It will be observed that the results all agree closely whether the silver was separated or not. and that hydrogen peroxide (as was to be expected) may be used as well as the sodium arsenite. The end-point in all these titrations is not as sharp as might be desired but I think it is sharper if the silver is not precipitated. If the silver is not precipitated, the titration must be done quickly, as the persulphate and silver nitrate in solution react to reproduce the color, if allowed to stand.

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THE CORROSION OF IRON.

BY W. R. WHITNEY.

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It is my object to add to the literature on this subject, the results of some observations of the action of water or steam under various conditions upon ordinary iron, coupled with some consideration of the principles involved.

Owing to the great use made of iron and steel, and the dependence placed upon them, it is not surprising to find that a great deal has been written upon the factors influencing their length of life when used for various purposes.

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 a state of solution, and, as we have no evidence of iron going into aqueous solution except in the form of ions (probably electrically charged atoms), we have really to consider the effects of conditions upon the potential-difference between iron and its surroundings. The whole subject of corrosion of iron is therefore an electrochemical one, and the rate of corrosion is simply a function of electromotive force and resistance of circuit. If now we apply Nernst's conception of the source of electromotive force between a metal and a solution, we must conclude from the measured potential-difference that iron in contact with an aqueous solution tends to dissolve, ionize, or oxidize with a force expressed as equivalent to about 10,000 atmospheres' pressure at ordinary temperature.

In other words, iron should tend to dissolve in any aqueous solution until the concentration of the electrically charged iron ions reaches such a concentration that the osmotic pressure is equal to the above value. This means that the saturated iron solution must be at least 450-fold normal, which is a concentration not practically obtainable. Thus far, the theory requires that iron should *tend* to oxidize in any aqueous solution. Whether it will do so or not depends on other conditions. Something may here be gained by a study of analogies. The dissolving zinc electrode of the Daniell or gravity battery, although possessing an enormous electrolytic solution-pressure, does not dissolve when the electric circuit is broken, but begins oxidizing immediately when connected through any external resistance to the copper pole. It is not enough then for oxidation or solution of the metal, that it have a *tendency* to dissolve; it must be in metallic connection with some other material capable of acting as an electrode, and this second electrode, if a positive element, must have a lower electrolytic solution pressure than the iron. Iron in contact with zinc and an aqueous solution will therefore not dissolve; but if copper replace the zinc, the iron will dissolve, the velocity of solution in these cases being determined by the resistance of the complete electric circuit. These two cases are often met with in practice. In marine boilers, zinc plates are sometimes suspended from the boiler tubes in the water, that they may be attacked instead of the iron. On the other hand, scrap iron is used very commonly to recover copper from solution in mine waters and other copper liquors, in which case the iron rapidly dissolves.

Hydrogen acts as a metal and is electrolytically classified in the group with copper when compared with iron and zinc. That is, if a cell were made up on the Daniell model, iron being used instead of zinc, and hydrogen in place of copper, the cell would generate a current when the iron and hydrogen electrodes were connected. Iron would then dissolve with a velocity dependent on the total resistance of the circuit. So also, and for the same reason, iron when placed in a solution containing hydrogen ions will dissolve as the hydrogen precipitates, just exactly as when placed in the copper salt solution. That iron does oxidize or dissolve in all solutions containing appreciable quantities of hydrogen ions is well known. This electrochemical relationship between iron and hydrogen is the primal cause of rusting.

This introduces at once an important point in connection with the subject. Pure water is believed to contain hydrogen ions to the extent of approximately 1 gram for each 10,000,000 liters and should consequently act qualitatively like any other hydrogen-ion solution in oxidizing iron. It is to this extent an acid. It would evidently be quantitatively a very feeble solvent on this basis, if for no other reason than the high electrical resistance of the solution. This is simply another way of saying that in such a dilute solution the hydrogen ions can come into contact with the iron only exceedingly slowly, this contact being necessary for the action. Whether the iron on oxidation or on dissolving remains practically *in situ* as an insoluble compound, oxide, hydroxide, carbonate, basic salt, etc., or is removed as rapidly as it is oxidized, depends on the nature of the surrounding medium. If it be simply in vapor or in moist air, removal of the iron is out of the question. If it be in contact with aqueous solutions, the removal of the iron will be determined by the nature of the negative ions in the solution. If insoluble compounds can form at the point of corrosion, the iron will not be removed. This is illustrated by the common precipitation of oxide or rusting due to the oxygen dissolved in the water; if no such insoluble compounds are formed, the iron will be eaten away, the surface remaining bright. Both of these processes are very common in practical experience.

