

## Birmingham Section.

Meeting held at Birmingham University, on Thursday,  
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MR. HARRY SILVESTER IN THE CHAIR.

## CORROSION OF INDUSTRIAL IRONWORK.

BY A. R. WARNES AND W. S. DAVEY.

We thought that a short paper dealing with some of the most important cases of corrosion of iron which have come under our notice, would stimulate other workers to publish their experiences and so ventilate a matter of extreme interest and importance to those connected with the chemical and engineering industries.

Considering its importance, the literature on the subject of industrial corrosion of iron appears to be very scanty:—R. Petit (Compt. rend., 1896, 123, 1278; this J., 1897, 128) mentions that iron is acted upon by very dilute solutions of calcium chloride, sodium chloride, potassium sulphate and calcium nitrate, and that the action becomes more pronounced in the presence of carbon dioxide. Carulla, in a paper on the "Corrosion of iron by raw tar," read before the Nottingham Section of this society (this J., 1896, 325), calls attention to two bolts taken out of the valve box of a pump that raised water from a well to supply a works. These bolts which were originally  $1\frac{1}{4}$  in. thick had become badly corroded, the corrosion in some parts being  $\frac{3}{8}$  in. in depth. The corrosion was supposed to be due to something communicated to the water by tar, as tar residues existed on the surface soil. Bolts in a pump used to raise tar at the same works were similarly corroded. Ammonium chloride was supposed to contribute to the corrosive action in both cases.

In several cases brought under our notice, and also in our own experience, we have not found the internal parts of tar pumps suffer from any marked corrosion, nor in one case of a water pump which raises approximately 40,000 gallons per day of water, contaminated with tar products. A portion of the end of a knocking stud taken from a tar pump after being in use for over five years showed practically no signs of corrosion.

Scheurer-Kestner (Bull. Soc. Chim. 1897, 1250—1252; this J., 1897, 141), deals with corrosion of cast and wrought iron by fused caustic soda under pressure. Laboratory experiments showed that pressure increases the rapidity of corrosion. A. Lange (Woch. f. Brau., 1899, 357; this J., 1899, 750) discusses the chemical action of liquid sulphur dioxide on the iron of cylinders of ice-making machines. Water appears to play an important part in the reaction, and the equation given by this worker is  $2\text{Fe} + 3\text{SO}_2 = \text{FeSO}_4 + \text{FeS}_2\text{O}_3$ . Henderson and Beilby (J. Chem. Soc., 1901, 1245—1256; this J., 1901, 1212) found that an exposure to the action of ammonia for seven days at a temperature of  $800^\circ\text{C}$ . rendered malleable iron so brittle that it could be broken like porcelain by a blow from a hammer.

Ed. Donath, in a paper on the "Production of ferro-cyanogen from gas-liquors" (J. Gasbeleucht, 1901, 880; this J., 1902, 51) states "We can see easily that gas-liquors exercise a corrosive action on iron, but this action apparently is more energetic when the water is heated. While the pumps which are used to pump up the cold ammoniacal liquor are corroded but slightly, it is by no means uncommon to observe strong corrosive action on the iron portions of the distilling apparatus. I have even seen . . . a Feldmann distilling apparatus, which had become so completely friable that at many places it was easy to pierce the thick sides with an ordinary knife. A portion removed with a knife consisted principally of graphite and Prussian blue, and it is highly

probable that this latter body was formed thanks to the presence of sulphides in the gas liquors, by the same process as in the purifying material."

In regard to the action of cold ammoniacal liquor on the iron portions of pumps we can confirm Lange's observations. In a valve taken from a pump which has constantly pumped ammoniacal liquor for over  $3\frac{1}{2}$  years, the greater part of the valve face still exists; hence it may be concluded that cold ammoniacal liquor is not a serious corrodent so far as iron is concerned. The corroded parts of the valve have taken on a granular appearance. We are also able to partly confirm the same worker's observation that portions of the cast iron columns of ammonia stills are corroded, in many cases becoming cellular, portions of the iron being eroded leaving cell like spaces. We cannot confirm the presence of Prussian blue in the corroded parts.

F. J. R. Carulla (J. Iron and Steel Inst., 1908, 76, 71) finds cast iron everlasting when used for ammonia stills, and instances the case of a still which had been at work for 18 years, the numerous cast iron cylinders of which showed no signs of wear. He also calls attention to the possibility of ammonium chloride attacking the iron of which tar stills are constructed, and the marked corrosion that takes place in castings of iron containing wrought iron chaplets when they are brought in contact with many chemical liquids.

