Fig. 13

modern. Some interesting specimens of corrosion furnished the author by the Sydney Harbour Trust, and taken from structures under their supervision, were here shown. The two iron service bolts were originally
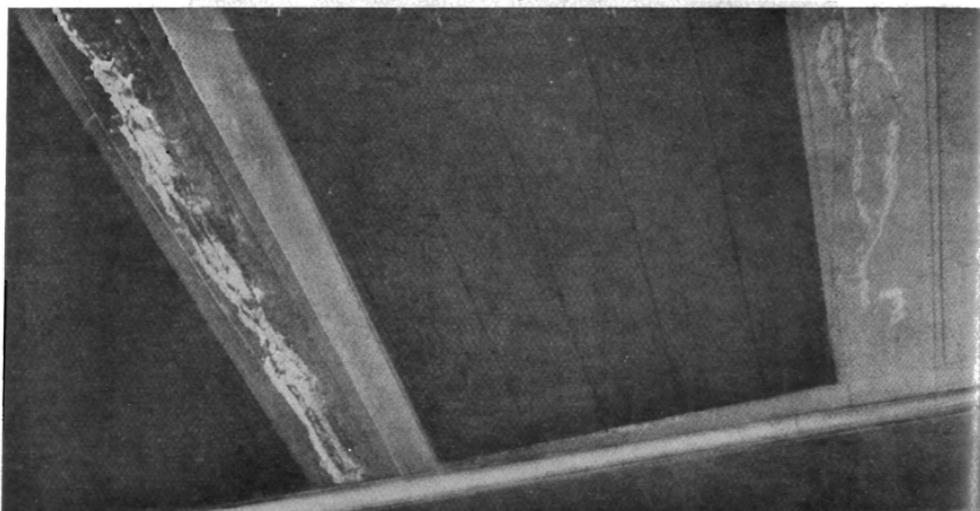
Fig. 14.

⅞ in. in diameter, but had been reduced by galvanic action to a diameter of ⅛ in. These bolts were temporarily placed through double walings which were sheathed with yellow metal, and the bolts were withdrawn after having been only two months in salt water. As an instance of accelerated corrosion this would be rather difficult to beat, and it was no doubt caused by the proximity of the yellow metal sheathing referred to. The portion of yellow metal bolt shown was one drawn from the old Pyrmont Bridge, after nine years' service in salt water. All the bolts of similar metal drawn from this structure and put in at the same time exhibited the same brittle nature as this. Other samples of corroded sheathing were also to be seen, the state of the metal in each instance being practically a record of the length of service each had seen.

To show the behaviour of metals in brine, tests, by M. B. Smith, had been conducted, covering not less than 100 days—in some cases a year or more—to allow full time for the reactions. The metals were

only seven-eights immersed in brine, as this simulated a condition very general in practice. The test pieces were $3\frac{1}{2}$ x $1\frac{1}{4}$ in. in size. The brine was renewed every seven days. The change in weight of the metals was noted at frequent intervals, and calculated in terms of change in weight per unit surface exposed to the action of the brine. The results of such tests on single metals were shown in Fig. 15, the curves representing the general or average behaviour of the respective metals in calcium brine at about 73 deg. F.
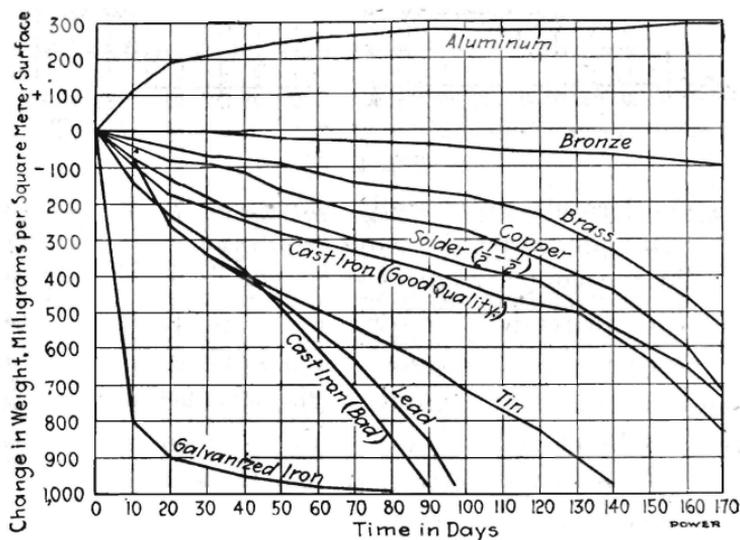

Fig. 15.

