The Water Department of New York City has studied recently and at great length the corrosive properties of the Croton water, particularly as influenced by the use of sulphate of alumina for purposes of decolorization. The free carbonic acid naturally present in such surface waters as the Croton supply is increased somewhat by the carbonic acid liberated through the application of sulphate of alumina. As small quantities of free carbonic acid, however, seem sufficient to institute corrosive tendencies of the water upon iron, the effect of added quantities, resulting from the use of sulphate of alumina, has been comparatively small.

A large share of the investigations has been devoted to the use of lime or soda to remove free carbonic acid and thus reduce the corrosive tendencies of the water. In fact, this process judiciously applied seems capable from laboratory experiences of forming coatings on the inside of a pipe system so that corrosion may be practically neglected.

Clear waters, such as those coming from underground sources and filtered surface waters, show an amount of iron dissolved from the piping which is probably no greater than that which occurs with many turbid and colored surface waters. But when the latter are used in an untreated condition the effect of corrosion seems to have been largely obscured by other physical characteristics. Hence the rapid increase in the use of filtered water has developed the need for additional care in the study of filtration projects.

The New York City investigations above mentioned were conducted by Drs. Jackson and Hale of the Mount Prospect Laboratory of the Water Department, and the same will appear in full in the 1912 Report of the Department.

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DISCUSSION ON CORROSION OF METALS.

FRANK E. HALE.

The question of corrosion of iron pipes by water supply was given an extended investigation of six months at Mt. Prospect Laboratory during the first half of 1912. These experiments are the basis for the following discussion.

CHEMICAL REACTIONS.

In order to understand the problem it is necessary to have a clear conception of the chemical reactions taking place. While the electric theory of solution tension of iron may be correct as the ultimate source of corrosion it is my belief that the cart has been put before the horse and that the electrical phenomena result from the chemical action. Certain it is that the presence of carbonic acid is the most potent factor, coupled with the presence of dissolved oxygen. The action of these two agents is modified by the presence of other salts, increased

by nitrates which furnish oxygen by reduction, decreased by carbonates which help to form protective coatings upon the pipe.

The chemical action takes place in the following order:

Solution as bicarbonate.   The first reaction is the solution of iron as bicarbonate by carbonic acid with the formation of hydrogen.

$$Fe+2\ H_2CO_3=FeH_4(CO_3)_2+H_2$$
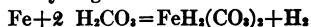
Formation of hydrogen.   The dissolved oxygen in the water which is near the iron surface oxidizes some of the hydrogen back to water.   After the oxygen near the iron is used up the hydrogen remains as a gas.   In the cold reaction of our experiments the amount of hydrogen oxidized was found to be about 20 per cent.

Oxidation and precipitation of dissolved iron as Fe_2O_3.   The dissolved oxygen at the same time oxidizes the soluble iron bicarbonate to insoluble red iron oxide setting free again the carbonic acid.

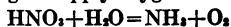$$4\ FeH_4(CO_3)_2+O_3+4\ H_2O=2\ Fe_2O_3+8\ H_2CO_3$$

Catalytic action of carbonic acid.   The carbonic acid, set free, again dissolves more iron and is again set free until all of the dissolved oxygen is exhausted.

Oxidizing power of Fe_2O_3.   The red iron oxide then acts as oxidizer until it is completely reduced to black magnetic iron oxide, setting free carbonic acid again.

$$FeH_4(CO_3)_2+Fe_2O_3+H_2O=Fe_3O_4+2H_2CO_3$$
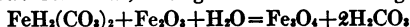
Final product is Fe_3O_4.   Reduction does not take place beyond this stage.   These iron products are expressed in the equations as oxides although differences of color, red, green, brown and black, coupled with varying stability on standing exposed to air, indicate that they probably exist as hydrates, with the exception of the final black magnetic oxide obtained by hot action.

