th>
<th>MgSO₄</th>
<th>Alk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emburse M.</td>
<td>21.6</td>
<td>Alk.</td>
<td>0.19</td>
<td>9.04</td>
<td>1.54</td>
<td>2.04</td>
<td>1.21</td>
<td>1.02</td>
</tr>
<tr>
<td>Mississippi R.</td>
<td>18.57</td>
<td>Alk.</td>
<td>0.31</td>
<td>4.01</td>
<td>6.1</td>
<td>3.16</td>
<td>3.28</td>
<td>1.85</td>
</tr>
<tr>
<td>Minnkow (W)</td>
<td>185.8</td>
<td>Alk.</td>
<td>1.77</td>
<td>22.96</td>
<td>7.01</td>
<td>31.81</td>
<td>27.59</td>
<td>94.4</td>
</tr>
<tr>
<td>Minnkow (E)</td>
<td>77.49</td>
<td>Alk.</td>
<td>1.4</td>
<td>39.12</td>
<td>23.92</td>
<td>8.62</td>
<td>4.12</td>
<td>1.03</td>
</tr>
<tr>
<td>Moundo (1)</td>
<td>23.32</td>
<td>Acid</td>
<td>1.16</td>
<td>7.14</td>
<td>5.24</td>
<td></td>
<td></td>
<td>9.72</td>
</tr>
<tr>
<td>Moundo (2)</td>
<td>30.54</td>
<td>Acid</td>
<td>1.42</td>
<td>6.9</td>
<td>6.42</td>
<td></td>
<td></td>
<td>15.15</td>
</tr>
<tr>
<td>Winona</td>
<td>77.54</td>
<td>Alk.</td>
<td>4.41</td>
<td>10.01</td>
<td>4.38</td>
<td>2.54</td>
<td>11.32</td>
<td>48.37</td>
</tr>
</tbody>
</table>

These waters are all used as feed waters in boilers, most of them being used by the I.C. Ry in their locomotives. Waters No. 5 and 6 come from Moundo-Polacki County and is used in a stationary engine boiler. It has a bad corrosive action on the boiler and is so acid that if allowed to stand in a tin bucket it soon eats holes in the sides and bottom. It does not carry very much salt in solution so we rank it not for its corrosive
action it would be a good feed water as it is not very
classified as poor. The water has an acid reaction when
tested with litmus paper and in the analysis the solu-
ble part showed a strong test with Ba(OH)₂ showing free
sulphuric acid. This then is the corrosive agent and
to overcome it sodium carbonate should be used.
The other waters analyzed were classified according
to their incrusting capacities, a water carrying 15 to 50
was called a good water, from 15 to 25 grains fair, 25 to 35
a poor and over 35 grains bad. Waters 1 and 2 were found
to be fair feed waters and an engineer using them would
not be troubled with a heavy scale forming in the
boiler. No trouble from corrosion would be experienced.
Water no 4 was found to be a bad water as it was found
to carry 54 grains to the gallon of incrusting material.
Some method could be devised to keep the salts in solu-
tion it would be serviceable with frequent blowing out.
Water No 3 carrying 90 grains of incrusting material is away beyond induction and water should not be used for field purposes. Water No 1 is a fair water. Its total solids are high but they are mostly soluble salts and can be gotten rid of by blowing and frequent cleaning the boiler. Its incrusting salts are about 22 grains per gallon.

That corrosion is a mighty evil and offers a wide field for investigation there is not a doubt. When one thinks of the countless number of boilers which are in use and of the vast number of these which are destroyed by this agent and what an understanding, such that would make possible a discovery of a corrective, would be worth it is to be wondered at that it is not more thoroughly investigated. As the knowledge of the subject now stands the causes of corrosion in general seem to be pretty
well known but when it comes to saying definitely just what it is which causes the trouble in a single water which is known to be corrosive it is a very difficult thing. The surest way of telling this is from a chemical standpoint—neither the engineer or the steam user can say what it is until he calls a Chemist to his aid with an analysis.

Some of the references used in this work were—

**Causes of Corrosion—Engineer May 1878 p 431**

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**Causes of Corrosion—June 1878 p 495**

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