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## AUTO ELECTROLYSIS AND ITS RELATION TO THE CORROSION OF IRON AND STEEL.

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The destruction of metals by corrosion was frequently set down to the formation of rust, or oxidization, but recent experiments carried out in different centres had demonstrated beyond question that electrolytic action played a more important part in the corrosion of iron and steel structures than was previously thought. The action was most insistent in places secure from observation and no notice was given of its existence as a rule (unless careful and systematic inspection was practiced) until the material failed. With surface corrosion, however, such as was met with on bridges and other work of a like nature, the prevention of this action could be more readily undertaken by the removal of the rust until a clean bright surface was obtained and the further application of an approved protective coating. It was generally conceded that there were but two theories worth considering that brought about the decay or corrosion of metals, viz., the carbonic acid and the electrolytic theories, respectively, the first being the one which was, until recently, generally upheld.

It was with the latter, however, that this paper principally dealt.

The Electrolytic theory of rusting, or corrosion, assumed that before iron could oxidise in a solution ferrous iron must first pass into the said solution; this, of course, could only happen when a current of electricity flowed

through a conducting wet medium, or as it was technically known, an Electrolyte.

This phenomenon showed that during the passage of the current through the electrolyte, there was a distinct progression of the ions towards the electrodes (ions being atoms, or groups of atoms, which were charged with static electricity), the charges not being in themselves apparent, since they were always of an equal positive and negative nature; the positively charged ion was called the cation, while that negatively charged was called the anion. Thus, if the electrolyte was a weak solution of hydrochloric acid, the hydrogen ions would migrate to the electrode, when, after depositing their electrical charge, the hydrogen escaped to the air in minute bubbles. This action was illustrated in Fig. I.

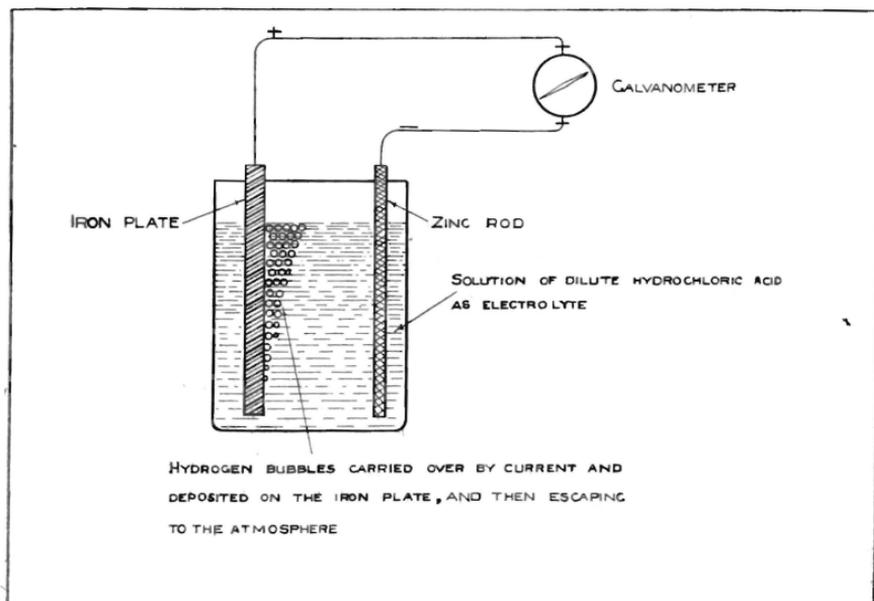


Fig. 1.

It was an established fact that every metal when immersed in water or subjected to moisture, tended to dissolve, some more rapidly than others, according to their

solution pressure; that is, the facility with which metal could enter into solution. A piece of iron immersed in water would have indications of what were known as polar areas, around which, it would be shown later by means of the now well-known "Ferroxyl" test, that an active condition existed; especially was this true of pieces of steel or iron that gave indications of having been strained, bruised or carelessly annealed.