There is no doubt that iron, even at ordinary temperatures, reacts with pure water, in accord with this conception. The experiments on this point, carried out by Deville[1] at high temperatures only, showed a balanced condition at various temperatures for the reaction

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

He found experimentally that water vapor in contact with iron must produce a certain concentration of hydrogen gas to be in equilibrium; in other words, if the hydrogen was continually removed, the iron could continually oxidize. Within the range of temperature employed (200° to 1000° C.), he found that the pressure of the hydrogen produced by the action between iron and water increased as the pressure of the water vapor was increased. As the temperature rose, the hydrogen concentration (or pressure) at equilibrium diminished; in other words, the lower the temperature in his experiments, the greater the tendency for oxidation of

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[1] *Ann. Chem.* (Liebig), **157**, 76 (1870).

the iron. According to these results, we should expect water to act on iron to generate hydrogen even at ordinary temperatures, and it is a well-known fact that very finely divided iron such as is obtained by dry reduction of iron salts, reacts with pure water and generates hydrogen.

This fact, that pure water causes solution of iron, is in accord with other experimentally discovered facts. Mr. G. O. Adams, in connection with a thesis presented to this institute in 1900, made analyses of various samples of gases collected from radiators in different houses where the hot-water gravity heating system is used, and where different water supplies are concerned, and always found a large quantity of hydrogen gas. In most cases, on opening the air-cock of the radiators the gas could be lighted with a match. A number of such mixtures were analyzed. These varied in composition, but were mainly mixtures of nitrogen and hydrogen with usually no oxygen. The hydrogen-content varied from 44 to 78 per cent. by volume. Measurable quantities of carbon dioxide or of hydrocarbons were not usually present.

It is very generally accepted by authorities on the corrosion of iron that the presence of carbonic acid is necessary; but, as water itself must be considered as not greatly different in hydrogen-ion-concentration from a carbonic acid solution in contact with air, it seems *a priori* probable that this accepted idea is incorrect.

Assuming the laws of Henry and Dalton to apply to the solubility of carbonic acid gas in water, also that the solubility of the pure gas under ordinary pressure is one volume for one volume of water (which is correct at 15° C.) and, finally that the normal content of carbonic acid in the atmosphere is 2 parts in 10,000 by volume, we should expect water in equilibrium with air containing this concentration of carbonic acid to contain 0.0002 volume carbon dioxide per volume of water. This corresponds to a concentration of the carbonic acid equal to 0.00001 mol per liter or 0.00002 normal. From the dissociation constant $(3040 \times 10)^{-10}$ determined by Walker,[1] and to which my attention was called by Professor Noyes, it follows that the first hydrogen of the acid is 16 per cent. dissociated at this concentration. From this it follows that 10,000,000 liters of water containing carbonic acid in equilibrium with ordinary air at 15° contains 16 grams of hydrogen ions, or only 16 times as many as perfectly pure water con-

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[1] *Ztschr. phys. Chem.*, **32**, 137.

tains. At the boiling temperature the carbon dioxide dissolved would probably yield a concentration of hydrogen ions even less than that in pure water, for not only is the solubility of the gas greatly diminished, but the dissociation of water is greatly increased by rise of temperature. Moreover, the distilling water would rapidly reduce the concentration of any carbonic acid capable of dissolving in water at 100° C.