Another chart, reproduced in Fig. 16, showed the results from a number of metals soldered together. The solder seemed to exert an effect similar to that shown by the zinc of galvanized iron, inasmuch as the solder went into solution in each case. The reaction on the metals other than solder was slight, compared with the effect on the solder. The combinations of dissimilar metals showed much greater losses than did those of similar metals. These tests were of nine months' duration, only 170 days' tests being shown on this chart, since
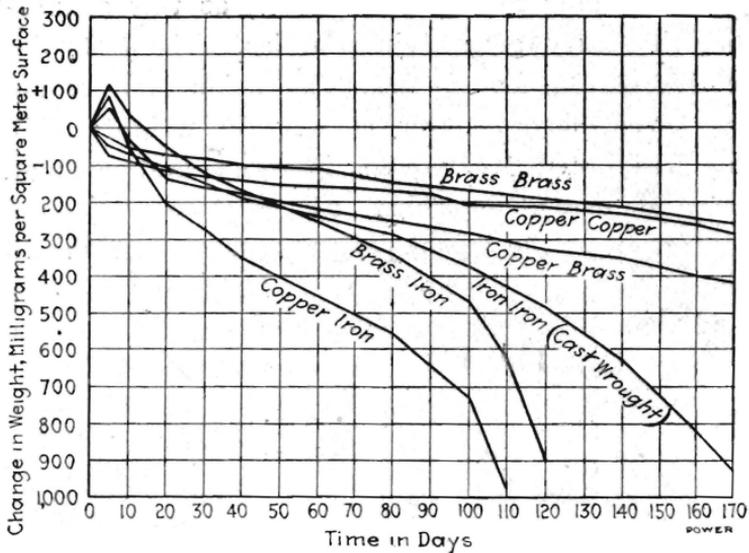
Fig. 16

the general results were well defined during this period. The brass-iron soldered couple continued to show less than did the copper-iron soldered couple in these tests.

In order to render the surface of iron plates or steel inactive or reduce the same to a passive state many expedients had been attempted. Those substances which developed hydroxyl ions in solutions, provided the concentration was sufficiently high, would prevent the rusting from taking place. Certain solutions of chromic acid and potassium bichromate also had the same effect. The use of the latter would keep the surface of iron passive for a considerable length of time, but it would eventually go back to its natural state and rust if left alone. They might now state from the various reasons set down here and elsewhere that the factors which stimulated corrosion were:—

1. Impure and segregated metal. Unhomogeneous or burnt metal which might contain blow holes.

2. Cold rolled or improperly annealed metal which might maintain an uneven, stressed or strained condition.

3. Contact action in which different types of iron and steel were used in one and the same structure.

4. The presence of hydrogen ions from any source whatsoever that might be brought in contact with the surface in water or in other electrolytes, in the presence of oxygen.

5. The concentration of active oxygen that was present in the wetting medium.

6. The presence of electrolytes generally in the wetting medium. Even hydroxyl ions and other inhibitors might appear as stimulators if in insufficient concentration.

7. The stimulating or depolarizing effects of certain coatings applied to iron and steel with the object of protecting the metal.

8. The effect of indentations, scratches or other injuries which became centres of corrosion.

9. The effect of extraneous or stray currents escaped from high potential circuits.

FACTORS WHICH INHIBITED CORROSION.

1. In most cases the reverse of conditions which stimulated corrosion.

2. Contact with certain substances in solution such as chromic acid and its soluble salts which produce a passive condition.

