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ON THE ACTION OF SLIGHTLY ALKALINE WATERS ON IRON.

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(Read at the Meeting, April 5, 1905.)

It has been the practice of one of us during the last ten or fifteen years, when examining waters intended for use in steam boilers, to make a trial experiment with the water, using a slip of thin steel 4 inches long by 1 inch wide.

A hundred c.c. of the water are placed in a boiling-tube, the steel slip—brightly polished with emery, not cleaned by chemical means—inserted, and the whole kept at 100° C. (or as near to that temperature as a water-bath will bring it) for twenty-four hours, after which the nature of the action is examined and its extent measured. In most cases a similar experiment is made at the air temperature. At the end of the time the deposit, if any, is washed off the surface of the metal, and the total amount of iron in solution and in suspension in the water is estimated.

Of course the test is a very imperfect one. It does not reproduce in any way the

THE ANALYST.

conditions obtaining in a steam boiler ; but some of those conditions, such as the high temperature and pressure, the rapid circulation, and the constant influx of fresh feed water, could not possibly be imitated without altogether prohibitive expense and trouble.

The plan has obvious advantages. It is simple and cheap ; requires but little of the water ; the conditions are under control, and can always be exactly reproduced ; any peculiarities in the action are visible, and its extent is easily and rapidly estimated.

In the somewhat limited number of cases in which such a method of testing is likely to be of use it has been found very fairly satisfactory. As a means of investigating the problems connected with the action of water upon iron and steel, there is a good deal to be said in its favour. The quantitative results obtained respond to almost every change in the conditions. They are affected by the chemical composition of the saline residue of the water, by its gaseous contents, by the temperature, by the duration of the experiment, by the concentration of the saline contents of the water, by the physical or chemical condition of the surface of the metal, by the electrical condition of the metal, and by the presence or absence of light. It is not unreasonable, therefore, to conclude that in the majority of cases in which a natural water has a corrosive action on the metal of a boiler, some indication will be given of the fact by this simple method of trial. In actual practice this conclusion has been fully borne out, though opportunities for comparison between the behaviour of the water in the laboratory and that in the boiler are not so very frequent, inasmuch as the majority of waters cause incrustation and do not corrode.

Having had occasion to apply the method to artificially softened waters, in which, as is almost invariably the case, the liquid was slightly alkaline owing to the presence of lime, caustic soda, or sodium carbonate, it was found that when the alkalinity exceeded a certain amount no action whatever occurred, and the surface of the metal was as bright at the end as at the beginning of the experiment. This inhibitive action is, we believe, generally known ; but we have nowhere seen any recognition of the fact that it has its limits, below which action does occur, although the water is still alkaline, much less any statement as to what those limits are. There seems to be a widespread impression that alkaline waters do not act upon iron at all, and the fact is usually regarded as one of the great advantages of the chemical treatment of hard waters.

We find, however, that with an alkalinity not exceeding a certain amount—dependent on the nature of the alkali present, and to a less extent on the temperature—not only does action occur equal in intensity to what would occur in the absence of any alkali, but that this action takes place in a very curious and interesting manner, for which at present we are unable to offer any altogether satisfactory explanation.

The following table (I.) shows the effect of adding to New River water small proportions of sodium hydroxide, lime-water, and sodium carbonate. The quantities added are expressed in parts of the alkali or carbonate per 100,000 of water, and also in cubic centimetres of decinormal solution per 100 c.c., and the amount of the action in milligrammes of Fe_2O_3 .

THE ANALYST.

227

TABLE I.—TWENTY-FOUR-HOUR EXPERIMENTS WITH NEW RIVER WATER TO WHICH HAD BEEN ADDED SMALL QUANTITIES OF ALKALINE SALTS.

AT 100° C.				AT AIR TEMPERATURE.	
C.C. of $\frac{N}{10}$ Alkali in 100 c.c. of Water.	Alkali by Weight in 100,000 Vols. of Water.	Area and Nature of Action.	Iron Removed, expressed as Milligrammes of Fe_2O_3 .	Area and Nature of Action.	Iron Removed. Mgs. of Fe_2O_3 .
<i>Series 1.—Sodium Hydroxide.</i>					
1.0	4.0	General.	23.0	General, but on one side only.	9.0
2.5	10.0	Local; large patches.	18.3	Broad ill-defined patches.	7.3
5.0	20.0	Local; smaller; well defined.	23.0	Projecting growths, well defined.	7.0
10.0	40.0	Ditto.	19.3	No action.	0
15.0	60.0	No action.	0	„ „	0
<i>Series 2.—Calcium Hydroxide.</i>					
0.5	1.85	General.	25.5	General.	9.0
1.25	4.6	Many small rounded patches.	25.3	Few rounded patches.	6.5
2.5	9.25	Long ill-defined streaks.	18.0	Streaks, ill defined.	7.0
5.0	18.5	Smaller well-defined patches.	21.0	Patches, well defined.	7.0
7.5	27.7	Round, sharply-defined growths.	18.5	Very little action.	7.0
10.0	37.0	Three small patches.	24.0	No action.	0
15.0	55.5	No action.	0	„ „	0
<i>Series 3.—Sodium Carbonate.</i>					
1.0	5.3	General.	22.5	General.	9.0
2.5	13.25	Many small spots.	21.3	General, but more pronounced in parts.	10.0
5.0	26.5	Well-defined streaks.	14.0	Long patches, ill defined.	7.5
10.0	53.0	Well-defined projecting patches.	15.0	Ill-defined patches.	5.0
15.0	79.5	Large ill-defined patches.	14.5	Well-defined patches.	7.0
20.0	106.0	Few narrow streaks, sharply defined.	20.2	Round, well-defined spots.	6.0
30.0	159.0	Few small spots and one narrow streak.	15.0	No action.	0
40.0	212.0	No action.	0	„ „	0