In the assembling of structures entailing the use of angle and plate work, it was not infrequent to find that certain members were showing signs of rapid corrosion, while others, adjacent or in direct contact, presented an almost unblemished appearance.

Some interesting figures, shown in Fig. 2, and obtained by J. P. Snow, from an American Signal Bridge, were typical of these phenomena.

This was due to the electro negative material in the structure being protected at the expense of the electro positive. The importance, therefore, of restricting the use of different grades of iron and steel in the one structure should never be overlooked. It had not yet been definitely determined whether the strained portion of the strip of steel was electro positive or whether it was electro negative, but Burgess (Trans, Am. Elec. Chem. Soc., 1908) practically determined that the strained portion of a metal plate was electro positive and corroded much more rapidly than the unstrained part. This might account for the accelerated corrosion of some portions of boiler plates; more especially where feathering and abrupt bends were met with.

Uneven rolling of plates for important pieces of work, such as steam boilers, vessels under pressure and members of structures inaccessible to observation should be carefully eliminated, and rejected by responsible parties.

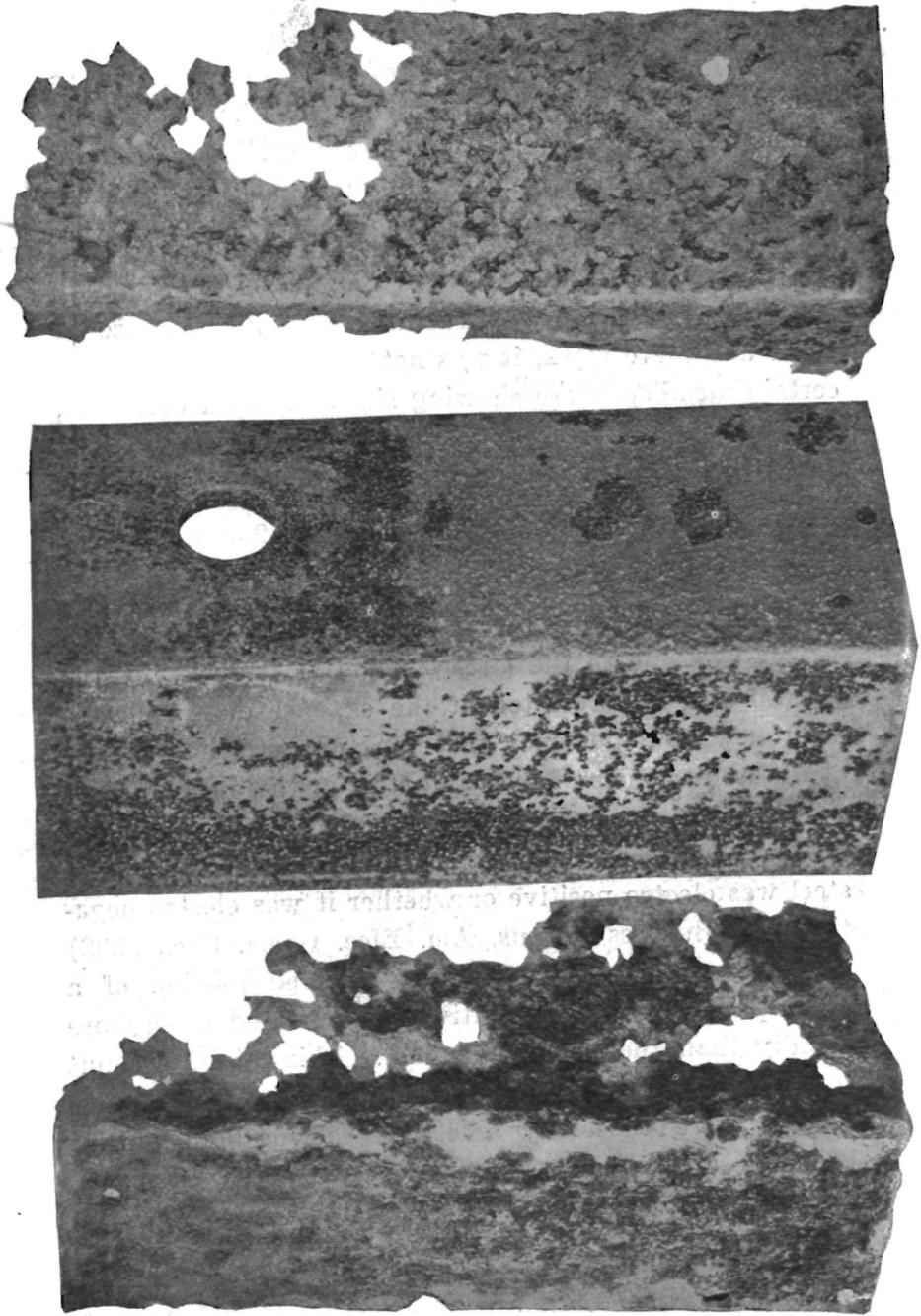


Fig. 2.

The careless bruising of plates should likewise be avoided, especially on the internal surface of shells of boilers, for there would at once be created a weak spot for the formation of an area liable to corrosion.

A reference to Fig. 6 would serve to indicate the reasons for this observation.

