

ELECTRO-CHEMISTRY APPLIED TO BOILERS FOR CORROSION PREVENTION.

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To the research scientist who is experimenting in pure science to more thoroughly understand the basic causes for certain phenomena, mankind is greatly indebted. However, in most cases, before his results can be successfully used, the scientist in the field is forced to do further experimental work. For example in 1903 Dr. W. R. Whitney of Massachusetts Institute of Technology (*J. Am. Chem. Soc.* Vol. 25, 1903) presented his hypothesis for the dissociation of iron but we are just now beginning to make practical application of his theory in the industrial world.

Dr. Whitney pointed out that "Practically the only factor which limits the life of the iron is oxidation under which are included all the chemical processes whereby the iron is corroded, eaten away or rusted. In undergoing this change, the iron always passes through or into solution, and as we have no evidence of iron going into aqueous solution except in the form of ions, we have really to consider the effects of condition upon the potential differences between iron and its surroundings. The whole subject of corrosion is simply a function of E. M. F. and resistance to circuit. The Velocity with which the process proceeds will depend on the temperature and on the hydrogen ion concentration of the water."

Since that time many research men have been investigating this problem with varying results. In most cases they have agreed upon the theory that the dissociation of iron is an electrochemical phenomenon. Many articles have been presented and books written on this subject, examination of which will show many erroneous and varied conclusions having been arrived at by the authors, and are responsible for considerable dissention in the research field.

In 1923 Dr. R. E. Wilson (*Ind. and Eng. Chem.* Feb. 1923) presented a paper before American Chemical Society, in which he discussed the various factors that affect the rate of dissociation of the iron and it is his opinion that improper recognition of these factors are principally responsible for the in-

correct conclusions. The factors that affect the dissolving of the iron, as given by Dr. Wilson are "Solution pressure of the metallic iron, hydrogen overvoltage, hydrogen ion concentration, velocity of flow, temperature, density, catalytic agents, oxygen, character of protective films, current density, passivating agents, metallic salts in solution, etc."

With incorrect consideration given to the effect these factors have upon the rapidity of the solution of iron, one can readily understand the possibility of an investigator arriving at improper or unsatisfactory conclusions.

The principal reaction in the corrosion of iron, as first pointed out by Dr. Whitney, is expressed in the simple equation



Since this is the basic reaction, any method of prevention must counteract it.

When the ionic hydrogen gives up its electrical charge to the iron, a galvanic couple is produced and the gaseous hydrogen plates out at the opposite or negative pole. As the hydrogen film accumulates and if it is not disturbed, the electrical potential of this pole will be raised to that where the iron went into solution (the anode) and the reaction ceases.

It has been found that certain metals, such as arsenic and tin, have the peculiar property of increasing the polarizing effects of the hydrogen film as it plates out upon the cathodic area, thus causing the more rapid establishment of the equilibrium between the cathode and anode. The removal of the hydrogen, or deplORIZATION as it is termed, caused principally by oxidation, will permit the plating out of more hydrogen, thus allowing iron to go into solution until the potential of the cathode area is again raised to that of the anode. The elimination of oxidizing agents or decrease in the hydrogen ion concentration of the liquid, has a direct effect upon the rapidity of solution of the iron.

These galvanic couples or small localized batteries are set up by difference in solution pressure along the metal surface resulting from heterogeneity, hydrogen ion concentration of the electrolyte and many other factors previously mentioned.

There is another distinct type of current flow known as electrolysis currents whereby the electrical energy is produced by some exterior source and passes from the iron to the electrolyte

causing the iron to go into solution in direct ratio to the E. M. F. At the same time hydrogen plates out on the negative pole where the current leaves the electrolyte and produces its polarizing effect the same as in the galvanic couple.

It is the specific purpose of the Electro-Chemical Polarization Process for the prevention of corrosion to maintain a plating of arsenic on the cathodic areas in a liquid bath that are to be protected, by using a counter electro-motive force taken from an external source and the secondary function of the imposed current is to maintain a polarizing film of hydrogen on the arsenic surface, in excess of that removed through oxidation or by mechanical or other means. The arsenic and hydrogen plating will eliminate any local galvanic currents and the E. M. F. of the imposed current is greater than the E. M. F. of any electrolysis currents reaching the liquid container.

This system of corrosion prevention has gone through the experimental stages in the railroad field, the first test installations being made in two Chicago & Alton Railroad Company's locomotive boilers at Bloomington, Ill., in 1924 under the direction of Mr. L. O. Gunderson, Chemical Engineer for the road.

Before explaining the mechanism of the process, I wish to give a few pertinent facts covering the losses to the railroads through corrosion of boilers. According to records the boiler corrosion problem is about as old as the boiler itself, but within the last few years it has become increasingly serious. One railroad official recently wrote, "If you desire to render a real service to the railroads of this country find out and tell them how to stop pitting and corrosion of locomotive boiler flues, shells and fireboxes, and all mechanical men will forevermore call you blessed."