When dealing with the corrosion of tar stills we shall have occasion to refer to the part which ammonium chloride plays in that action, but in this place we would like to confirm Carulla's observations in regard to wrought iron chaplets in castings. It was found that the cast iron pipes used to connect the swan-necks of tar stills to the condenser coils rapidly corroded at the point where the chaplets had been introduced, and in some cases the chaplets were eaten right out. It is most likely that the rapid corrosion which takes place at the chaplets is due to marked local electrolysis; corrosion of all metals is probably more or less due to electrochemical action. A remedy was found in this case by using pipes which were cast vertically without the use of chaplets.

In a paper on "Tests for the action of chlorides on cast iron" (this J., 1909, 508), Carulla describes the action of ferrous chloride and ammonium chloride liquors on cast iron, and a method of determining the extent of the action in each case. G. K. Davis (J. Iron and Steel Inst., 1908, 76, 81) describes the action of hot ammonium chloride solution on wrought iron. A. T. Lincoln deals with the electrolytic corrosion of brasses very fully in the Journal of the American Electrochemical Society, vol. ii., 43 (see this J., 1908, pp. 167 and 946).

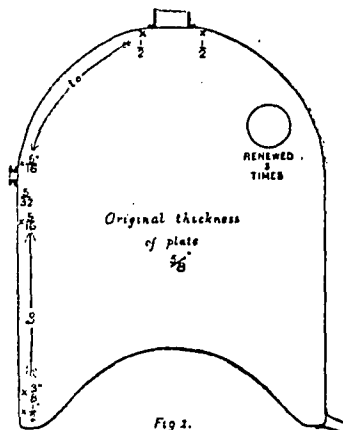


Fig. 2.

To the tar distiller the corrosion of his stills is a continued source of anxiety and expense, and he would

welcome an alloy at a reasonable price that will resist for a longer period than wrought iron or mild steel the corrosive action of the vapours which are given off during the distillation of tar. The diagram will give some idea of the extent of the erosion in a tar still after working for five years. The plate under the manlid-stool has had to be renewed three times during this period, being eroded completely through each time. The plate under the charging block stool is another spot which gives a great deal of trouble. It will be seen from the diagram that for one foot below the stool the plate is only  $\frac{1}{2}$  of an inch in thickness, being in fact the thinnest part of the whole still, neglecting of course the portion under the manlid-stool.

The mechanism of the process of corrosion of the iron of tar stills is, without doubt, a complicated one, and it is somewhat difficult to form a theory to fit in with all the conditions that may exist in the still from the commencement to the finish of the operation. We are of the opinion that the dissociation of ammonium chloride, ammonium sulphide, ammonium hydrosulphide, and ammonium cyanide, and the subsequent action of the dissociation products upon the iron, is the chief cause of the corrosion. The rate of the action is probably increased by electrochemical conditions (self-corrosion). It is quite possible also that strain contributes towards corrosion by producing a certain amount of molecular instability in portions of the iron plates, thus rendering these parts more easy of attack. The plates are eaten away at a greater speed at those points where excessive condensation takes place, for instance under the manlid-stool, and this is due, in all probability, to the continuous flow of liquid removing the final products of corrosion more rapidly at these points than they are removed elsewhere, and thus exposing a fresh surface of iron to the attack.

It is thought that the process of corrosion goes on at a greater rate during the latter portion of the distilling operation, principally during the period when steam is used to assist in the distillation. The final products into which the corroded iron is converted appear to be chiefly ferrous sulphide and ammonium ferrocyanide. Ammonium thiocyanate occurs in small quantities, and traces of ferrous chloride and Prussian blue have been found in portions of the corroded iron. It is considered that the steam introduced into the still plays no other part than that of producing ionisation of the ammonium chloride, etc., and increasing the power of action of the products of dissociation.

As far as possible it has been endeavoured to prove the theories just enunciated. To secure like conditions to those existing in a tar still during work, in glass apparatus is next to impossible.

On the undersides of manlids of stills after working, a deposit of a dirty, brown colour was noticed. Several samples of this material were collected and examined, when it was found that over 50 per cent. consisted of ammonium chloride. The composition of two samples is given in Table 1.

TABLE I.

	Ammonium chloride	Carbon	Soluble in benzene. (anthracene, naphthalene, &c.).
1.	per cent. 52.31	per cent. 5.03	per cent. 42.06
2.	54.30	5.07	40.03 } by diff.