The following experiment bearing upon this point is one which may have been frequently tried by others, but is worthy of note. To learn whether carbonic acid was necessary to iron-rusting, a clean bottle was steamed out for a time to remove soluble alkali from the glass and was then filled with pure distilled water which was kept boiling by passing steam through it for fifteen minutes. While still boiling, a bright piece of iron was placed in the bottle. A stopper (in some cases rubber and in others cork) carrying a tube open in a capillary several inches above the stopper, was inserted into the bottle and firmly fastened in place, the water being kept boiling. Finally, the glass capillary was heated hot by means of a blowpipe and sealed by squeezing the walls together. The bottle was then allowed to cool to a temperature of about 80° C., and the neck of the bottle was finally covered with paraffin to prevent leaking. It was thought that in this way the oxygen, carbonic acid and other gases in the water were completely removed. Bottles containing iron and sealed in this manner have stood without any visible change for weeks. In some cases a little air was subsequently admitted to bottles which had stood in this way with the iron apparently unaffected, and within a few minutes the water became cloudy and assumed a yellow color. Ordinary rust rapidly deposited upon the glass and in spots upon the metal. In fifteen or twenty minutes the production of rust throughout the bottle was perfectly evident. It seemed plain from the rapidity of formation of oxide and its precipitation on the glass, that the iron had dissolved in the water before the addition of the air, and that the latter simply permitted the formation of the insoluble oxide.

Mr. J. A. Collins, in connection with his thesis of 1898, performed a similar experiment which shows that the iron is dissolved in the water and that its appearance as rust is a secondary phenomenon due to the action of oxygen on the solution. A cleaned iron pipe 0.5 inch by 15 inches, sealed at one end and having a screw cap to fit the other, was filled with boiling distilled water, and the boiling continued by heating the pipe until half the water had boiled away. While still rapidly distilling, the cap was screwed on tightly and the tube heated to about 125° C. for an hour. On cooling and removing the water from the pipe, it was found to be perfectly clear and colorless, but, on exposure to air in a glass vessel, it rapidly precipitated rust. The pure water had dissolved iron in some form from the clean metallic surface, and this had remained in solution until precipitated by the oxygen of the air. In experiments with air-free water in contact with iron, in glass bottles and flasks, Mr. Collins let into the flasks containing only the pure water together with its vapor and the bright iron, air which had been freed from carbonic acid by being exposed to the action of a barium hydroxide solution in a closed bottle for twelve hours, the bottle being repeatedly shaken to hasten the absorption. In case of this treated air, the production of rust in the flasks was evidently as rapid as with ordinary air.

A similar experiment with purified oxygen gave the same result. One is forced to conclude from such results that if the rusting is due in any way to carbonic acid it is rapidly brought about by such a quantity of this gas as is left in air or oxygen after treatment with a barium hydroxide solution; in other words, by an inappreciably small quantity. As this acid could owe its activity solely to its hydrogen ions, because of the fact that the carbonate ion has no rusting or dissolving action on the iron, it is interesting to note that in the case of recently boiled water, the hydrogen-ion content due to carbonic acid may well be as low as the hydrogen ion content due to the dissociation of pure water.

Iron dissolves in pure water qualitatively just as in a solution of copper sulphate, hydrogen being deposited in place of copper. The velocity with which this process proceeds will depend on the temperature and on the hydrogen-ion-concentration in the water. When this concentration is so great that the potential-difference exceeds a certain value, the hydrogen will be evolved as gas, separating from the liquid at the surface of the iron as bubbles. This potential value depends on the state of the surface, so that it is usually higher than the theoretical value for polarization by hydrogen where the gas is in equilibrium with the solution. Below this value, the hydrogen, which is nevertheless being deposited upon the iron, but at a concentration below that corresponding to atmospheric pressure, slowly dissolves in the water, forming an ordinary solution of it, and escapes by diffusion. Its solubility will presumably be proportional to its pressure even though this is below atmospheric pressure.

It was shown by Faraday that an electromotive force below that necessary for visible electrolysis of a solution, was still capable of producing a continuous though feeble current which was then attributed to metallic conduction of the solution. Helmholtz, by his studies of polarization, showed this to be due to actual electrolysis proceeding as above stated. This polarization phenomenon should greatly limit the velocity of solution of the iron, even if no other complicating effect due to the production of an insoluble compound, an oxide or hydroxide, in case air be present. This is usually the case in practice. The production of a compact adherent coating of oxide on the surface of the iron generally retards the corrosive action. Especially is this true at temperatures of steam where the magnetic oxide is formed. This oxide always forms as an adherent solid coating on the iron and seems to be interrupted only by cracks caused by its unequal coefficient of expansion compared with the iron. The red oxide or rust is always flocculent and spongy and, besides not protecting the iron, actually seems to increase the velocity of corrosion in its vicinity. It is common to attribute to the red oxide or rust a catalyzing effect on the corrosion of iron.