Nitrate as source of oxygen.   After all dissolved oxygen has been used up nitrates are completely reduced to ammonia serving to supply oxygen.

$$HNO_3+H_2O=NH_3+O_2$$

Final action of carbonic acid.   After all possible sources of oxygen are exhausted, the carbonic acid dissolves more iron, which is probably thrown out of solution finally as insoluble basic carbonate of iron, since after complete reaction there is only about 0.2 to 0.7 p.p.m. iron in solution, no free carbonic acid, no dissolved oxygen, no nitrate, sometimes no bicarbonic acid, and under some conditions caustic lime is present.   The alkalinity of hard waters is reduced to about 25 p.p.m.

Sources of dissolving or active carbonic acid.   The carbonic acid for the solvent action may be derived from three sources, the free carbonic acid, the bicarbonic acid, and the neutral carbonate.   In the latter case the carbonate hydrolyzes so that there are in solution neutral carbonate, lime hydrate, and carbonic acid.   This takes place when the water reaches the stage that only neutral carbonate is present.   The carbonic acid set free dissolves the iron. The presence of lime hydrate was proven by titration with phenolphtalein and methyl orange.

Source of active carbonic acid affects rate of corrosion.   The rapidity of corrosive action is affected by the source of carbonic acid in order as given above, and the amount of soluble iron present during the active stages of corrosion varies with the above order of source of carbonic acid.

Carbonic acid set free by alum.   Another source of carbonic acid is that set free in alum treated waters.   This is really mostly bicarbonic acid set free.   The amount set free per grain of alum per gallon is not as sometimes stated 6.8 p.p.m. but about 3.5 p.p.m. (determined by analysis).   This is probably due to the formation of a basic carbonate of aluminum, $AlCO_3(OH)$, rather than the hydrate, $Al(OH)_3$.   The compound formed probably varies somewhat with the temperature and may be mixtures of $AlCO_3(OH)$ and $Al_2(CO_3)$ $(OH)_4$. Probably $Al(OH)_3$ forms only upon boiling, as in chemical analysis.   The amount of free carbonic acid given, 3.5 p.p.m., agrees with the results obtained at the Little Falls Filter Plant.

It must be understood that the facts as given above apply to new pipe with a *clean iron surface* and to *complete reaction.*

Water as a source of oxygen. Attempts to remove dissolved oxygen from water appear to me to be hopeless as well as expensive, because a consideration of the above reactions brings out a fact that seems to me to have escaped general attention, and that is that 75 per cent. of the oxygen in the iron oxides formed by complete reaction, if all the hydrogen were set free, comes from the water and not from the dissolved oxygen, and the greater part of the hydrogen is set free.

Large amount of iron corroded relative to amount of dissolved oxygen. A very large amount of iron is corroded for each part per million of dissolved oxygen through the catalytic action of carbonic acid and water. For example 10 p.p.m. of dissolved oxygen produces 126 p.p.m. Fe_3O_4, expressed as Fe, whereas if the hydrogen were oxidized and not set free, the amount which 10 p.p.m. oxygen could produce would be only 31 p.p.m. iron. In our experiments 75 per cent. to 80 per cent. of this theoretical amount of iron was produced, the difference from theory being due to oxidation of hydrogen. This is a variable quantity, but about 85 per cent. of the hydrogen oxidized was oxidized during the first fifteen minutes, which substantiates the idea expressed previously that oxidation of hydrogen takes place only at the surface of the iron while dissolved oxygen is present near the iron. The presence of hydrogen gas is easily shown and has been proven by many investigators. Any hydrogen set free means an equivalent amount of oxygen obtained from the water to oxidize the iron.

Effect of kind of iron relative to complete reaction. The experiments were carried out with Byers wrought iron pipe (protected with an inside coat), Reading wrought iron, Black mild steel, and galvanized wrought iron. The first three showed no differences in the corrosive action when carried to completion, but the steel appeared to corrode most rapidly. The galvanized iron showed great resistance at first, but gradually, especially with alkaline water, the action increased somewhat, though in the time of our experiments the highest amount was only about one-third that of the other pipes.

RATE OF CORROSION.

Remarkable speed of reaction. Experiments with regard to speed of reaction brought out some surprising facts.

About 50 per cent. of the iron produced by corrosion in the cold is produced in two to three hours. With Croton water (5 p.p.m. free carbonic acid) the action is practically complete in fifteen hours.