A piece of plate had an abrupt indentation on one side, and under the ferroxyl indicator the bruised part showed up blue, or electro positive, to the remaining surface of the plate. The specimen was really an exaggerated one that enabled them to see how a pocket could easily be formed for no apparent reason other than that "the plate had developed a weakness." Upon a close examination this would be found to be corrosion due to the above described cause, and the consequent bulging accompanying a weakened plate under pressure.

Before proceeding with a description of the result obtained by use of the Ferroxyl indicator the author thought that a brief explanation of the application of this most important adjunct to the engineer would be appropriate.

Substances which, when immersed in water showed a change of colour when subjected to a reaction, were called indicators.

In the particular instances referred to the substance phenolphthalein in the presence of hydroxyl ions turned a faint pink colour, and these ions were always found around a negative pole of a galvanic circuit after the hydrogen ions had disappeared.

This product could be relied upon to indicate the negative pole of a circuit.

In order to accentuate the effect of the Electrolytic action taking place on a piece of iron or steel, "Walker" added to the phenolphthalein indicator a trace of potassium ferricyanide, and gave them the beautiful effect

known as Turnbull's blue compound. He further demonstrated that by the use of gelatine a fairly permanent indication could be obtained: The following figures showed modifications of some experiments by "Cushman, Walker, and Bresch."

Figure 3 indicated a reversal of polarity from the ordinary, the bent wire nail in this case denoting that the middle portion has had the skin tightened by the

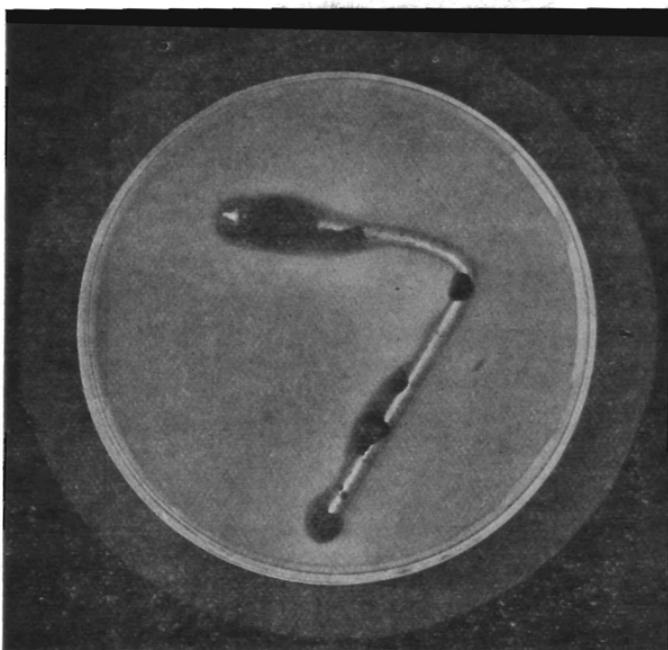


Fig. 3.

single bend. In other cases with a double and a treble bend this portion showed up blue, indicating that the metal had been strained beyond its elastic limit and went rapidly into solution.