The peculiarity of the action consists in this—that whereas with quantities below those given in the table the iron slips are acted upon fairly uniformly all over, rust being formed on the surface of the plates, and then, owing to their nearly vertical position, settling slowly down to the bottom of the vessel; with larger but still very small proportions of alkali the action on the iron assumes a local character. At first

THE ANALYST.

the localization is extremely slight, but with increasing alkalinity not only do the areas acted upon get smaller, but they get to be more and more sharply defined; finally, when a certain strength of alkalinity is reached all action ceases, and at this stage no deposit is observable in the liquid, and the surface of the metal remains as bright and untarnished after twenty-four hours as at the beginning of the experiment, only a trace of iron being found in solution in the liquid, and none in suspension, after several days.

If in those cases in which action has taken place the amount of iron removed from the metal slips be estimated, it will be found to be—with the smaller proportions of alkali that produce any degree of localized action—not markedly different from that produced by the water alone. As the alkalinity increases the quantity diminishes slightly, but not at all in proportion to the area of action. Frequently when the area acted upon is not $\frac{1}{100}$ part of the total surface of the plate, it will be found that the iron removed has only diminished by about 5 per cent. of the maximum amount. When the higher limit of alkalinity is reached the quantity of iron removed diminishes with a sudden drop almost to nil—*i.e.*, to quantities which give no visible precipitate with ammonia. Coincident with the increased localization of the action is a tendency for the oxide of iron (or carbonate?) formed to adhere to the surface of the metal instead of slowly subsiding to the bottom of the liquid, and this tendency goes on increasing until the rust projects from the surface like the growth of a mould, and these growths get firmer and more closely adherent as they get fewer in numbers and smaller. In most cases they are of a dark-green or even blue colour beneath the surface, but if examined *in situ* without shaking they are generally found to be covered with a loose layer of bright-red oxide. A qualitative examination is sufficient to show that the greater part of the iron they contain is in the ferrous state, and it seems fairly certain that a ferrous salt is first produced, to be afterwards oxidized to ferric when it ceased to be in contact with the metallic surface. When rubbed off, the growths leave evidence of their action on the metal in the form of dark-coloured patches, which can be felt as distinct and generally sharply-defined depressions on the surface of the plates.

For the purpose of studying the phenomena under somewhat simpler conditions, a number of experiments have been made with distilled water instead of New River water. The dissolved salts in the latter are more or less precipitated by the alkaline hydroxides and salts which formed the subject of the experiments recorded in Table I., and the dissolved gases are greater and more variable in amount, so that the alkali added does not represent the alkalinity of the solutions. With distilled water the dissolved gases are the only uncontrolled constituents.

We have determined, for all the ordinary alkaline hydroxides and carbonates used, or likely to be used, in water softening, the degree of alkalinity at which this local action begins and finishes, and we have noted certain points in connection with the nature of the action, which appears to differ both in kind and in intensity with different bases (see photographs).

Table II. shows the results of experiments made in the cold, and at, or just below, the boiling-point, with potash, soda, ammonia, lime, and baryta; and Table III. with sodium carbonate.

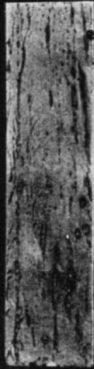
AMMONIUM HYDRATE.



0.87



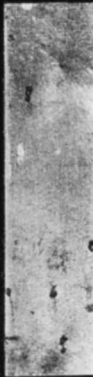
1.75



3.5



8.75



17.5

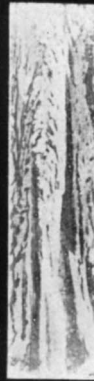
BARIUM HYDRATE



2.13



2.13



4.27

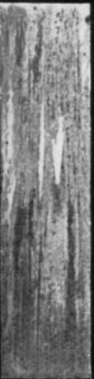


8.55



21.37

SODIUM CARBONATE



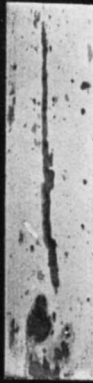
2.65



5.3



13.25



26.5



53.0

Photographs shewing the action of alkaline waters on steel plates. (Half natural size)
The bright parts represent the polished, i.e. uncorroded surface.
The figures give the proportion of alkali in 100,000 volumes of water.



79.5

TABLE II.—TWENTY-FOUR-HOUR EXPERIMENTS WITH DISTILLED WATER TO WHICH ALKALINE HYDROXIDES HAD BEEN ADDED.