3. Alkaline solutions of all kinds in which the concentration of hydroxyl ions was sufficiently high, but this protection might be overcome and the equilibrium conditions reversed in very strong boiling alkaline solutions.

4. Contact with more electro positive metals.

5. Electrolysis under certain specific conditions and those which inhibited corrosion.

Regarding the last item, viz., the use of electrolysis for the prevention of corrosion of iron and steel, it might be of interest to members to hear the results of some experiments carried out by the author in collaboration with Dr. G. Harker, in July, 1910, at the instance of the Colonial Sugar Refining Co., to see if protection by the action was possible. The experiments were carried out on the principle of the Cumberland process, which consisted of the placing of an insulated bar of wrought iron suspended in a boiler to act as the anode, and a current of electricity of about 2.4 amperes at the pressure of about 8 volts being passed via this bar through the water to the shell, the latter acting as the cathode of the current.

In Table 2 were set forth the results of some preliminary experiments carried out with small iron and steel plates 1½in. x 1½in. x ⅛in. A small storage battery was employed for the supply of the current which during the series described in Table 2 was delivered at a pressure of 3.3 volts. The resistance of the circuit given in the second column of the table was made up of that of the solution plus that purposely supplied from a Standard Resistance Box (Fig. 17). The anode and cathode plates were placed 5cms. apart in a beaker, with about 115c.c. of solution, and the resistance between the plates was found to be about (3), (22), and (370) ohms. for sea water, acid solution and ordinary tap water respectively. The alteration of resistance during the process of the experiments, owing to a change in the composition of the solution, was only of moment in the case of the two experiments in acid solution using iron anodes and no account was taken of it in these preliminary trials.

For purposes of comparison it should be stated that the corrosion of the steel and iron when simply placed
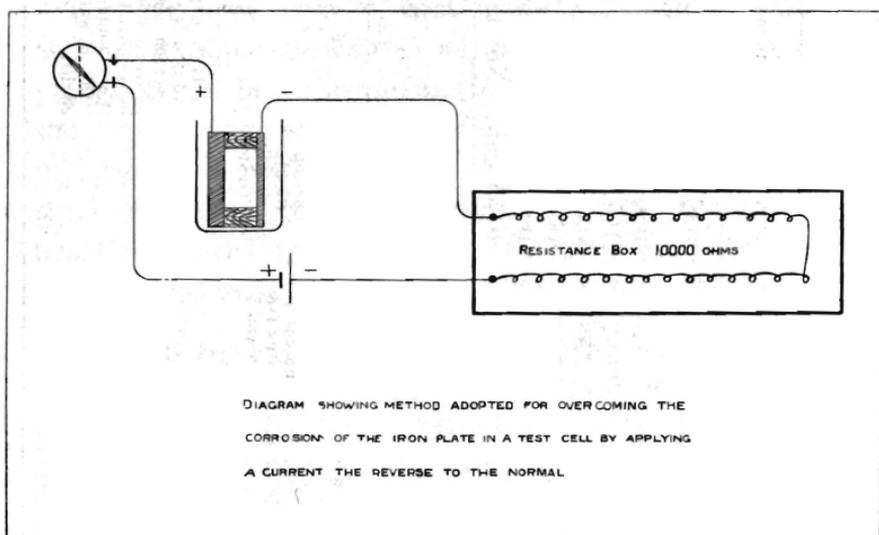
DIAGRAM SHOWING METHOD ADOPTED FOR OVERCOMING THE
CORROSION OF THE IRON PLATE IN A TEST CELL BY APPLYING
A CURRENT THE REVERSE TO THE NORMAL

Fig. 17.

in a beaker for 24 hours with about 115 c.c. of solution
was found to be:—

	Steel.	Wrought Iron.
Acid Solution	.08	.01
Sea-water	.0033	.0032
Ordinary Water	Not Taken	.0028

Different pieces of steel made from the same plate gave
very varying results but the figures were a sufficient
average for purposes of comparison.