Figure 4 showed the action taking place upon several ordinary wire nails. Here the positive nodes, as they were called, were distinctly indicated by the dark blue colour,

the negatives by the faint pink, which was really the hydroxyl ions indicated by the phenolphthalein.

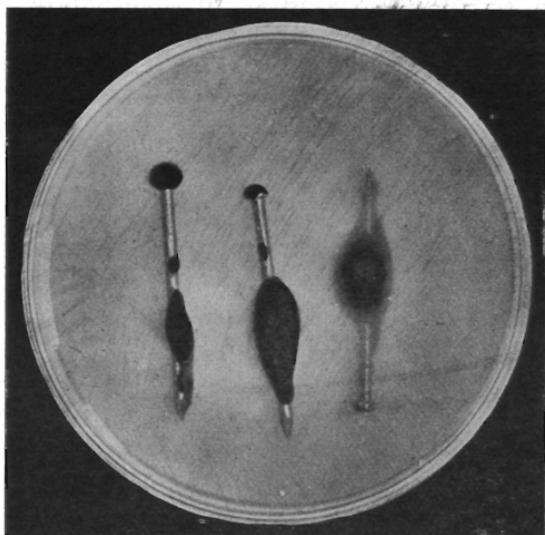


Fig. 4.

Figure 5 illustrated the comparative rate at which a piece of pure iron wire and a piece of hard steel would

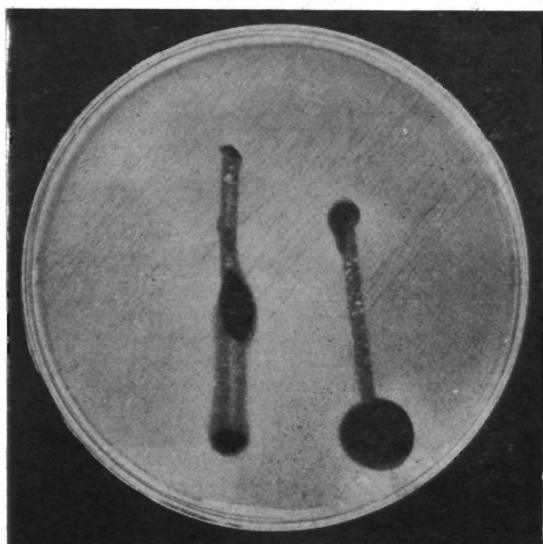


Fig. 5.

pass into solution, the difference in colour probably being an indication of the respective rate of each.

Figure 6 represented a piece of steel plate that has had the surface bruised or broken as previously mentioned.

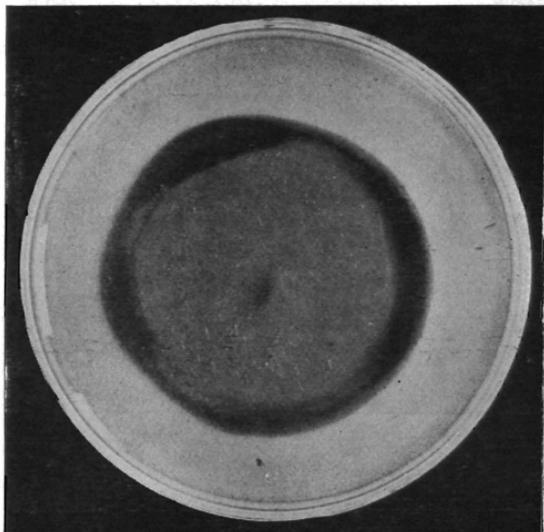


Fig. 6.