AT 100° C.				AT AIR TEMPERATURE.	
C. C. of $\frac{N}{10}$ Solution per 100 c.c. of Water.	Alkali by Weight in 100,000 Vols. of Water.	Area and Nature of Action.	Iron Removed, expressed as Milligrammes of Fe_2O_3 .	Area and Nature of Action.	Iron Removed. Mgs. of Fe_2O_3 .
<i>Series 1.—Sodium Hydroxide.</i>					
0.25	1	Liquid turbid; action general, but slightly localized, in streaks.	20.3	Ill-defined streaks one side; general the other.	5.3
0.50	2	Liquid turbid; action general, but more pronounced in parts.	14.5	Fairly general, tending to streaks.	6.7
1.0	4	Long narrow patches.	18.5	Distinctly local; irregular patches.	7.0
2.5	10	Narrow patches.	19.3	One small projecting growth.	2.8
5.0	20	Two small streaks.	5.8	No action.	0
10.0	40	No action.	0	" "	0
15.0	60	" "	0	" "	0
<i>Series 2.—Potassium Hydroxide.</i>					
0.25	1.4	Long thin streaks over whole plate.	17.8	General, but tendency to streaks.	5.0
0.5	2.8	Thin streaks, less than above.	13.7	Long thick streaks, well defined.	6.2
1.0	5.6	Thin streaks, still less.	13.7	Few short thin streaks.	5.8
2.5	14.0	One large patch.	12.8	No action.	0
5.0	28.0	No action.	0	" "	0
10.0	56.0	" "	0	" "	0
15.0	84.0	" "	0	" "	0
<i>Series 3.—Calcium Hydroxide.</i>					
0.125	0.46	General on one side; patchy the other.	19.0	General, but tending to streaks on one side.	7.5
0.25	0.92	In narrow wavy streaks.	17.0	General, but more pronounced in parts.	8.5
0.50	1.85	In long patches.	20.8	Long patches.	6.5
1.25	4.6	In long streaks.	22.0	A very few patches.	9.5
2.5	9.25	Well-defined streaks.	20.5	" " "	7.5
5.0	18.5	Very little action.	3.5	Little apparent action.	5.0
7.5	27.75	No action.	0	No action.	0

THE ANALYST.

Series 4.—Barium Hydroxide.

0.25	2.13	Long narrow fern-like streaks.	15.7	General; one broad, ill-defined patch.	5.3
0.50	4.27	Broad, zebra-like markings.	20.0	Streaks and spots; form projecting growth.	7.3
1.0	8.55	Thick streaks projecting.	14.4	One thin streak.	5.2
2.5	21.37	One broad patch on one side; one spot on the other.	11.3	No action.	0
5.0	42.74	No action.	0	No action.	0
10.0	85.48	" "	0	" "	0
15.0	128.22	" "	0	" "	0

Series 5.—Ammonium Hydroxide.

0.25	0.85	Almost general, but some streaks.	19.7	General, but streaks just apparent.	7.5
0.50	1.7	Streaks along whole length.	17.0	Long patches, ill defined.	7.5
1.0	3.4	Well-defined streaks.	11.0	Long streaks, also spots.	7.0
2.5	8.5	Very thin streaks.	11.5	Few thin streaks and spots (projecting).	6.0
5.0	17.0	Few dots only.	11.5	Few spots.	5.0
10.0	34.0	No action.	0	No action.	0
15.0	51.0	" "	0		

TABLE III.—TWENTY-FOUR-HOUR EXPERIMENTS WITH DISTILLED WATER TO WHICH SODIUM CARBONATE HAD BEEN ADDED.

AT 100° C.				AT AIR TEMPERATURE.	
C.C. of $\frac{N}{10}$ Solution per 100 c.c. of Water.	Weight of Salt in 100,000 Vols. of Water.	Extent and Nature of Action.	Iron Removed, expressed as Milligrammes of Fe_2O_3 .	Extent and Nature of Action.	Iron Removed. Mgs. of Fe_2O_3 .
0.25	1.32	General; darker streaks visible.	22.0	Ill-defined patches.	8.5
0.50	2.65	Many long thin streaks, bright in between.	15.0	Long, broad patches.	7.5
1.0	5.3	Long patches.	16.3	Long patches.	7.0
2.5	13.25	" "	14.0	" "	5.5
5.0	26.5	Few broad patches.	14.5	Streaks.	6.0
10.0	53.0	Broad patches of smaller area.	16.5	Large well-defined spots.	6.5
15.0	79.5	Few patches.	17.5	Very sharply - defined spots.	7.0
20.0	106.0	Broad patch one side, one spot on the other.	16.5	Few spots.	6.0
30.0	159.0	Long broad patch one side, spots on the other.	18.5	No action.	0
40.0	212.0	No action.	0		
50.0	265.0	" "	0		

Though each alkali has a more or less marked individuality as regards the pattern formed on the slips (shown fairly well in the photographs), and even the colour and tenacity of the growths of oxide, the same sequence of changes occurs with each as the proportion of alkali rises.

The figures in the tables show that the amount of iron removed is practically independent of the area attacked, so that the more restricted the area, the deeper the excavation that occurs there.

We have not yet made any definite experiments on the point, but from one or two isolated observations it would seem probable that, as the area of action gets less and the products of the action assume the form of growth-like projections from the metal, the proportion of ferrous iron increases. At all events, with a water of neutral reaction we could get no evidence of the presence of ferrous iron at all, while with the projecting "growths" ferrous iron was in greater quantity than ferric.

The colour of the oxide supports this view, inasmuch as the rust from neutral distilled water is always reddish-brown, while with the dilute alkaline solutions, and more especially with baryta, it is of a dark blue-green colour. In one case a growth of a light blue colour was observed—a not very surprising result, inasmuch as Nicolardot (*Journ. Chem. Soc.*, 1905) has shown that a white Fe_2O_3 can be prepared.

The fact that alkaline solutions are capable of acting in the way described is of considerable theoretical interest, as well as of possible practical importance.

To deal with the purely scientific aspect of the matter, it is necessary to consider the explanations that are usually given of the rusting of iron. According to the view originally proposed by Traube (*Berichte*, xviii., 1877-1887), and more recently advocated by Dunstan (*Proc. Chem. Soc.*, 1903, p. 150), oxygen and water react with the metal, *both* being *necessary*, and ferrous hydrate and hydroxyl are formed. The latter reacts again with iron, forming a hydroxide of the formula $\text{Fe}_2\text{O}_2(\text{OH})_2$, which, according to Dunstan, represents the ordinary composition of iron rust. Neither of these workers has been able to detect the presence of hydrogen peroxide, but this is (to them) explained by the rapidity with which that substance is acted upon and destroyed by metallic iron.