The results given in Table 2 showed that the corrosion of
wrought iron and steel in ordinary water or in sea-water
could be prevented—as judged by constancy of weight
of the cathode piece—by even small currents when iron
was used as the anode. In acid solution no loss of weight
took place with a current of 0.15 ampere with iron as
the anode, but with platinum as anode the current did
not wholly protect the cathode, and reference would be
made to this later. In the sea-water experiments a green
coating of ferrous hydroxide nearly always formed on
the cathode, and the difficulty of removing this no doubt
accounted for the slight gain of weight observed in some
cases.

TABLE II.

	Solution.	Resistance of Circuit.	Current in Amperes.	Anode.	Cathode.	Loss of Weight of Anode, gms.	Loss of Weight of Cathode, grams.	Time in hours.
A	$\frac{4N}{100}$ Sulphuric Acid	22 ohms.	·15	Platinum ...	Steel	...	·0036	24
B	do.	do.	do.	do.	Wrought Iron	...	·0060	21
C	do.	do.	do.	Wrought Iron	do.	9·662	·0107 gain	5
D	Water from Tap ...	370 ohms.	·009	do.	do.	·1537	·0038	20
E	Sea Water	3 ,,	1·0	do.	do.	7·5721	·0010 gain	6
F	do.	30 ,,	·1	do.	do.	1·3967	0·0	17
G	Dilute Acid ...	22 ,,	·25	do.	Steel	·5921	·0155 gain	Not taken

TABLE III.

	1	2	3	4	5	6	7	8	9
	Solution.	Resistance of Circuit.	Voltage of Battery.	Current in amperes calculated from 2 and 3.	Time in Hours.	Loss of Iron Anode, Grams	Current calculated from 5 and 6.	Loss on Cathode (Steel cylinder) Grams.	
A	$\frac{4N}{100}$ Sulphuric Acid	414 – 454	3·8	·00918 to ·00837	72	·7218	·0096	·52	In both exps. C. and D. a deposit of greenish ferrous hydroxide had to be removed from the cylinder. In "D" it was very slight.
B	do.	14 — 60	3·8	·27 to ·063	18	1·2663	·067	·25 gain	
C	Sea Water... ...	40	4·0	·01	72	·8328	·0111	...	
E	do.	1000	4·0	·004	72	·3058	·0041	...	
D	do.	1500	4·0	·0027	72	·2094	·0028	·03	

The experiments were first made with acid solutions as information was wanted as to whether Cumberland's process could be of use in protecting boilers if fed with sour water from sugar factories. The results appeared in Table 3, and although the acid solution used was of much greater strength than would ever be met with in practice, it was quite clear that the steel cylinder could be protected by using currents of quite moderate strength.

In the first experiment 400 ohms resistance was added to the circuit from the Resistance Box in order to reduce the strength of the current to about 0.01 ampere, in the second the resistance of the cell only was employed.

The alteration in the resistance of the cell owing to solution of iron was shown by the second resistance figure.

An interesting point brought out by these experiments was that the quantity of current actually used, calculated from the voltage of the battery and the resistance of the circuit, was approximately equivalent to the current calculated from the amount of iron removed from the anode. The electrochemical equivalent of iron was .00029 grams per sec. per ampere, in other words 1.040 grams of iron were carried by a current of one ampere per hour, and hence from the loss of iron from the anode it was possible to calculate the current flowing. This suggested that, in applying Cumberland's process it might be possible to determine the strength of current for any given case by finding the rate of corrosion of the steel in the given solution, and then calculating from the electrochemical equivalent of iron the opposing current required.

Some experiments were carried out (see Table 3) with the object of finding out the amount of current required to inhibit the corrosion of the plate in sea-water, and also of determining whether the quantity was the same as that calculated by the method just described.

The cylinder was first immersed in sea-water for 72 hours and was found at the end of that time to have lost 0.3 grams. Assuming that, in order to keep the iron from dissolving, an amount of electricity had to be passed through the circuit equivalent to that produced by the dissolution of 0.3 grams, they found that 0.288 amperes were required, necessitating a current of .004 amperes per hour for 72 hours.