There are approximately 72,600 locomotives operated on the American railways and the losses due to flues, boiler sheets and staybolts being made unserviceable through pitting and grooving are conservatively estimated to reach \$12,000,000 annually.

There are six or more technical committees attempting to analyze the causes for corrosion and trying to find a means of prevention. Many specially prepared steels, irons and alloys such as copper content steel, nickel steel, Molybdenum steel, leadized steel and several others have been experimented with but today we are unaware of a metal suitable for the severe boiler stresses, which will in all cases withstand the corrosive action of a boiler water.

Attempts to inhibit corrosion by treating the boiler feed water with various chemicals such as soda ash, lime and soda ash, zeolite, arsenic, mercury and chromium have produced erratic results. Deaerating or de-activating apparatus that will remove 100% of the dissolved oxygen has not yet been developed for locomotive application and, due to the exactness of control required to obtain gas free water, it is rather doubtful as to whether such equipment is practical for locomotive service.

In studying boiler corrosion you will find the majority of destruction due to the local or galvanic couples on the metal surface. Because of its localized nature this type of corrosion known as "pitting" is very severe for the metal is soon penetrated and made unserviceable whereas the surrounding surface is in perfect condition. The other type of corrosion known as grooving appears to be due to or accelerated by electrolysis currents caused by thermal differences in the boiler or stray currents from various exterior sources.

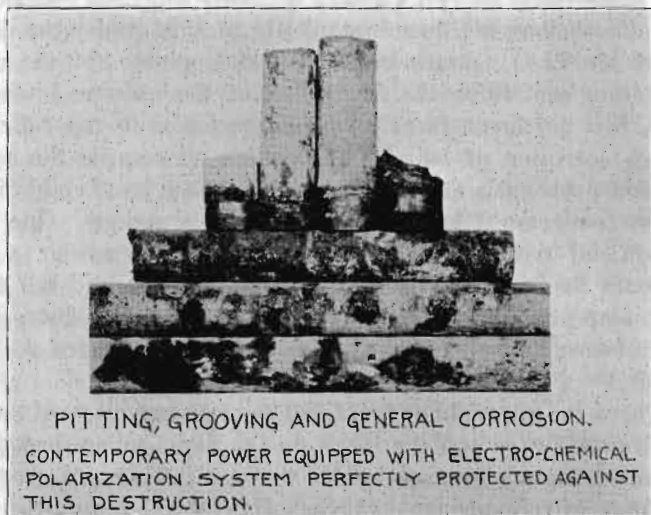


FIG. 1.

Figure 1 shows flues attacked by the various types of corrosion just mentioned.

The city water at Bloomington, Illinois, the poor quality of which you are all familiar with, produces destruction of the boiler metal such as shown in Figure 1 in as short a period as 9 months after flue application. This causes a damage to the

boiler interior amounting to from \$500 to \$1500 annually. The original test installations on the Chicago & Alton gave immediate protection against the corrosion damage and only slight changes have been made up to the present time.

The operation of the system is best described by referring to Figure 2.

The positive pole of a turbo-generator is connected to resistor coils and fuses located in a metal box on the interior of the locomotive cab and from this box a connecting wire runs to two electrodes protruding through the boiler shell at points diagonally opposite each other. These electrodes are securely connected to two thoroughly insulated and rigidly clamped iron anodes, both of which are at all times below the surface of the boiler water. The negative pole of the generator is grounded to the boiler shell, thus causing the direct current to flow through the resistors to the anodes and from the anodes through the boiler water to the water-immersed portions of the boiler and back to the negative pole of the generator thus completing the electric circuit. This causes the metallic portions in the boiler to function as the cathode area of the electric circuit and as long as the E. M. F. of the imposed current is greater than the E. M. F. of any stray or electrolysis currents the cathode area will be protected from the deleterious effects of such currents.

There are from 3000 to 5000 sq. ft. of exposed metal surface on the boiler interior, consequently there is greater possibility of galvanic couples being set up due to difference of potential caused by speck impurities such as slag, carbon, etc. Since the counter-current does not prevent these local couples it is necessary to resort to the use of some metal such as arsenic that has a high discharge potential when hydrogen is plated upon it so that the potential of the cathode areas will soon be raised to that of the anode when conditions are satisfactory to produce the potential differences. Several research men have brought out the fact that a metallic body acting as a cathode in an electric circuit does not stop local galvanic couples from functioning. This can very easily be demonstrated by beaker tests.