Traube asserts, as a well-known fact, that iron is not oxidized when put into alkaline solutions, and states that it decomposes hydrogen peroxide when in such a solution without being itself oxidized. Moody more recently (*Proc. Chem. Soc.*, 1903, p. 240) has found that pure freshly-distilled hydrogen peroxide does not act on iron unless an acid, such as carbonic acid, is also present.

Dunstan (*loc. cit.*) explains this passivity of iron towards alkaline solutions by saying that all the substances which inhibit rusting do so by virtue of their power of decomposing the peroxide. If, therefore, dilute solutions of alkalis *do* act on iron, either hydrogen peroxide is formed, in spite of the presence of the alkali (in which case, according to Traube, it should not act on the iron), or the hydrogen peroxide is not formed, and the hydroxylation theory becomes untenable. It must be borne in mind, however, that Dunstan was dealing chiefly with the *atmospheric corrosion* of iron, and that he used apparently highly purified iron in his experiments.

To ascertain whether small quantities of hydroxyl could survive the action of the slight alkalinity of the solutions employed, we made up two solutions, containing

THE ANALYST.

respectively 0.15 and 0.7 parts of hydrogen peroxide per 100,000 of distilled water; 100 c.c. of each strength were heated in a water-bath for twelve hours, and two similar quantities, to which 1 c.c. of $\frac{N}{10}$ sodium hydroxide had been added, were treated in the same way. At the end of the time some of the original solutions which had not been heated and the four solutions that had been heated were tested for hydrogen peroxide, and abundant evidence of the presence of that substance—or, at all events, of a peroxide—was obtained in every case. The peroxide is not destroyed by even 5 per cent. soda after heating in the water-bath for four hours. From the way in which the experiments were carried out as little as 0.015 per 100,000 could have been detected. The action on iron (as measured by Fe_2O_3 removed) was not materially increased by the presence of the hydroxyl, and when the added alkali was raised to 15 c.c. it was entirely inhibited, just as if no peroxide had been present, although the latter could be easily detected at the close of the experiment (twenty-four hours).

It seems quite plain, therefore, that the hydrogen peroxide theory, as far as this particular form of rusting is concerned, cannot be sustained, unless as a mere pious belief unsupported by any sort of proof, other than the indirect one of analogy, for it cannot be proved to be present under ordinary circumstances, and when added it neither increases the action nor gives rise to it when it would otherwise not occur.

The other theory of the rusting of iron has its most recent exponent in Moody (*Proc. Chem. Soc.*, 1903, pp. 157 and 239), and is to the effect that the primary action is due to the interaction of iron and carbonic acid, and that rust is formed by the subsequent oxidation of ferrous salt. He shows that when iron is exposed to water and oxygen—previously freed as far as possible from carbon dioxide—the volume of oxygen remains practically unchanged, but that on admitting carbon dioxide it diminishes rapidly and the iron rusts.

It is as difficult to believe that carbonic acid is any more necessary to the reaction than hydrogen peroxide, in view of the experiments recorded in Table II., more especially those in Series 3 and 4. To make quite sure that the amount of carbonic acid gas dissolved in the distilled water was not greater than the quantity of baryta added, a special experiment was made in which 0.5 c.c. of baryta water was added to 100 c.c. of the water, and a steel slip immersed in the liquid. At the end of the twenty-four hours, when the usual characteristic action had taken place, titration of the clear solution, using phenolphthalein as indicator, showed alkalinity still present, corresponding to 0.4 c.c. $\frac{N}{10}$ $\text{Ba}(\text{HO})_2$, a loss of only 0.1 c.c.

In view of the extreme insolubility of barium carbonate in hot water, it is not unfair to assume that neither free nor combined carbonic acid took part in the reaction.

Further, it would appear from another experiment that in the presence of what must be regarded as a large excess of free carbonic acid, iron is *not* acted upon, for we find that sodium bicarbonate acts in a similar way to the normal carbonate if only enough of the salt is present—*i.e.*, a stage is reached when the iron is entirely untouched after being immersed in the solution, either hot or cold, for twenty-four hours.

We have distinct evidence that localized action occurs with this salt, but in a far less striking manner than is the case with the *normal* carbonate. With 10 c.c. of

THE ANALYST.

233

a normal solution the action is general, but at the same time small; with 15 c.c. of normal bicarbonate solution per 100 of distilled water the plate remained absolutely bright and untarnished after being in the cold for twenty-four hours, and it gave no evidence (judging by the mercuric chloride test) of the presence of any normal carbonate at all—*i.e.*, the whole of the bicarbonate remained unchanged. A hot solution of the same strength was also without action, although much normal carbonate was formed—*i.e.*, a large amount of carbonic acid must have been present, or, at all events, must have passed out of the liquid.

TABLE IV.

C.C. of Bicarbonate (Normal Solution).	Bicarbonate per 100,000 Vols. of Water.	Mgms. of Iron Removed.
1	84	{ cold 8.5 action general. hot 12.5
5	420	hot 13.5 } " " slight tendency to
7.5	630	hot 12.5 } local action.
10	840	{ cold 7 } ditto more
15	1,260	{ hot 8 } marked. hot 0

According to Moody, oxygen and water without carbonic (or other) acid will not cause rusting. According to Dunstan carbonic acid and water without oxygen is also without effect, while the various experiments we have made certainly indicate that carbonic acid is not necessary, though there can be no doubt that it plays an important part under the ordinary conditions of rust formation. Some further experiments go to show that the actual *quantity* of the dissolved gases has very little to do with the matter, for we find that after twelve hours at water-bath temperature no further gases are evolved from water; and yet when distilled water was first boiled and then heated for four hours on the water-bath in an open vessel, the action on iron after twenty-four hours was 25.3 mgms., as compared with 22.2 with the same water not previously heated. Similar experiments with water containing 2.5 c.c. $\frac{N}{10}$ NaHO gave, when heated beforehand, 13.2 mgms., and when not so heated 17.8. As water entirely free from gases will not act on iron, it seems probable that a minute quantity of gas is necessary to start the reaction, which then goes on continuously. It is obvious, however, that under the term "rusting" a number of different reactions are included, and much more work is required before a satisfactory explanation of them all is likely to be forthcoming.