The carbon appeared to be in the graphitic state and contained a trace of iron. In the water soluble portion, which was faintly acid to litmus, a trace of ferrous iron and a large trace of sulphates were found in addition to the ammonium chloride. Ferrocyanides and thiocyanates were absent. Large quantities of ammonium chloride and ammonium sulphide were found in some of the liquors which come over during the working of the still (see Table 3). It is a well-known fact that ammonium chloride and ammonium sulphide dissociate at high temperatures into ammonia and hydrochloric acid, and ammonia and

sulphuretted hydrogen respectively, and it is quite reasonable to suppose that the hydrochloric acid and sulphuretted hydrogen set free will attack the iron of the stills, especially in the presence of steam which is to a certain extent superheated owing to the temperature of the still.

It is considered that ammonium chloride exerts a greater action upon the iron than ammonium sulphide, and the following experiments were carried out to prove this. Solutions of ammonium chloride and ammonium sulphide in water were prepared at such a strength that the amount of hydrochloric acid combined with the ammonia in the former salt was exactly equivalent to the amount of sulphuretted hydrogen combined with the ammonia in the latter. Pieces of wrought iron of known weight and area were totally immersed in the solutions, and the temperature then raised to 80° C., and kept as near as possible to that point for 4 hours. The pieces of iron were then removed, carefully wiped, dried and reweighed. The results are shown in Table 2.

TABLE II.  
Ammonium Chloride.

	Original weight of iron. Grms.	Area sq. c.m.	Loss in grms.	Loss grms. per sq. c.m.
1.	18.6805	18.78	0.0197	0.001
2.	18.6608	18.78	0.0189	0.001

Ammonium Sulphide.

	Original weight of iron grms.	Area sq. c.m.	Loss in grms.	Loss grms. per sq. c.m.
1.	16.9288	17.26	0.0146	0.00084
2.	16.9142	17.26	0.0150	0.00086

The fact that traces of ferrous chloride were found in the scrapings taken from plates in different parts of stills is also a support to the theory that ammonium chloride plays an active part in the corrosion.

Electrochemical action has not been proved up to the moment, as pressure of work has prevented the making of experiments. Arrangements are being made, however, to investigate this matter. It seems quite reasonable to suppose that electrochemical action does take place.

The electrochemist believes that when a metal is brought in contact with an electrolyte, and ammonium salts are electrolytes, electrolysis will take place upon the surface and rapid corrosion will be the result.

Many experiments have been carried out by J. Thickens, of the University of Wisconsin, with the object of proving that strained iron is more susceptible to corrosion than unstrained iron. In all cases he found a marked difference in the rate at which the strained portions of iron corroded compared with the unstrained. Mild steel showed a greater corrodibility than wrought iron. He found that in the presence of an electrolyte the strained portion of the iron became the anode and the unstrained the cathode.

We have observed that those portions of tar stills which are subjected to unequal strain due to expansion and contraction corrode much more rapidly than the general body of the apparatus. In the cases under investigation it is particularly noticeable at that portion of the stills next to the downtake flues. In this position there are three plates which have corroded across the corners in deep grooves. At those points in the stills where the greatest condensation takes place, the plates are badly corroded into grooves, and the general erosion takes place with greater rapidity. The plates in these positions are much cleaner, being in most instances practically free from a scale of sulphide of iron such as is found on the greater portion of the still plates. This, it is thought, supports the theory just given.

The results of an examination of the ammoniacal liquors which distil over during the process of tar distillation are given in Table 3. It will be noticed that the

amount of ammonium chloride and also the amount of iron as ferrocyanide are greatest in the liquor which comes over during the end of the distillation. It is at this stage that steam is passing into the still and the temperature high, and it seems quite within reason to assume that the action of corrosion is at its height during this period, especially when the results given in Table 2, and the fact that steam (water) and also high temperatures increase the amount of dissociation of substances capable of dissociating are considered.

TABLE III.

	Liquor collected when still commences to work.	Liquor collected at finish of crude naphtha.	Liquor collected during the working of heavy creosote. Steam passing into the still.
Ammonium chloride	0.13 grms. per 100 c.c.	0.053 grms. per 100 c.c.	2.02 grms. per 100 c.c.
Ammonium sulphide	0.40 grms. per 100 c.c.	2.20 grms. per 100 c.c.	0.54 grms. per 100 c.c.
Ammonium ferrocyanide	trace	0.04 grms. per 100 c.c.	0.056 grms. per 100 c.c.
Ammonium thiocyanate	trace	trace	large trace

The final products of corrosion are found chiefly in the shape of loose scale on the plates. Small quantities occur in the oils which distil over and in the ammoniacal water, in the former case as ferrous sulphide in the form of a fine black powder or in coagulated masses, and in the latter as ammonium ferrocyanide. An examination of the scale removed from several plates in various positions showed that ferrous sulphide was the chief final product. Ferrous chloride and Prussian blue occur in small traces. The following is the result of the analysis of scrapings taken from the top ring of plates.