Three experiments with sea water, "C," "D" and "E" were performed, using currents of .01, .004, and .0027 amperes respectively. According to the above theory the first current should be larger than necessary to prevent corrosion of the steel, the second about correct, and the third too small. And this proved to be the case.

In the first experiment the steel was completely protected, but the current employed was much larger than necessary, and the excess of iron removed from the anode formed a greenish mud of ferrous hydroxide which partly remained on the cylinder. In the second experiment the strength of the current seemed to have been judged very correctly. The plate was quite protected and very little ferrous hydroxide was formed. In the third experiment the current was weak. No ferrous hydroxide was produced, and the cylinder lost slightly in weight. It therefore seemed likely that in employing Cumberland's process the current required to prevent corrosion could be obtained by observing the rate of corrosion of the iron or steel vessel under the given conditions. A current somewhat in excess of that calculated should be employed so as to make certain of protecting the vessel. In the case of a boiler it would, of course, not be possible to determine the loss directly, but if a sample of the steel of which it was made was obtainable the rate of corrosion of this sample in the given liquid under somewhat similar conditions could be ob-

tained, and the current necessary to prevent the corrosion of the sample determined. The current required for the boiler compared with that for the sample, would bear a fairly direct proportion to the area of the boiler surface exposed to the liquid as compared with the area of the sample, and consequently the current required to prevent the corrosion of the larger vessel could be determined. Assuming that the steel of a boiler would corrode at a rate equal to the rate of corrosion of the experimental steel cylinder in sea water, and that the surface exposed to the water was 2500 square feet, then the surface of the cylinder being 1.25 sq. feet, the current required would be $\frac{.004 \times 2500}{1.25} = 8$ amperes. This figure was somewhat higher than Cumberland's estimate of 1 to 2 amperes at 4 to 8 volts pressure, but it must not be forgotten that in determining the rate of corrosion of the experimental cylinder there was free access of air to the sea water, and this effect might possibly outweigh the influence of the higher temperature of the water in a boiler. Sea water was also more corrosive than ordinary boiler water, and it was quite probable that Cumberland's estimate of 1 to 2 amperes was not too low, but naturally a good deal would depend on the nature of the feed water and the material of the boiler itself.

Up to this time the explanation put forward by Cumberland that by making the plate to be protected the cathode positive ions of iron were prevented from entering the solution appeared quite satisfactory; the only disturbing experiments were those in which platinum was used as the anode, in which, although the current employed was far in excess of that required to protect the plate, corrosion still took place to a slight extent. To obtain further information on this point some experiments were conducted with zinc. A rod of zinc was

placed in a small beaker filled with $\dfrac{N}{5}$ H_2SO_4 and its
rate of solution determined by immersing it for one hour
and then re-weighing it. It was then connected to the
negative pole of the battery through a suitable resistance
to, and a strip of platinum was connected to the positive
pole; the two were then immersed and left for one
hour. Even when a current was used three or four times
as strong as that calculated to be sufficient to prevent
corrosion the rate of corrosion was only diminished to
about half its previous value. Thus a rod of zinc was
found to behave as follows:—

                                        Loss in weight.
                                          Grams.
Immersed 1 hour without current .. .012 ⎫
                  using   ,,   .. .0064 ⎭ 1st test.
                  without   ,,   .. .015 ⎫
                  using   ,,   .. .0092 ⎭ 2nd test.

The temperature only varied from 15° C. to 15.5° C.
The electrochemical equivalent of zinc being 1,22
grams per hr., the current required for .015 gram would
be about .012 amperes, while that actually employed was
nearly 3 times as great. When a zinc rod was substituted
for the strip of platinum as the anode a gain of .002
gram was obtained in one hour, and this gain would
have been much greater if the effectiveness of the cur-
rent had not been reduced by the solution of zinc from
the anode itself.

In another experiment in which the zinc dissolved more
rapidly the rate of solution was determined in two suc-
cessive experiments to be .2774 and .2786 grams in 30
minutes. The current required was calculated, the re-
sistance, about 8 ohms in this case, adjusted so as to
give a current just slightly in excess of that calculated,
and a zinc anode was used, presenting a much smaller
surface than the cathode. The anode lost .3412 grams

in 30 minutes, while the cathode lost only .0264 grams and would doubtless have been completely protected but for the solution of some zinc from the anode by the action of the acid.