It will, of course, at once be objected that the experiments were made with impure iron—in this case steel. We have not yet been able to get, in the form of slips, any iron of known purity, but we have found that sheet-iron and Siemens steel and also steel wire alike give the characteristic action within the limits of alkalinity we have established.

In summing up the result of his work (*loc. cit.*), Dunstan makes the statement (whether as the result of experiment or as a commonly-accepted opinion is not clear) that when the iron is impure, or when another metal is present, electrolytic

THE ANALYST.

action occurs; the electro-positive metal suffers oxidation and hydrogen gas is evolved. If the latter is a necessary condition of electrolysis, then no electrolysis takes place in connection with the phenomena under discussion; for if a boiling tube, prolonged at what would be its closed end by a narrow tube of $\frac{1}{16}$ inch internal diameter and about 4 inches long, closed at its distal extremity, be inverted over a steel slip immersed in water, of slightly alkaline or neutral reaction, and heated in the water-bath for twenty-four hours, the gas that collects in the narrow portion of the tube does not differ in volume by $\frac{1}{50}$ c.c. from that given off by the water alone in the absence of the steel slip.

To turn to the practical aspect of the question, it is quite obvious that, assuming that these curious phenomena we describe really take place under the conditions which obtain in boilers, feed-water tanks, etc., they would constitute a very serious objection to the use of chemical processes of water-softening, and also to the employment of alkaline waters of any sort for steam-raising purposes, for even the smallest degree of alkalinity in a feed-water will, by the concentration that takes place in the boiler, be raised to thirty or more times its original amount (Cribb, ANALYST, July, 1900), and therefore the whole range of alkalinity with which action occurs is well within the conditions that would occur in practice.

A glance at some of the plates is sufficient to show that even in the space of twenty-four hours (and especially where the area of attack is small) the metal is eaten away to quite an appreciable depth. Now, it is generally admitted that (leaving on one side the question of incrustation), the rusting action is a continuous one, although it slackens down considerably after the first onset, and the following figures (Table V.) show that this is so, and therefore, either hot or cold, it is quite plain that, given the right strength of solution, most serious pitting *might* be caused.

TABLE V.—ACTION OF DISTILLED AND NEW RIVER WATER DURING VARIOUS PERIODS AT THE AIR TEMPERATURE.

Period.	Distilled Water. Mgms. of Fe_2O_3 .	New River Water. Mgms. of Fe_2O_3 .
12 hours.	6.5	—
24 „	8.0	9.1
48 „	—	14.4
168 „	25.8	—
240 „	39.5	56.0

It is important, therefore, to inquire how far, if at all, this could take place in practice.

As regards the metal, we find that sheet-iron, Siemens-Martin steel with the "skin" on, as actually used for making boilers, and the steel with which most of the experiments in connection with the paper were made, act practically alike. Even the "skin" does not prevent the local action in any way, and the action goes on at the same rate, or even more energetically, therefore the nature of the metal is no bar to the action.

THE ANALYST.

235

The action of the dissolved salts likely to be met with in natural waters other than alkaline salts is similarly without any inhibiting effect.

As shown in Table VI., the figures represent mgms. of Fe_2O_3 removed from the steel plates after immersion in solutions of the salts named, and of the strengths specified, for twenty-four hours at the water-bath temperature.

TABLE VI.

Strength of Solution,	10 Parts per 100,000.	100 Parts per 100,000.
Sodium chloride ...	19.0	25.0
Sodium sulphate ...	18.5	28.0
Sodium nitrate ...	18.0	61.5
Sodium phosphate ...	18.0	16.5
Potassium nitrate ...	22.0	—
Calcium chloride ...	17.0	31.5
Calcium sulphate ...	25.5	54.5
Magnesium chloride ...	28.0	23.5
Magnesium sulphate ...	25.5	26.5
Ammonium chloride ...	12.0	47.5
Ammonium carbonate ...	30.0	22.0
Distilled water alone ...	19.0	22.0
New River water alone ...	25.0	30.0

Of course, only the salts of the alkalis and alkaline earths could be present under the conditions which give rise to local action.

In the case of boilers, especially high-pressure boilers, the high temperature prevailing increases the amount of decomposition undergone by practically all the saline constituents of natural waters (Cribb, ANALYST, 1900), and, therefore, it would naturally be expected that the possibility of pitting would increase rather than diminish as the temperature rises. To ascertain whether the local action of alkalis actually does take place at temperatures above 100°C ., we have so far only made one experiment. It consisted in heating a steel slip immersed in distilled water, containing 4 parts per 100,000 of sodium hydroxide, to a temperature of 110°C . for some hours. The usual action characteristic of that degree of alkalinity took place. We hope, however, to have the opportunity before long of employing a still higher temperature; but there is no reason for doubting that the action at temperatures above 100°C . will be more, and probably considerably more, than it is at the normal boiling-point.