If the primary rate of corrosion of iron independent of subsequent formation of insoluble substances is simply dependent upon the concentration of the hydrogen ions of the water, anything which reduced this concentration should also reduce the corrosion. The principles of equilibrium of chemical reactions when applied to the dissociation reaction of water should show how, practically, to accomplish this reduction. In this case the product of the concentration of the hydrogen and hydroxyl ions must remain constant in any aqueous solution, for the principle involved declares this product to bear a constant relation to the concentration of undissociated water molecules and this is itself evidently constant in aqueous solutions. From various measurements we are led to believe that the product of the concentrations of the hydrogen and hydroxyl ions is approximately 10^{-14}. In pure water the concentration of each of the two water ions, hydrogen and hydroxyl, is therefore evidently 10^{-7}. If additional hydroxyl ions are added to the water in any way, the concentration of the hydrogen ions must correspondingly diminish, so that the product may remain constant. Thus the corroding power of the water, if due to the hydrogen ions, would be reduced. This reduction of the hydrogen ion concentration may be brought about by the addition of any alkali to the water. That the corrosion is thereby diminished is a well-known fact and one that already receives many practical applications. Iron and steel tools in process of manufacture, between the roughly ground state and the final polished condition, are often kept under water saturated with lime. This prevents the rusting which would quickly take place if they were left in moist air. The effect of the lime must be attributed solely to the hydroxyl ions which in turn reduce the concentration of the hydrogen ions of the water. Neutral salts of calcium do not exert this effect and hence it can not be attributed to the calcium compound nor to the calcium ion. Other soluble alkalies do it equally well and these contain, in common, only the hydroxyl ion.

One of the most common components of the many boiler-compounds which are used to prevent pitting and corrosion in boilers, where the water used is very pure and consequently does not form a protecting layer of scale upon the iron, is some form of alkali. The alkalies usually used are caustic, slaked lime, carbonates, borates, aluminates, etc., which are in every case compounds readily undergoing either dissociation or hydrolysis and producing hydroxyl ions thereby. Thus again the concentration of the hydrogen ions is reduced. Conversely, the concentration of hydrogen ions would be increased by the addition of any salt whose hydrolysis would produce hydrogen ions, and for this reason magnesium chloride, ammonium chloride, and similar compounds may increase the corrosive effect of waters containing them.

Free alkali added to a boiler water not only greatly reduces the concentration of the hydrogen ions, from whatever source, thus diminishing the electrochemical reaction of interchange between hydrogen and iron in the boiler itself, but also produces another valuable effect. If a steam or hot-water heating system is fed with a water which is not naturally alkaline, a part at least of the carbonic acid, which it always contains, will be driven from the water on boiling and pass to the cooler portion of the system to be redissolved in condensing water. Thus the return pipes of the system will be subjected to the action of this acid or hydrogen-ion solution. No protecting scale of salts from the water being produced in these return pipes, such as is almost always produced in the boiler itself, the corrosive action will be most marked in the return pipes, and especially where the pipes are exposed to the action of continuous supplies of the water in motion. This will prevent the establishment of equilibria and the iron will be continually removed. It ought also to be removed according to the previous discussion, though more slowly, even if no carbonic acid or other acid were present, because of the hydrogen ions of the pure water. This reaction could again be reduced by the presence of volatile alkali in the condensed water, but in practice this latter is usually a negligible effect compared with the effect of volatile acid.

I wish now to show that the effect of the carbonic acid is actually a cyclic one, the same molecule of acid doing unlimited corrosive work, and that the very harmful corrosion of return pipes in many heating systems may be directly attributed to this usually inconsiderable and unnoticed ingredient of the water. To make this point clear, let us imagine a steam-heating system made up of a boiler, with steam pipes leading to various heating stacks and radiators from which return pipes bring the condensed steam back to the boiler below the water-level. For simplicity, we assume that the plant is run without the addition of water after the boiler has been originally charged. In other words, no steam is blown out into the air and the plant is not used, as some are, to incidentally supply hot water for foreign uses, which thus requires a continual water feed. Our closed system usually contains, when in actual running condition, a number of dead-ends where gases have accumulated and where the pipes are cold. This may be observed in many radiators of common type. Into this colder portion of the system, the gases such as oxygen, nitrogen and carbonic acid, which were originally in the feed water, will collect. Here they will dissolve in the condensed water which is to return to the boiler, the carbonic acid being especially soluble. The carbonic acid or its active hydrogen will cause the solution of iron from the return pipes and this iron will be carried back towards the boiler as bicarbonate of iron, being held in solution just as is calcium carbonate in water containing carbonic acid. This may be represented by the reaction