Mr. F. N. Speller in his researches has found this condition to exist and in his book "Corrosion, Causes and Prevention" 1926, page 433, says, "Local electro-chemical action will continue on a surface which is within the protective influence of an externally applied current. It is therefore, unsafe to rely too much on electrolytic protection without taking other precautions."

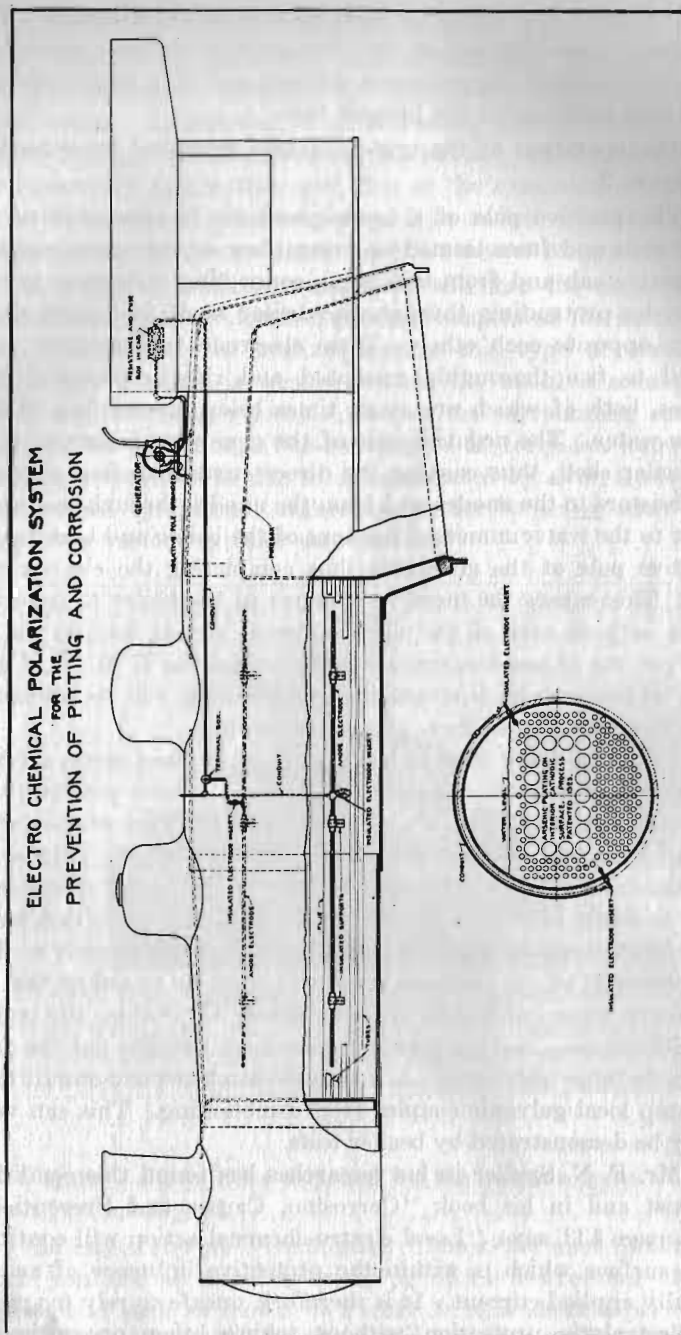


FIG. 2.

In the Electro-Chemical Polarization system of protection the extra precaution was taken with the use of arsenic. The arsenic plating is maintained by adding from 2 to 4 pounds of a soluble arsenic salt to the boiler water or electrolyte each month. Since arsenic plates out on iron by immersion it eliminates the necessity for definite current density to get the plating, and from the practical point of view this as a most desirable condition.

The imposed current is used during period the locomotive is in service to maintain the arsenic plating and on top of this a plating of monatomic hydrogen. This produces a high discharge potential on the arsenic surface which tends to establish a potential equilibrium. Incidentally a surplus of hydrogen is kept on the cathodic surface to combine chemically with oxidizing agents entering with the fresh boiler feed water. The direct current used amounts to about 2 volts and 2 to 3 amperes to each electrode giving a current density of around two milliamperes per square foot of protected surface.

The cost of current will vary from $\frac{1}{2}c$ to $2c$ per hour. For an average locomotive the annual cost of protection by this process will run from \$18.00 to \$36.00, which includes the cost of the arsenic compound. You will no doubt agree that this is a very low cost for protection and can readily understand why it is being applied to all locomotives on the Chicago & Alton Railroad.

Figure 3 shows pieces of three flues removed from C. & A.