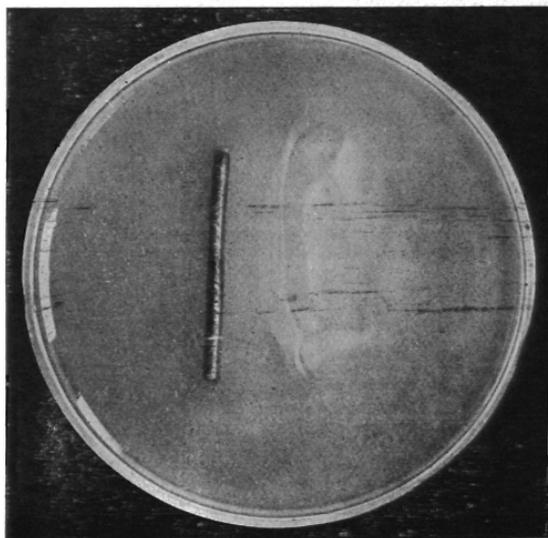


Fig. 7.

Figure 7 showed the protective action of a piece of zinc when connected as a couple to a piece of iron. It would be seen that the zinc was going into solution (indicated by the white area, which was zinc oxide), while the iron strip was being protected. This action would continue until the zinc was exhausted, when the iron would be attacked.

In Figure 8, two iron wire nails were placed on either side of a copper strip, and it would be seen that the nails were going into solution at the distinct nodes of positive

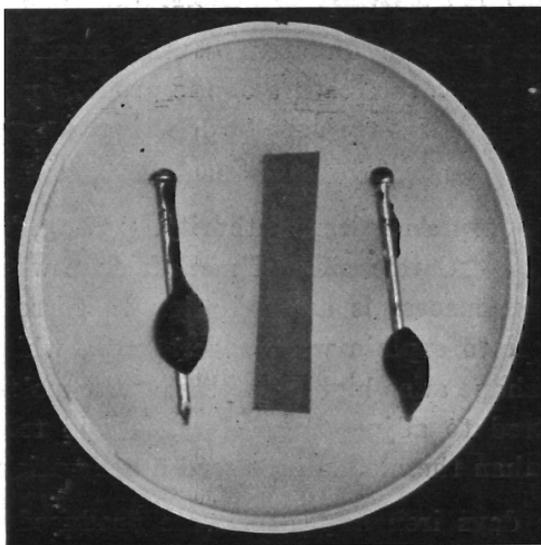


Fig. 8.

potential. If the nails were in direct electrical connection with the copper as the zinc and iron were shown to be in Fig. 6, then there was no doubt but that the whole area of the nails would show up the blue colour.

The foregoing remarks on the ferroxyl test would clearly show that at certain points, compared with others, on iron or steel surfaces, there existed a difference in the solution pressure, or that these parts were electro posi-

tive to others and that electrolytic action could be made to appear visible.

It was a popular theory that the present product of the steel furnace was less resistant to corrosion than the iron or steel of 50 years ago; but who could say that modern conditions had not also something to do with this state of affairs? Superabundance of sulphuric acid from waste gases or the introduction of the electric railway and lighting system into a city, and the consequent leakage from the same no doubt must have a bearing upon this debatable subject; but they could not get away from the fact that the methods of manufacture had a strong tendency to produce quantity at the sacrifice of the quality which was the feature of the production of many years ago, before international trade rivalry sprang into operation.

A well known American authority, "Sang," said on this subject:—"Carelessness of manufacture which tends to heterogeneousness is an invitation to corrosion, and in itself goes to explain why modern steel, which is tortured into shape at so high a speed that the molecules are not permitted to adjust themselves, is said to be more corrodible than the metals produced a generation ago.

In those days iron and steel were produced in small quantities without the addition of other metals, and were rolled slowly and allowed to cool naturally.

Moreover, the tonnage craze from which the quality of products in so many industries to-day is suffering, is causing to be put on the market a great mass of material only a small portion of which is inspected."

However, a reaction was now taking place, and there was every reason to believe that a metal now being manufactured by certain firms with the following ingredients—

Carb.	Mang.	Sul.	Sil.	Phos.
.015	.020	.017	.0	.002

or with a total of .054 per cent. of chemical impurities—would resist corrosion as well as the forged iron made years ago.