$$Fe + 2CO_2 + 2H_2O = H_2Fe(CO_3)_2 + H_2.$$

In the case of the bicarbonate of calcium solution, it is well known that boiling it decomposes the salt and liberates half of the carbonic acid, leaving a precipitate of calcium carbonate. In case of the soluble bicarbonate of iron, as will be shown later, the decomposition of the compound by heat, liberates all of the carbonic acid instead of half of it and produces the insoluble oxide or hydroxide of iron. Whether this decomposition of the soluble iron salt takes place in the boiler after the solution has returned to it, or in the return pipe where the proximity to the boiler produces a sufficiently high temperature, is of no immediate importance. In either case, the carbonic acid is all set free and must immediately return with steam to the cooler parts of the system; there again it will dissolve in the condensate, again render soluble some iron and carry it towards the boiler and so forth. In each cycle of this kind hydrogen will be set free which will remain in the cooler parts of the system, as it is but slightly soluble in water. It seems necessary, therefore, that in common practice a very small quantity of carbonic acid must often cause an unlimited amount of corrosion, without in any way losing its power to continue the process. The process of corrosion of the iron in this case will amount *in toto* to the union of iron with the oxygen of water and liberation of hydrogen, the carbonic acid acting merely as a catalyzer, where the mechanics of its action is apparent. This peculiar condition of affairs has been observed by us in certain large heating systems where we have found, first the carbonic acid of the feed water; secondly, much carbonic acid mixed with hydrogen, nitrogen, and oxygen in dead-ends or cold parts of the system; thirdly, water in the return pipes, where very rapid corrosion of the piping was taking place, in which much dissolved bicarbonate of iron was found; and, finally, much precipitated oxide of iron in the boiler and hottest parts of the return pipes.

It has been possible also to reproduce these phenomena in the laboratory in various ways and in some cases in glass apparatus where the complete cycle becomes practically visible. In connection with his thesis, Mr. C. L. Wright arranged an apparatus of which a sketch·is shown. Pure distilled water was boiled in the flask A, and various quantities of air and carbonic acid mixtures were enclosed in the system which was kept nearly at atmospheric

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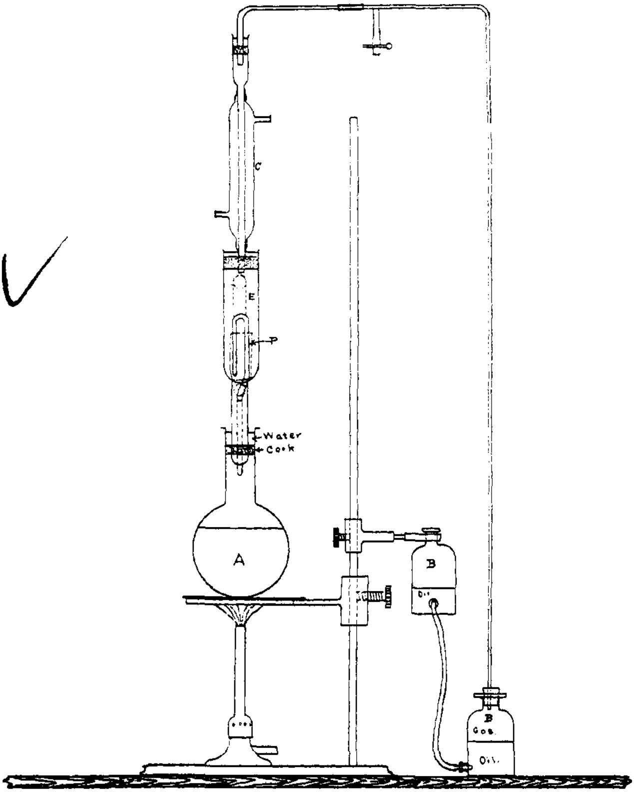

pressure by the liquid seal made by the bottles B connected with the condenser C. The steam condensed and took up a little of the carbonic acid; this solution came into contact with a piece of cleaned iron pipe, P, from which the outer layer had been removed in the lathe. This iron was supported in an extractor, E, between the condenser and the boiler in such a way that it was alternately covered with the water and uncovered by the intermittent siphon action of the extractor.