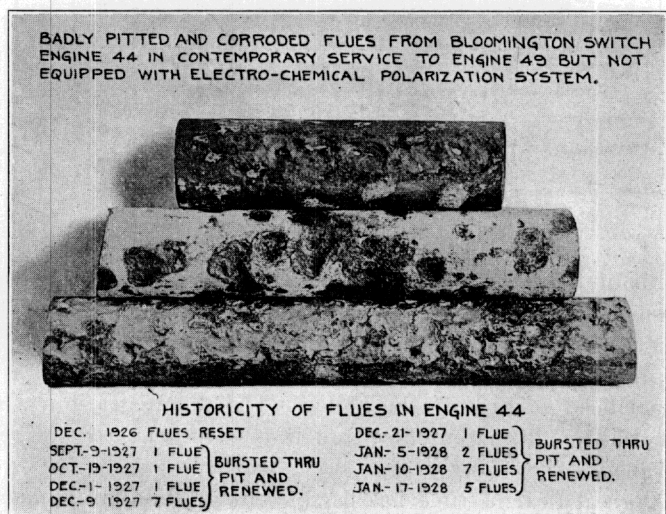


FIG. 3.

switch engine 44 at three different times. This engine is not equipped with the electrodes and you can see the deleterious effects the Bloomington, Ill., city water has when used in unprotected locomotive boilers.

In Figure 4 a group of flues removed from C. & A. switch engine 49 is shown to illustrate the complete absence of corrosion on the flues after installing the protective systems as compared with the severely corroded flues removed just prior to making the installation. This engine has been in contemporary service with engine 44 (Fig. 3) using the same water, etc., the only difference being the use of the counter current and arsenic in the 49. This surely is conclusive proof that the system does work and and due to its simplicity and low cost is a very practical installation.

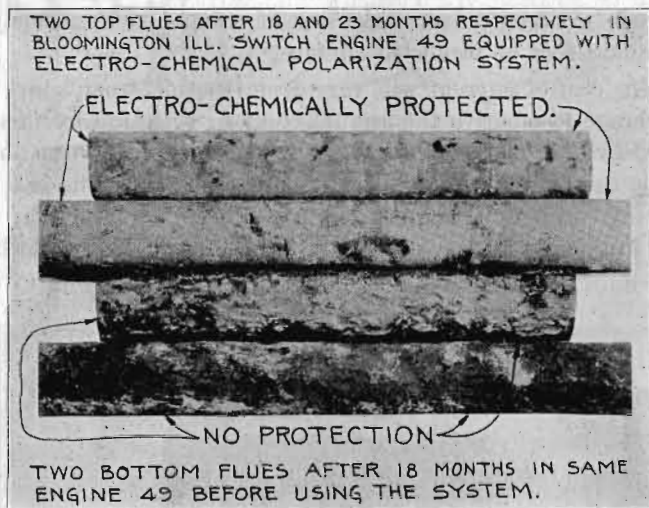


FIG. 4.

About 35 engines have now been equipped with this anti-corrosion scheme and in every instance the boilers have been kept free from pitting, grooving and general corrosion. The iron pipe anodes on the boiler interior disintegrate and in a way are sacrificed to protect the boiler. The disintegration is slow due to the small current flow and it is only necessary to renew them about every four years.

A great deal of time has been spent in the development of apparatus that has permitted the practical application of our

knowledge of the electro-chemical theory for the dissociation iron. However, the actual operating results have been gratifying and it appears as though the industrial worlds corrosion loses can be greatly reduced by using the Polarization Process or some modification of it.

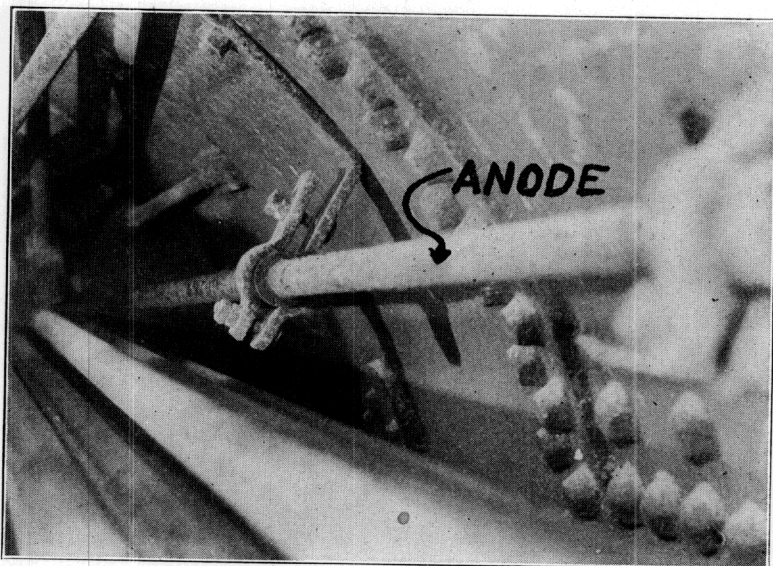


FIG. 5.