Even if the higher temperatures occurring in steam boilers brought about no increase in action, it is quite obvious that the rate of corrosion occurring in our laboratory experiments might have the most serious consequences even after a comparatively short period of working. Take, for instance, a 100 horse-power boiler with 600 square feet of water surface. Assume that it is fed with New River water, which according to Table VI. removes a little over 25 mgms. of Fe_2O_3 in twenty-four hours. This would mean 6.7 ounces of metallic iron removed in a single day and night. Each square inch of $\frac{1}{4}$ -inch boiler plate only weighs 1.22 ounces.

THE ANALYST.

There are, on the other hand, some facts which would tend to lessen, if not altogether to prevent, pitting in a boiler, and there can be no doubt that these are largely operative, otherwise pitting would be universal with all softened waters from the cause under discussion.

The first is that most softened waters give a deposit when heated, which is generally sufficient to cover the plates and tubes with a more or less protective coating. If it is not, steps are taken to produce such a coating by what may be called artificial means. Secondly, the rapid circulation, especially in the case of tubular boilers, would almost certainly prevent anything in the nature of the growths seen in the laboratory experiments. There are, however, in most boilers, and especially in the non-tubular kinds, certain places where the circulation is very much slower, and it is in the experience of most engineers that it is in these spots that pitting most frequently occurs.

It would be unnecessary to refer to this point at such length but for the fact that in using the steel slips we have found that when local action has started in certain areas, and the growths attached are rubbed off the surface of the slip, action does not always commence again in the same place. When the slip was polished with emery before replacing it in the liquid, the action never commenced at the same spots.

Finally, there is another very interesting reason why action is less likely to occur in boilers and closed vessels, and that is that it is unquestionably less energetic in the dark.

The figures we bring forward in support of this are neither so numerous nor so striking as we should like, but we have never made a single experiment in which the stimulating effect of light is not apparent—that is to say, in which the amount of corrosion has not been less in the dark than in the light.

The following table shows side by side the result of exposing the same kind of steel to the action of the same liquid for the same time in ordinary daylight and in absolute darkness. The figures represent as usual mgms. of Fe_2O_3 removed.

TABLE VII.

	Duration.	In the Dark.	In the Light.
Distilled water	12 hours	4·5	6·5
Tap-water	24 hours	7·5	13·5
Distilled water, MgCl_2 , 20 per 100,000	„	5·2	7·2
„ „ NaHCO_3 , 84	„	6·0	8·5
„ „ Na_2CO_3 , 53	„	5·0	7·0
„ „ $\text{Ca}(\text{HO})_2$, 9·2	„	7·2	11·5
„ „ NaHO , 4	12 hours	2·0	4·2
Distilled water	240 hours	9·5	39·5
New River water	„	21·7	56·0
Distilled water + 4NaHO per 100,000	360 hours	16·0	48·5

THE ANALYST.

237

The difference is considerably greater than would appear from the above, inasmuch as during somewhat less than half the total duration of the experiments (except, of course, the first) all the liquids were necessarily in the dark.

The further investigations we propose to undertake will, we hope, throw more light on this interesting point.

DISCUSSION.

The PRESIDENT (Mr. Bevan) said he should like to know more definitely how the authors accounted for the corrosion taking place in patches, except on the electrolytic theory, which, although their experiments seemed conclusive, he did not regard as being entirely disposed of. It would be interesting to know the actual composition of the iron, because, if the iron were chemically pure, it would be difficult to see how the action could take place in patches; while, if it were not chemically pure, it was pretty obvious that in certain places there might be a little more or a little less of one constituent or another, which, of course, would give rise to electrolytic action. In the case in which the corrosion took place on one side only, was the plate exactly vertical? Possibly the degree of exposure to light had some influence.

Mr. CRIBB said that he did not mean to imply that the action took place necessarily on one side only. It was curious, however, that this did sometimes happen. He did not think the difference with regard to light would be sufficient to account for it.

Mr. ARCHBUTT thought that it would have been better if the authors had started with steel boiler plate of known analytical composition, and had used strips from the same plate throughout the experiments. He also thought that it would have been better if the water had been freed from gases, as would be the case in a steam boiler. Although the authors had found corrosion to be so general in their experiments with alkali, whether in the caustic form or in the form of carbonate, he did not think that this was the case in actual practice, for, if it were, one would expect the boilers in the country generally to be in a much worse condition than they really were in. In certain cases, however, serious corrosion did occur from causes which at present could not be explained, and therefore any investigation which would help to throw light on these obscure causes would be useful. In a case within his knowledge in which pitting had occurred in boilers using Manchester water it had been remedied to a large extent by scraping out the magnetic oxide that had been formed in the pits, brushing these places over with petroleum, and using in the boilers about 1 pound of sodium carbonate per 1,000 gallons of water evaporated. The fact that this practically stopped the corrosion seemed to indicate that the action of the alkali in a boiler was not quite the same as under the conditions of the author's experiments. It might be mentioned that pitting and corrosion were nearly always local, pitting being sometimes so serious in boiler tubes as to result in holes right through the tubes. As a rule, in boiler plates also corrosion took the form of local pitting. He had at present under observation, however, an extraordinary case in which the barrels of locomotive boilers were corroded all over below the water-line. The boilers took water from several different sources, and all of these had been investigated, but no reason for the corrosion was at first apparent. No mineral or fatty

THE ANALYST.

acid could be traced as the cause. None of the waters were artificially softened, and no chemical or disinfectant was used in the boilers. The water of which the largest quantity was used came out of the Derbyshire limestone, and contained about 21 grains per gallon of total dissolved matter, including 7.55 grains of calcium carbonate, 3.99 grains of magnesium carbonate, 1.94 grains of magnesium sulphate, 4.74 grains of sodium sulphate, 1.19 grains of sodium chloride, and 0.95 grain of silica. The free carbon dioxide amounted to only 0.52 grain, and the dissolved oxygen to 0.66 grain. It would not be thought that such a water would seriously corrode boilers. He was, however, forced to conclude that such water was liable to corrode bare boiler plate, and that, unless the plates are protected by a scale, corrosion was more or less bound to occur. The scale which this water formed was particularly soft and porous, and did not protect the plates. It might be also that there was some organic acid in the water. Both of these causes would be met by softening the water with lime, which would remove the greater part of the carbonates but would leave the sulphates behind, thus encouraging the formation of a small quantity of thin, hard scale, whilst the excess of lime would neutralize any organic acid that might be present. An experiment on these lines now had been in progress for several months, and perhaps at some future time he might be able to communicate the result to the Society. Meantime he should be interested to hear if the authors could suggest any other explanation of the corrosion.