Morning rust and new service. This explains the greater tendency in house services, especially in new services, to show rusty water when first drawn in the morning, since the action is complete over night.

Influence of carbonic acid upon rate of corrosion. The rate of corrosion is increased proportionately to the increase in free carbonic acid. The action cold was complete in seven to eight hours with Croton water containing 25 to 50 p.p.m. free carbonic acid. The total iron was also somewhat increased with the higher free carbonic acid.

The carbonic acid hastens the action by dissolving the iron more rapidly. There being more iron in solution, oxidation is hastened. Analyses for soluble iron and dissolved oxygen proved this to be true. The carbonic acid increases the total iron by forming more basic carbonate of iron which is left unoxidized after available oxygen is exhausted.

Alum-treated water showed no appreciably greater corrosive action either in speed or total amount of iron than untreated water. This is due to the comparatively slight increase in free carbonic acid (3.5 p.p.m. per grain of alum per gallon).

Retardation of rate of corrosion by neutralization of carbonic acid. Neutralization of the free carbonic acid by lime hydrate or by sodium carbonate retards the corrosive action.

Neutralization of the free and half-bound carbonic acid by lime hydrate, provided there is no excess caustic, still further retards the corrosive action, and also reduces the total iron produced by cold action 33 per cent. and by hot action 50 per cent.

Neutralization of carbonic acid retards corrosion by reducing the amount of dissolving agent, hence the amount of soluble iron present at any moment and thus slows up the oxidation.

Increased rate of corrosion caused by a slight excess alkali. The slightest excess caustic (a few p.p.m.) up to considerable excess hastens corrosion to almost identically the same degree as does increasing the free carbonic acid to 25 to 50 p.p.m. A large excess of soda ash acts likewise. This action of alkalies has been noted by Cushman and others.

Excess alkali hastens the corrosion by hastening the absorption of oxygen by the iron in solution, though this is smaller in amount at any time. Until the excess of alkali is sufficient to prevent hydrolysis of carbonates the corrosion takes place. Analyses proved that the oxygen is absorbed faster and that only traces of iron are in solution at any time. Compare in this connection the Levy method of determining dissolved oxygen in water, *i.e.*, oxidation of ferrous salts in alkaline condition.

Amount of excess caustic necessary to completely stop corrosion. The excess of alkali necessary to stop corrosion completely is 100 to 125 p.p.m. excess lime hydrate over that needed to neutralize the free and half-bound carbonic acid. Only slightly more is needed to stop corrosion hot than cold. This amount of excess alkali acts by completely preventing solution of iron, for the oxygen still oxidizes the surface of the iron and is completely gone in 24 hours, although no iron over the original amount appears in the water.

The above facts show that whatever helps to put iron into solution is the real cause of red water trouble. It is the iron in the water, dissolved or suspended, which causes trouble, not the iron clinging to the pipe.

Heat hastens rate of corrosion. All corrosive action was hastened by heat (120°-150°F.) so that complete reaction was accomplished in 1½ to 3 hours on the clean iron surface.

Heat hastens corrosion in at least four ways,—by hastening the chemical action of solution of iron, by increasing the amount of free carbonic acid since heat sets free the half-bound carbonic acid of the alkalinity, by creating convection currents that cause the dissolved iron to diffuse more rapidly and hence come in contact with the dissolved oxygen faster, and by hastening the oxidation and precipitation chemically of the dissolved iron.

Action of hard water. The water of the Flatbush Water Company, which has a hardness of about 140 p.p.m., contains only two-thirds as much oxygen as Croton water and 10 p.p.m. free carbonic acid, produced corrosion as rapidly as Croton water on the clean iron surface and a total amount proportional to the oxygen and carbonic acid content as required by theory. Yet in service this water causes no complaint and is generally free from iron and turbidity. This is undoubtedly due to protective scale formed on the pipe, probably consisting of both iron oxide and carbonate of lime. As previously stated the alkalinity of hard waters is reduced to about 25 p.p.m. when the action goes to completion.