		Soluble in water contained	Insoluble in water and benzol consisted of
Soluble in benzol,	10.82%	Ferrous chloride	FeS 92.28%*
Soluble in Water	0.30%	Ammonium chloride	C, 7.63%
FeS and C	82.79%	in traces	
		Ammonium sulphate in traces	

\* In some cases a small trace of Prussian blue was found along with the ferrous sulphide and carbon.

## DISCUSSION.

The CHAIRMAN said that at the end of a boiler where there was rapid expansion and contraction "grooving" always occurred; but he had understood that that was due to a mechanical rather than to a chemical reason. A small crack was developed and, at last, it became a groove.

Mr. A. E. TUCKER said he had come to the definite conclusion that the corrosion of iron and steel was entirely an electrical action, involved and obscured by the chemical actions which also accompanied it. Modern research showed that alkaline materials and certain oxidising bodies prevented the inception of oxidation, and therefore corrosion under most circumstances. He was convinced that where iron was strained by mechanical causes it always exhibited greater tendency to corrosion than unstrained iron. In strained iron the pores were opened and a rough surface was produced which was more subject to corrosion. This result was further illustrated by the well-known immunity of highly polished surfaces, such as razors, to the action of ordinary exposure to damp or foul air, which, on rough surfaces, would bring about

rapid corrosion. He had seen some new carpenter's tools which had been submerged in a Cannock colliery for five or six years; when the pit was reopened the tools still appeared to be new. Again he commended the authors of the paper to recognise the electrical condition as being above all the explanation of corrosion of their tar stills; this action would be intensified by the character of the materials used in them. He had found that several acids under certain conditions produced the same result as phosphoric acid now used for anti-rust processes. This showed that the immunity from rusting in the articles operated on was not due to the formation of a phosphide or phosphate of iron, as had been suggested, but rather to an alteration in the physical condition of the surfaces.

Mr. H. L. HEATHCOTE said the electro-chemical explanation of corrosion must undoubtedly play a great part in that and other cases of corrosion. But he failed to see how in the present instance, at such high temperatures, it could be regarded as the most prominent factor in bringing about the corrosion referred to. He was inclined to look at the effect of the increase of volume due to corrosion. When the outside of the iron or crevices in the irregular surface of the iron became corroded the volume of the products, he thought, would be enormously greater than that of the original iron. The pressure exerted by these products would be enormous. The effect of this expansion was shown very well by Professor Carpenter in his work on the expansion of cast iron, when alternately heated and cooled. He was inclined to think that these stresses were, in the present case, much more important than those due to the simple expansion due to heating and cooling, if any steps were taken to coat the iron previous to using it. There was no doubt that one or other of the methods for coating iron with a phosphate coating would afford an efficient preventive of rust, especially if the coat, which was porous to a certain extent, was impregnated with oil or other ingredient which was hard to remove.

Mr. W. T. COLLIS observed that the rapid rate at which tar stills disintegrated was phenomenal and most expensive. With regard to electrical action the corrosion varied according to what was worked in the stills. Some oils were almost as destructive as tar. In reference to the plate, across which a straight groove was cut, he had usually noticed the mischief in a patch. That patch might be a foot square with one central point which would be very thin. He did not think that could be put down to electrical action.

Mr. E. A. MANN said that not only was the wear and tear of the still itself to be taken into account, but the very heavy expense entailed in the way of brickwork and fittings when replacement became necessary. He had no doubt that ammonium chloride was the greatest factor in the matter. Similar stills used for distilling light oils and creosote, which contained a large amount of sulphur compounds but were practically free from chlorides, showed nothing like the same amount of wastage. He instanced a case where a  $\frac{1}{2}$ -in plate was cut completely through under the charge block of a tar still in less than three months.

Mr. A. R. WARNES, in reply, said his belief was that the grooving in this instance was due neither to electrical nor chemical action, but to mechanical causes. He believed a certain amount of electrolytic action did take place, but he and his fellow author hoped to prove that, and also deal with the matter with regard to the question of stress and strain. So far as the plates under notice were concerned, it did not look as if they were swollen. They had not tried treating iron with solutions, but steel treated with chromates had been tried in connection with the corrosion of iron, and found to be very resistant in regard to atmospheric influences, but it eventually lost that power—in one case, in about six months. They had tried nickel steel which was very hard and difficult to work. They had placed nickel steel in a still, and up to the present the results were in favour of this material. They hardly hoped, however, to use it because of the expense and the difficulty of working it.