Mr. DIBDIN said that, in connection with the boilers at the pumping-stations of the London County Council, it was at first thought that magnesium chloride seemed to facilitate pitting as much as anything. This was particularly the case with some deep well waters, and especially with that from a trial well sunk at Crossness. The water there was brackish, and contained a good deal of magnesium chloride, derived, no doubt, from tidal water entering through a fault in the strata. The most effective preventive of this action on the boilers was found to be the use of an alkaline solution of tannin, made by boiling bark with caustic soda. The pitting seemed to take place with almost every kind of water, even when distilled in the ordinary process of condensation—New River water, tidal water, or water supplied, say, by the West Middlesex or East London Water Companies. He had often thought over the matter, but must confess that the only conclusion he had been able to arrive at was that the corrosion was due entirely to electrolytic action, and that it would, therefore, vary with the character of the iron. It seemed to him that, if the authors' experiments could be made in the reverse direction—namely, by taking varying quantities of iron and water of constant composition—a good deal of light might be thrown on the subject.

Mr. JULIAN L. BAKER suggested that, bearing in mind the medium in which the protuberant growths were developed, these possibly consisted largely of an anaërobic form of mould or bacterial growth. He should like to hear whether any of the experiments had been made under aseptic conditions.

Mr. CRIBB said that in every case where these growths developed in the cold they also occurred in the corresponding experiment at 100° C.

Mr. JOHN WHITE said that a short time ago he had submitted to him a piece of an iron branch water-main 3 inches in diameter. It had been used for about six

months for a fairly pure public supply, which, however, contained some vegetable matter. After that time the pipe had become so "made up" that a lead pencil would not pass through it. The only conclusion he could come to was that, as the water contained free oxygen and carbonic acid, oxide of iron was formed, which attached itself to the walls of the pipe, and this caused the deposition of organic matter as well. The deposit was not an ordinary incrustation; it contained about 60 per cent. of oxide of iron, the remainder being water and organic matter.

Mr. J. H. B. JENKINS inquired whether the authors stated in their paper the extent to which corrosion took place with New River water and distilled water respectively to which no alkali had been added. The addition of caustic soda to London water would form carbonate with the bicarbonate present in the water, so that at a certain stage there would be present only the normal carbonates of soda and lime. Perhaps the authors could indicate in the tables when that stage was passed, and caustic alkali could be assumed to be present in the water. He had noticed in examining polished steel sections microscopically that the sulphide dots or threads always found in commercial mild steels became nuclei for corrosion, by which the sulphide was decomposed. After rubbing such corroded sections afresh there would probably be no longer any sulphide spots left in the earlier positions, but others would be exposed at the new surface, so that the next points of corrosion would be expected to appear at fresh places. In connection with the experiments in the light and in the dark, he should like to hear whether the temperature was about the same in each case, because generally one would expect the temperature to be somewhat higher in the daytime.

Mr. CRIBB said that the results of experiments with New River and distilled water alone were given in Tables VI. and VII. He thought that the point when all the bicarbonate in the New River water was converted into carbonate would probably have been either reached or passed when 5 c.c. of $\frac{N}{10}$ alkali had been added. With regard to the experiments in light and darkness, various methods had been adopted to insure equal temperature or nearly so.

Either the dark experiment was made in an incubator at 20° C. (*i.e.*, was slightly warmer than the other) or the two cylinders were placed side by side, one being under a cardboard cover and the other exposed. He thought that the differences of temperature would in most cases be far too small to produce any appreciable effect on the results.

Mr. JENKINS, continuing, said that in the boilers of which he saw most—namely, locomotive boilers—the possibilities of galvanic action were undoubtedly great, because the fire-box inside the boiler was of copper. In nearly all cases, however, unless the water was quite soft, a protective scale was formed, which kept the water from contact with the metal surfaces. Very often they met with cases in which, if the scale had been broken or was not sufficiently hard to be impervious, galvanic action occurred. When pitting and corrosion took place, it was generally at those parts of a boiler where the circulation was least vigorous. He thought that this was due to the fact that in those places the gases which came out of solution when the water was heated remained in contact with the metal for the longest time. In a locomotive boiler this was generally below the level of the fire, near the foundation ring, or along the belly of the boiler.

THE ANALYST.

Mr. HERBERT E. BURGESS suggested that the local character of the action might be accounted for by the presence in certain places of a thin coating of grease. If the plate happened to be touched with the fingers, the grease therefrom would form a protective coating, and he suggested that it would be well to wash the metal with chloroform before the experiments were made.

The PRESIDENT thought that the peculiar pattern of the corrosion was against Mr. Burgess's theory.