It was thus clear that in the case of zinc, as in that of iron, the weight of the cathode could be maintained by a current calculated from the actual corrosion of the cathode in the given solution, provided that the ions of the anode were carried through the solution. If a larger current than that calculated be employed the deposition from the anode would increase the weight of the cathode. In all the experiments with iron and zinc anodes the cathode metal was dissolving, but its weight was being made up at any rate in the acid solutions by deposition from the anode, and this was clearly demonstrated in the last zinc experiment described, in which the deposit of zinc on the cathode derived from the anode could be plainly seen. During the progress of the experiment the cathode was dissolving in the solution and giving off hydrogen gas just as freely as when it was immersed in the acid solution by itself without any current passing. That the iron or zinc should be dissolving from the cathode while simultaneously deposition of the same metal was taking place seemed rather strange at first sight, but was not so when they considered the action which took place when a piece of iron was immersed in a solution of copper salt. Here the ions of iron passed into solution and the copper ions took their place.

That the passage of a current was in itself not sufficient to keep the cathode protected was shown by the experiments with iron and zinc in which platinum was used as the anode. At the same time the connection of the iron or zinc to the negative pole of the battery did diminish the solution of the metals, but the diminution was much more marked in the case of iron than zinc.

If they took it that the piece of steel used in the first experiment described in Table (2) would have lost .08 gram in the acid solution if left to itself, then since only .0036 gram was lost when a current of .15 amperes was employed, the loss of metal was under 5 per cent. of what it would have been in the absence of the protecting current. Probably it would be possible in the case of both iron and zinc, by sufficiently increasing the voltage, to prevent the solution of the metal completely; but the process would be too expensive to apply on a large scale. The deposition of hydrogen ions from the platinum anode would undoubtedly tend to protect the cathode from the action of the acid, and, furthermore, after the iron or zinc had reached a certain concentration in the solution there would probably be a tendency for the current to re-deposit them on the cathode.

During the progress of the first experiment described in Table (2) 5 c.c. of solution was taken from the beaker at intervals and tested with potassium ferrocyanide in order to determine whether the quantity of iron in solution continuously increased or whether it reached a certain concentration and then remained stationary. The first test was taken a few hours from the beginning of the experiment and showed the same amount of iron as in all the subsequent tests, proving that only a certain quantity of iron passed into solution. In the experiments with the steel cylinder in sea water it was found impossible to weigh the cylinder with certainty with an accuracy greater than .015 gram. Furthermore, the passage of a current through sea water generated sodium hydrate which would not only tend to reduce the corrosion of the cylinder itself but would also precipitate iron ions passing from the anode. It was therefore doubtful in these experiments whether any iron was deposited on the cylinder itself, but, even making allowance for the

occurrence of experimental errors in the weighing, the loss from the cylinder could only have been very slight.

Although the experiments described had shown that Cumberland's process did not actually prevent metal from entering the solution from the cathode, but that, where the weight remained constant, deposition was taking place from the anode, still the tendency of the metal to pass into solution was much diminished. Whether or not the deposition of fresh metal from the anode took place evenly over the surface of the cathode, forming a coating which might continually be removed and so protect the main body of the metal, was a matter which could only be decided by further investigation.

In connection with factor No. 4 in the series of inhibitors it was on record that a large saltwater pump gave considerable trouble due to corrosion of the C.I. body near the G.M. valve plate until one day a steel spanner was accidentally enclosed and left in contact with this plate. The next overhaul of the pump disclosed that the corrosion of the C.I. body had been arrested but that the spanner had pretty well disappeared, for evidently being more electro positive than the cast body of the pump, it went into solution, so protecting the same at the expense of its own life.

It was not the author's intention to discuss the use of protective coating, pigments, etc., as this was a subject on which much could be said and was deserving of special thought.