In fact, a metal called “No-Co-Ro” was said to possess the following distinctive features as against ordinary steel and charcoal iron:

The test of this material, set down in Table I, was commonly called the acid test, but too much reliability should not be placed on the conclusions arrived at by the use of it, for since corrosion was only a surface action depending upon the removal of the hydrogen from the said surface, it could easily be seen how even a slight trace of impurity, e.g., arsenic, would slow down the solubility of the iron to a marked extent.

Table I—Twelve Hour Corrosion Tests.

	In Sulphuric Acid.	In Hydrochloric Acid.
Steel	$\left\{ \begin{array}{l} 15.1220 \\ 7.6360 \\ \hline 7.4860 \text{ Loss} = 49.50\% \end{array} \right.$	$\left\{ \begin{array}{l} 15.7900 \\ 8.2850 \\ \hline 7.5050 \text{ Loss} = 47.53\% \end{array} \right.$
Charcoal Iron	$\left\{ \begin{array}{l} 17.4840 \\ 14.7930 \\ \hline 2.6910 \text{ Loss} = 15.33\% \end{array} \right.$	$\left\{ \begin{array}{l} 15.0620 \\ 13.1673 \\ \hline 1.8947 \text{ Loss} = 12.58\% \end{array} \right.$
“No-CO-Ro” Metal	$\left\{ \begin{array}{l} 17.4720 \\ 17.3930 \\ \hline .0790 \text{ Loss} = .452\% \end{array} \right.$	$\left\{ \begin{array}{l} 20.7900 \\ 20.4050 \\ \hline .3850 \text{ Loss} = 1.85\% \end{array} \right.$

Again, the action of even a dilute acid was rapid in comparison with the slow rusting that accompanied corrosion under natural conditions.

The question had frequently been put to the author, as to whether a reliable acceleration test could be obtained, but he could say that most authorities seemed to agree that such a test had yet to be found. Corrosion

was a comparatively slow process, and any attempt to hasten the process by artificial means would surely result in the production of an entirely different phenomena.

Notwithstanding the many points which were still the subject of controversy, all investigators appeared to be of the opinion that iron would not rust in water unless oxygen was present, and unless water was present rusting would not take place in air or oxygen.

Rain water and mist showed great activity in the oxidisation of metals, and water when saturated with air was strongly corrosive to iron and steel. This point had a very strong bearing upon the corrosion of boiler shells and tubes; pitting could be probably entirely avoided if the air could be removed from the feed water prior to its entering the boiler. This could be best brought about by the use of open feed water heaters, connected to the dry vacuum pumps of the condenser—by the use of slow-running automatic pumps or, as was the recent practice in the Navy, the use of high-pressure centrifugal pumps.

It would have been noticed that corrosion was very pronounced at what was known as the "water-line" or when the metal was subjected to alternately wet and dry spells, as at the water-line of iron columns, ships' bottoms, and boilers, etc.

This was due to the water in contact with the atmosphere being largely saturated with oxygen and a corresponding increase in the corrosive action on the metals. A deeply-buried metal would rust if there were free oxygen present, but after that had been consumed, as it were, and no further supply maintained, rusting would cease.

This had often been proved by the removal of old pipes, etc., that had shown remarkable preservation.

Again, other pipes corroded rapidly and caused no end of annoyance to the user. The exhibits shown of corroded pipes would convey a good idea as to what extent corrosion would extend; the  $1\frac{1}{4}$  in. pipe shown in Fig. 9 was fouled up completely and presented a remarkable appearance on one side where electrolytic action had surely taken place. The  $\frac{3}{4}$  in. shown in Fig. 10 was

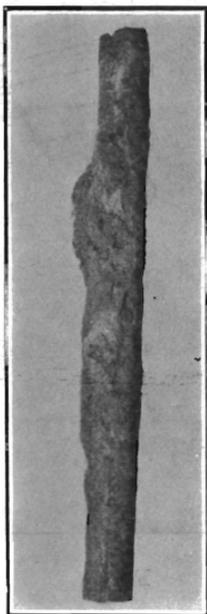


Fig. 9.