In the first few experiments a precipitate was soon formed in the boiler which was not analyzed, but which was evidently a mixture of hydroxide of iron and silica from the glass. Subsequent experiments in the same apparatus differed in result from the first one and showed that, in the absence of free oxygen, the boiler water simply became black and opaque but showed little or no precipitate. The glass tube leading from the condenser to the boiler was also quickly coated with a black deposit of iron oxide. It was evident that iron was being dissolved and the resulting compound decomposed in the boiler, and in the hot return tube, but it was at first thought peculiar that the precipitate which appears when the glass or flask is a new one, was not produced in subsequent experiments with the same apparatus. This led to attributing the actual formation of a precipitate in the first case to the presence of dissolved glass. The dark color could only be due to the iron. The clear, black, filterable solution obtained from such previously used apparatus was then shown to be a colloidal solution of iron oxide by the following method: Small quantities of such salts as sodium and barium chloride were added to portions of the clear, black water, and they caused an immediate coagulation and a consequent heavy precipitate, coupled with complete decolorization of the solution. This precipitate, well washed by decantation with pure water, was treated with dilute sulphuric acid in a closed vessel and pure air passed through this and then through a vessel containing a barium hydroxide solution. The failure to produce a precipitate of barium carbonate in this barium hydroxide solution showed that the original compound did not contain a carbonate. The precipitate was shown to contain iron by dissolving it in acid, oxidizing and precipitating the ferric hydroxide by ammonia. The formation of this colloidal solution of ferrous oxide is in exact accord with the principles which determine the formation of colloidal solutions in general. It is a general principle that whenever any substance which is by nature insoluble, is formed in water, it will tend to remain in a colloidal or suspended state until coagulated by electrolytes.

In the production of most precipitates in common laboratory reactions, there are always sufficient electrolytes present to account for the coagulation of the insoluble substances, if we may judge by the concentration usually necessary where measurements have been made. Where this is not the case, a colloidal state usually results. In the case at hand, there are practically no electrolytes present when the soluble ferrous bicarbonate is decomposed by heat, as this process requires the presence of but exceedingly small quantities of soluble salts in the solution at any one time. The insoluble ferrous oxide consequently remains in the colloidal state. This colloid may be precipitated by salts dissolved from the glass vessel, if of sufficient concentration, as was the case with new glass apparatus, and in this respect this colloid is like many others, such as platinum and silica.

The ease with which the soluble iron salt is decomposed by heat was well shown in the glass tube connecting the condenser and boiler, the return pipe of the above experiment. Above the stopper of the flask, where this tube was fairly cool, the glass remained clear, but below the stopper where the tube was heated by the steam of the flask, it was covered deeply with a black deposit, probably ferrous oxide. The deposition of this substance at this part of the return tube, commenced almost immediately on starting the experiment.

An experiment carried out in this way where pure water and carbon dioxide were used, where analysis showed the gaseous mixture to contain 11 per cent. carbon dioxide, produced such rapid corrosion of the iron that within a few days nearly a third of the exposed surface had been eaten away to depths of several hundredths of an inch, at which rate an ordinary pipe would not last more than a few months. It is not surprising that carbonic acid should dissolve iron under these conditions, but the fact that this corrosive action is a cyclic one, in which under suitable circumstances even a trace of carbonic acid may dissolve an unlimited quantity of iron without losing its corrosive power. has not received sufficient attention.

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A PROPOSED METHOD OF TESTING WOOD TREATED TO RESIST FIRE.

BY CHAS. F. MCKENNA.

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In the spring of 1902 an effort was made by the Bureau of Buildings of the Borough of Manhattan, New York City, to secure more certitude as to the qualities of the so-called fireproof wood which was being delivered in the city for use in high buildings.

Methods of test which have been in vogue for some time in the Bureau of Buildings were stated to be inadequate for the proper discrimination between well-treated wood and that which was