Consumption of oxygen as related to speed of corrosion. Dissolved oxygen disappears rapidly in all cases. In the first fifteen minutes 23 per cent. to 37 per cent. were used up due to oxidation of both hydrogen and dissolved iron.

The relative speed of oxidation is best seen in comparing percentages of oxygen used up in 1½ hours.

Temp.	Croton water	Free CO₂	Bicarbonic acid	Lime hydrate excess	Oxygen used up.
1 hot	untreated	5 p.p.m.	10 p.p.m.	....	100%
2 cold	modified	0 p.p.m.	0 p.p.m.	27 p.p.m.	87%
3 cold	modified	25 p.p.m.	10 p.p.m.	....	87%
4 cold	untreated	5 p.p.m.	10 p.p.m.	....	78%
5 cold	modified	0 p.p.m.	10 p.p.m.	....	75%
6 cold	modified	0 p.p.m.	0 p.p.m.	....	68%

It is noticeable that the increases of dissolved oxygen used up in No. 3, No. 4 and No. 5 is approximately proportional to the increases in free carbonic acid in the water.

Relation of oxygen to color and composition of precipitate. So long as there is oxygen in solution the reactions take place rapidly and almost proportional to time and the iron precipitate is red (Fe_2O_3). After exhaustion of the oxygen the reaction becomes slower, the red oxide being reduced to the lower black oxide, turning green to brown to black. The color of the precipitate gives a good indication of the progress of the action.

Relation of oxygen and carbonic acid to soluble iron. While there is dissolved oxygen present there is iron in solution depending upon the amount of active carbonic acid. Soon after the oxygen disappeared it was but rarely that more than 0.5 to 1.0 p.p.m. iron was in solution. The amount of soluble iron present while dissolved oxygen was present was as follows:

Croton water	Free CO_2	Bicarbonic acid	Lime hydrate excess	Soluble iron
modified	0 p.p.m.	0 p.p.m.	27 p.p.m.	0.35 p.p.m.
modified	0 p.p.m.	0 p.p.m.	....	0.76 p.p.m.
modified	0 p.p.m.	10 p.p.m.	....	3.50 p.p.m.
untreated	5 p.p.m.	10 p.p.m.	....	5.50 p.p.m.
modified	25 p.p.m.	10 p.p.m.	....	7.90 p.p.m.

It is obvious that the amount of dissolved iron is greater with increase in the active carbonic acid.

Relation of amount of oxygen to corrosion. The amount of oxygen within wide limits does not seem to affect the *rate of corrosion* materially, but the total amount of iron removed from the pipes in complete reaction, other factors remaining the same, is directly proportional to the dissolved oxygen in the water.

<div align="center">PROTECTIVE COATINGS.</div>

When iron pipe is exposed to the continuous action of water, as in service, a protective coating forms according to the nature of the water.

Coating delays corrosion. Its action is to delay corrosion rather than to stop it and to reduce the amount of iron appearing in the water. The corrosion goes on slowly but the oxides cling to the iron increasing the amount of scale.

Protective character of coating varies with the water producing it. In cold action the greatest protection was acquired experimentally in ten days and then remained constant. Flatbush and Brooklyn waters caused a better protective coating than Croton water. The iron produced in 24 hours dropped from 114 and 85 p.p.m. respectively for the two former to 21 p.p.m. Fe., for the Croton and its modifications from 56–102 to 29–36 p.p.m. Fe. Croton was tried in four modifications,—untreated, with free carbonic acid neutralized by sodium carbonate, with free carbonic acid neutralized by lime hydrate to bicarbonate, and treated with one grain per gallon of alum.

In hot action the protective coating formed in two days. Flatbush water reached the lowest level of 3 p.p.m. iron with an average of 8. Brooklyn water reached 4 p.p.m. iron with an average of 9. Untreated Croton fluctuated high and low with an average of 41 p.p.m. iron. The alum treated Croton averaged 26. The soda neutralized Croton averaged 15 with a minimum of 11, and the lime neutralized Croton averaged 23 p.p.m. Fe. All the averages, cold and hot, include results from the tenth to the twenty-first day.