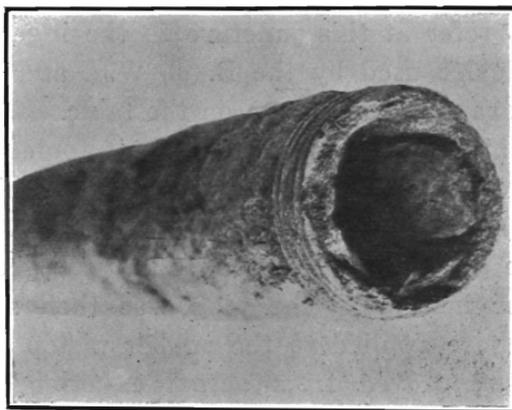


Fig 10.

one taken up after a short term of service, having fouled or corroded up on the inside only in this instance. The heap of nodules illustrated in Fig. 11, and coated with

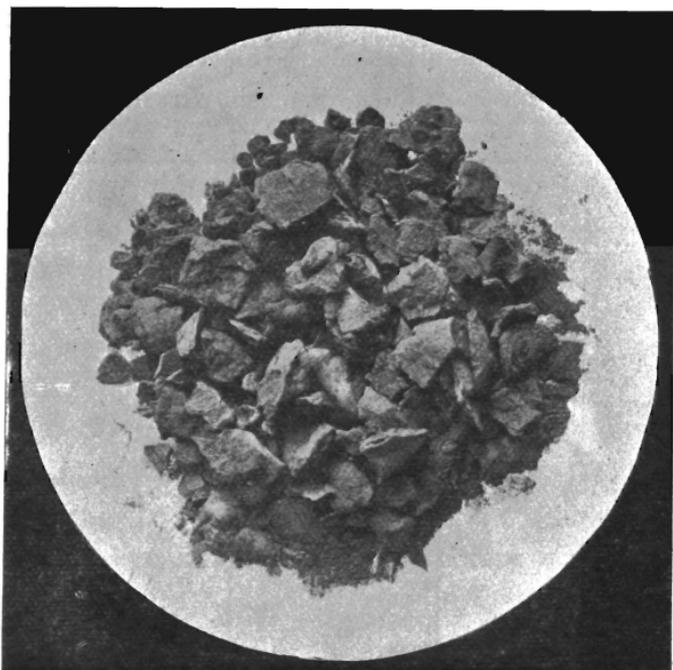


Fig. 11.

ferrous hydroxide, had been taken from a 4in. pipe after six years' service in the tropics. It might be of passing interest to refer at this juncture to the ingenious pipe-cleaning device used by the B. of W.S. and S., and of which an example was shown on the table. This apparatus was claimed to clean pipes even if fouled to 60 per cent. of the pipe area. The operation of cleaning was as follows: The pipe was broken somewhere above the position where the stoppage or restriction was greatest, and the cleaner inserted. The pipe was then sealed, and water pressure applied to the rubber piston as it were. It had been proved from actual experience that the cleaner then progressed with the stream of water in the

pipe, breaknig off and turning the scale and other matter into a soft slurry which was readily discharged with the water from the nearest hydrant. A thorough cleaning once every five years was said to be sufficient in this city's service, and the largest size main could be as easily cleaned as a small 4in. bore branch line.

Interest naturally centred upon the action that strong currents from such sources of power as tramway circuits, electric lighting and other power lines would have upon the various pipe systems in a city like Sydney, but investigation at the various centres seemed to point to a clear record as far as interference from these sources was concerned. No direct evidence could be ascertained that corrosion due to either the tramway or lighting systems existed. This was no doubt due, especially in the case of the earthed tramway circuit, to the excellent system of negative feeders and well bonded connections that the authorities maintained.

Too much credit could not be given to those who controlled these systems for the excellent results so far attained.