Mr. CRIBB, in reply, said that he himself should be inclined to consider that these phenomena were due to electrolytic action were it not for the difficulties in the way of accepting that explanation. With a material like Siemens-Martin steel it must be due to the distribution of the different impurities (*i.e.*, substances other than iron) throughout the mass of the metal, and therefore, assuming that one alkali would have the same chemical action as another, there was no particular reason why different alkalies should produce different electrolytic effects; and therefore the patterns should be the same. They were, however, very different. As far as he knew, the distribution of the different constituents of steel was a microscopic and not a macroscopic matter, and therefore any patterns due to electrolysis might be expected to be microscopic and not macroscopic.

Mr. JENKINS remarked that lines of impurity, such as sulphide threads, would be found drawn out in the direction of rolling of the steel plate. This happened to be the same direction as the corrosion streaks developed in the author's experiments. Supposing that other strips were cut so that their long dimensions were *transverse* to the direction of rolling, would the direction of corrosion streaks be altered?

Mr. CRIBB said he had noticed with Siemens-Martin steels in the case of which the "skin" was allowed to remain on the front and the sides had been cut through, the local action took place on the sides as well. There was no connection between the pattern on the sides and that on the front. That was one of the difficulties standing in the way of the electrolytic theory. Practically the same character of pattern was obtained with different pieces of metal when the same alkali was used. With regard to the analytical composition of the metal, many of these experiments had been made a long time ago, when testing the value of the method as a purely empirical process for getting at the corrosive powers of different waters. The slips of metal used, however, were in all cases of the same composition, and they might be able to analyse one later on. Mr. Dibdin's suggestion would be rather difficult to carry out, as it was not easy to get in a convenient form samples of iron of varying and known composition. They had, however, been able to show that with actual steel boiler-plate the same phenomena occurred. They did not, of course, contend that every time an alkaline water was used in a boiler this local action would necessarily take place, and they had pointed out the causes which would be likely to prevent it. It was curious that, in spite of the widely-accepted opinion as to the corrosive effect of magnesium chloride, there was scarcely any evidence in its favour except that derived from the analysis of boiler waters themselves. A 1 per cent. solution of magnesium chloride, when heated, had no more action on metal than plain distilled or tap water. As a matter of fact, it did not decompose when boiled. He admitted that it apparently did decompose under high pressure, but he had not

been able to make any laboratory experiments under those conditions, except one or two conducted in an autoclave which, however, failed to yield any conclusive results. Mr. Jenkins's suggestion that the impurities formed nuclei which were removed by rubbing afforded a very reasonable and probable explanation. The rubbing, however, was very slight, and, moreover, the action, especially when it was beginning, was hardly of a nature suggesting the existence of nuclei,* inasmuch as it commenced in the form of patches without anything in the nature of a nucleus. It was only when the alkalinity was reaching its higher limits that small dots were produced. He did not think that grease could have had any influence in these experiments, because all the plates were systematically and carefully cleaned with emery, and were never touched afterwards except at the edges. The strength of the alkali, too, would in some cases be sufficient to saponify any slight traces of grease. He was afraid he could not suggest any explanation of the curious case of corrosion mentioned by Mr. Archbutt.

ADDENDUM.

Mr. Archbutt writes that, having by the courtesy of the authors been permitted to read the paper more carefully since the meeting, he does not feel convinced that the chief corrosive agent was not, after all, carbonic acid, the action of which ceased when the amount of alkali added was sufficient. The authors do not appear to have determined the amount of free CO_2 originally present in the water, and therefore it is impossible to say what relation the amount of alkali which was found to stop corrosion bore to the free CO_2 . Is it not possible that in highly-dilute solutions bicarbonates may be mildly corrosive to iron and steel, and need the presence of a certain amount of free caustic or monocarbonated alkali to restrain their action?

In the experiment with baryta, the amount added was just enough to neutralize 1.1 parts of free CO_2 per 100,000 parts of distilled water. Supposing more than this were originally present in the water, some of the barium carbonate may have been held in solution, and in the subsequent titration have neutralized acid. Therefore it seems that the experiment, as described in the paper, does not necessarily prove that the baryta removed all the carbonic acid.

To prove their case conclusively, the authors would need to show that distilled water which has been freed from every trace of carbon dioxide and oxygen by boiling, and has been prevented from reabsorbing any of these gases, is more corrosive to iron when slightly alkaline than when no alkali is added.

Referring again to the case of locomotive boiler corrosion, which had formed the subject of some of his previous remarks, he had within the last few days had an opportunity of inspecting two locomotive boilers, one of which had been supplied during the last nine months exclusively with the water of which the analysis had been stated, and the other with the same water after softening with lime. The difference in the appearance of the two boilers was striking. The boiler which had used the untreated water was already extensively corroded, whilst the boiler which had used the treated water was in very good condition, being only pitted in a few

* Since reading the paper experiments have been made with steel wire under the microscope, and most distinct evidence of nuclei, round which the action seemed to centre, has been obtained.

THE ANALYST.

places here and there. Both boilers at the commencement of the experiment were nearly new and quite free from corrosion.

Mr. Cribb, in answer to the first point in Mr. Archbutt's "addendum," writes that the solution in the experiment referred to was titrated directly, using phenolphthalein, which does not react with barium carbonate. Also that in Table II., Series 4, an experiment is recorded in which local action occurred, the barium hydroxide added being equivalent to no less than 5.5 parts of CO_2 per 100,000.

Water really free from CO_2 and O does not act on iron at all. The boilers referred to in the final paragraph obviously confirm the author's contention that local action and pitting may occur in actual practice when artificially softened waters have to be employed.

The action of the water of which Mr. Archbutt gave the analysis before treatment was probably due solely to the small proportion of dissolved gases. The water in boilers is always being reinforced with fresh feed-water, and consequently there is always enough gas in solution to cause action, either general or local. In this case there was not enough of the scale-forming compounds to form a protective coating.