Action of carbonic acid upon pipes with coatings. The pipes which had acquired a protective coating from these different waters were subjected for 24 hours to the action of untreated Croton water and to Croton water containing 20–27 p.p.m. free carbonic acid.

The water with increased carbonic acid produced an average of 38 p.p.m. iron from the pipes with scale formed in cold action against 24 p.p.m. produced by untreated Croton (5 p.p.m. CO_2). On the pipes with scale produced in hot action about the same relative quantities were produced, 34 against 22 p.p.m. Fe., showing that water containing the greater amount of carbonic acid causes more corrosion upon pipes protected by scale.

The scale produced by Flatbush, Brooklyn, and soda neutralized Croton water proved the more protective.

GENERAL SUMMARY.

Extensive corrosion takes place rapidly in new pipe while the iron is fairly clean from incrustation. This explains the abundance of complaints of iron rust in new service installation.

Concerning the kind of pipe there is little doubt that steel pipe is most readily attacked, wrought iron next, and galvanized iron the least. The latter is far preferable for use. Lead pipe should never be used any more than absolutely necessary because of the danger of accumulative poisoning with minute amounts of lead (less than 0.5 p.p.m.).

The chief agent in dissolving the iron is carbonic acid, as it is also the chief agent in holding iron in solution.

The chief agent in carrying the rusting to the greatest extent is oxygen.

Through the catalytic action of active carbonic acid, about 70 per cent. of the oxygen in the iron rust comes from the water by chemical decomposition, hydrogen gas being set free. The remainder only, about 30 per cent., is furnished by the dissolved oxygen in the water.

Waters which give the most trouble are very soft and contain considerable free carbonic acid.

Hard waters rarely cause complaint as they form an excellent protective coating on the pipes.

The action in distribution services probably never reaches completion on account of protecting scale of oxide, etc., which retards corrosive action. The scale varies with different waters in protective properties. Tap samples in New York City have shown no appreciable diminution in dissolved oxygen or in free carbonic acid, so that only slight corrosion can have taken place in proportion to volume of water and possible reaction. Even hot services have shown the usual amount of carbonic acid and more oxygen than would saturate the water at the temperature when drawn.

Since in distribution services there is no exhaustion of oxygen, any increase in free carbonic acid may mean a possible increase of soluble iron in the water, which would be precipitated in the hot water supply.

Neutralization of free and half-bound carbonic acid is impracticable as it tends to hasten corrosion if there be the slightest excess of hydrate, removes zinc when hot from galvanized pipe, interferes with alum precipitation and color removal, and produces considerable precipitation of calcium carbonate in the water, which would deposit in the pipe system, meters, etc., unless previously removed by filtration or sedimentation.

Neutralization of only free carbonic acid is feasible, since it retards corrosion and reduces the amount of soluble iron

Either soda ash or lime oxide may be used. Both reduce the corrosive action, cold or hot. Only sufficient lime should be used to form bicarbonate. This reagent increases the hardness 1.1 p.p.m. for every 1 p.p.m. free carbonic acid neutralized to bicarbonate. About 5.3 pounds CaO per million gallons of water are required for each 1 p.p.m. carbonic acid. It is best handled dry. It costs about two cents per million gallons per 1 p.p.m. carbonic acid.

Soda ash is more soluble, can be handled in concentrated solution and consequently in small sized tanks, and probably with better regulation of dosage, would not increase the hardness, but on the contrary would decrease the lime sulphate in the water, changing it to sodium sulphate, thus improving the water for boiler use and for other industrial purposes. It also apparently helps to form a better protective coating on the pipe. About 20.2 pounds soda ash per million gallons of water are required for each 1 p.p.m. carbonic acid. This would cost about 20 cents per million gallons for each 1 p.p.m. carbonic acid. Soda ash has been used successfully on a small scale to obviate red water trouble. The great difference in cost is due to greater molecular weight, less combining power, and greater cost per pound. The cost must be considered in connection with the degree and advantage of the change of sulphates to carbonates, etc.

Aeration of water by splashing followed by neutralization of residual free carbonic acid (about 5 p.p.m.) is probably the best practice.

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