The modern ferro-concrete structures that were now being erected throughout the world needed to be carefully watched for fear of electrolysis taking place due to the stray currents mentioned, and tests should be periodically carried out with instruments capable of detecting extremely small differences of potential. It was at local points of increased potential that trouble was likely to occur, for currents as low as one millovolt actually hastened corrosion. Figures 12, 13, 14, were typical examples of what would happen if reinforcing happened to be in contact with a lighting or power circuit; at the anode of the circuit the concrete was blistered and finally thrown off, leaving the iron exposed. Upon a close examination of the parts a film of rust would be found directly

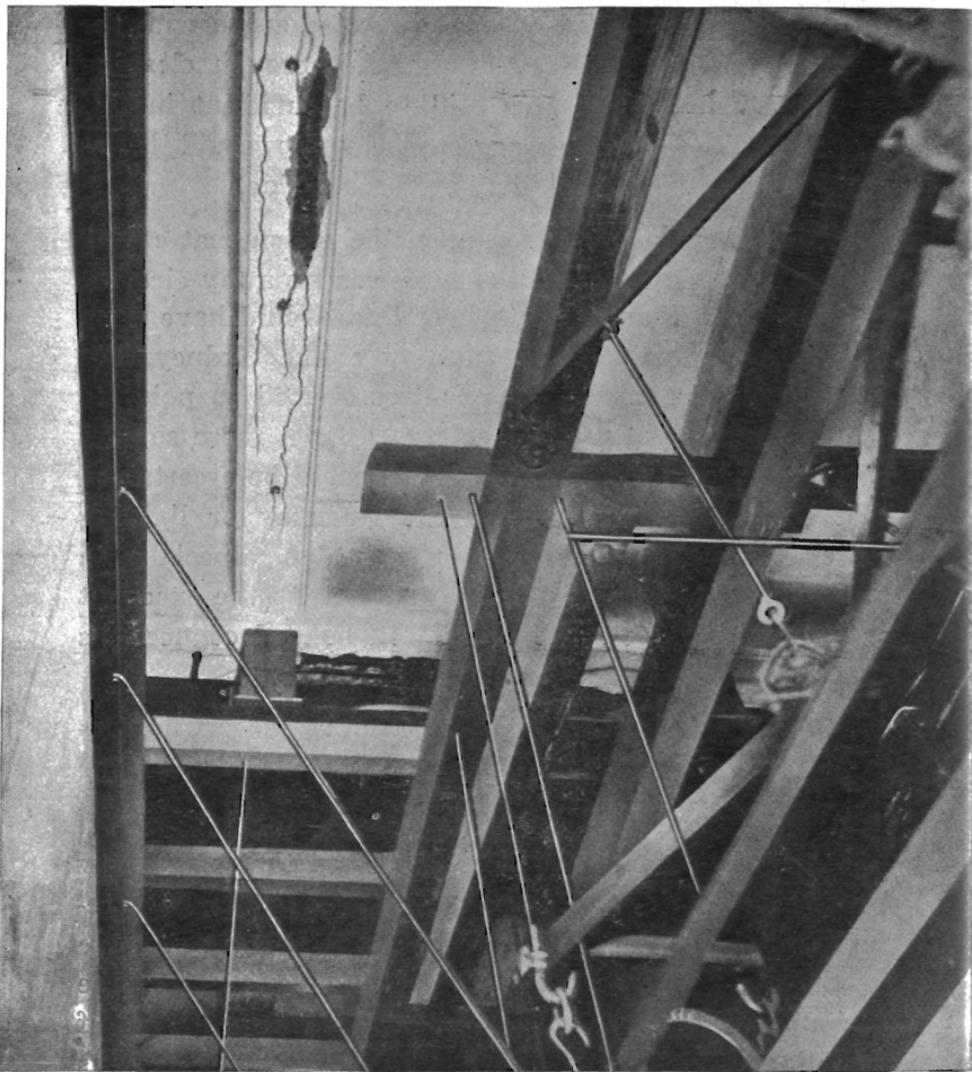


Fig. 12.

in contact with the metal, and it was the expansion of the gases that caused the segregation of the concrete, and the ultimate destruction of the member. So far as could be gathered no great damage had yet been caused by such an occurrence, but this was no doubt due to this type of building construction being fairly