SYNOPSIS

This thesis considers an investigation into the nature and magnitude of corrosion of mild steel by condensing vapours from solutions of ammonium salts at 80°C. Tests with drops of condensate on steel specimens are described and it is advised that they be used as a simple preliminary before elaborate corrosion tests are applied in industrial practice. Two types of corrosion were found - by differential aeration cells and by direct attack. The type of corrosion depends on the nature of the condensation on the material to be examined, i.e. whether dropwise or film-type. Corrosion varied from extremely high rates of attack by sulphur dioxide bearing vapours to complete protection by purely ammoniacal vapours. The attack is not controlled by ammonia but by the acid constituent of the vapours.

UNIVERSITY OF CAPE TOWN

THE CORROSION OF MILD STEEL
by
CONDENSING VAPOURS
from
SOLUTIONS OF CERTAIN AMMONIUM SALTS.

BY

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INTRODUCTION

Corrosion by condensed vapour in chemical plants, where apparatus is in contact with a condensable gas near its dew point, is often a major problem, resulting in increased maintenance costs and loss of time for repairs. This particular type of corrosion has, for example, been found in a tar distillation by-product plant for the recovery of benzole forerunnings from gas works crudes. Vapours rising from the hot solution in the residue receivers of the boiler still, condense on the cold surfaces of pipe lines, and cause serious deterioration of the plant by corrosive attack. Corrosion of this nature should not be confused with impingement attack or erosion, which takes place in condensers and plant where the gases may travel at a considerable velocity. (1)

The investigation set out in this thesis, was carried out to determine the nature and magnitude of corrosion by the condensing vapours of ammonium salts, which were the chief causes of corrosion in the case described above. As a general basis for investigation, conditions were reproduced similar to those under which corrosion took place, i.e. a slow stream of air and vapour from a hot solution condensing on the cold surface of a test specimen.

A description will be given of the method and apparatus that was used to fulfil this aim, and the way in which the controlling factors from the corrosion standpoint were considered and due provision made for them. Detailed accounts of the corrosive attack for each salt studied will be accompanied by theories to explain the mechanism of the corrosion.

REVIEW of LITERATURE

The Corrosion of Iron by Water.

Numerous theories have been advanced to account for the corrosion of iron, only a few of which have been accepted as meeting the conditions under which rusting takes place, and explaining the phenomena that occur.

According to one theory, pure iron will not corrode in contact with pure water even in the presence of oxygen. Perfectly pure water is not regarded as being an electrolyte. The presence of a fourth substance, an electrolyte, even in traces, is deemed to be essential for corrosion to occur. J.A.N.Friend (2) lent strong support to this theory. It is electrochemical in nature, but the following is the more generally accepted electrochemical theory.

According to this theory, (3)(4)(5)(6)(7), the reaction takes place through a cell between two areas on the metal surface. At the anode surface, the metal goes into solution, while one or more corresponding reactions go on at the cathode surface at the same time. The current passes from the anode to the cathode through the solution and back to the anode through the metal. Electrons flow in the opposite direction. It is assumed that water and air or oxygen are the only requisites for corrosive attack. Water is supposed to be slightly ionised.

$$H_2O \rightleftharpoons H^{\cdot} + OH'$$

When iron is immersed in water, an exchange of electrons occurs between the hydrogen ions and the iron atoms so that the water in the proximity of the metal contains ferrous ions and hydroxyl ions corresponding to a solution of ferrous hydroxide. The discharged hydrogen ions form molecular hydrogen.

$$Fe + 2H^{\cdot} + 2OH' \rightleftharpoons Fe^{\cdot\cdot} + 2OH' + H_2$$

If the solution is aerated and oxygen has access to the ferrous hydroxide, it is oxidised to hydrated ferric hydroxide and deposited as rust.

In order for this theory to be true, it is necessary for iron to continuously pass into solution, and this depends upon i. the solution pressure of iron, and ii. the solubility product $[Fe^{\cdot\cdot}][OH']^2$. According to J.W.Mellor (8) the reaction $Fe + 2H^{\cdot} = Fe^{\cdot\cdot} + H_2$ is in equilibrium when $k_1 = [Fe^{\cdot\cdot}][H^{\cdot}]^2 = 67 \times 10^{-14}$ and since, for water at 18°C, $[H^{\cdot}][OH'] = 0.56 \times 10^{-14} k_2$, $k = [Fe^{\cdot\cdot}][OH']^2 = 2.1 \times 10^{-14}$. This assumes that the ferrous hydroxide is completely ionised. If the true value of the solubility product of ferrous hydroxide is less than k, some hydroxide will be precipitated before equilibrium is reached, and iron will continue to pass into solution. On this basis, Mellor maintains that the electrochemical theory has not been satisfactorily proven, since the value of the solubility product of ferrous hydroxide is not accurately known - values lie on either side of the above figure. Calculated and experimental results that have been given in literature are:- 1.64×10^{-14}(9), 8.7×10^{-14}(10), 9.54×10^{-15}(11), 3.9×10^{-15} - in the absence of oxygen - (12), 7.93×10^{-15}(13), 3.2×10^{-14}(14), 1.6×10^{-19}(15), and 4.8×10^{-16}(16).

The source of Mellor's value of 67×10^{-14} for the equilibrium product $[Fe^{\cdot\cdot}][H^{\cdot}]^2$ is not quoted; and the results of H.O.Halvorson and R.L.Starkey (17) show that it is not constant and varies with pH. They determined the equilibrium concentrations of both ferrous and ferric ions in contact with metallic iron in solutions of differing pH values. Their results are as follows:-

pH	3.0	4.0	5.0	6.0	7.0
$[Fe^{\cdot\cdot}]$	2.7×10^{2}	2.70	2.7×10^{-2}	2.7×10^{-4}	2.7×10^{-6}
$[Fe^{\cdot\cdot\cdot}]$	6.1×10^{1}	6.1×10^{-2}	6.1×10^{-5}	6.1×10^{-8}	6.1×10^{-11}

From these figures, it may be calculated that the equilibrium product $[Fe^{\cdot\cdot}][OH']^2$ is equal to 2.7 x 10^{-20}. This value is below all of the values for the solubility product quoted above,,and hence, no precipitation of ferrous hydroxide will take place. This does not mean, however, that corrosion cannot occur. Oxygen is one of the requisites of corrosion; and the ferrous hydroxide in solution is oxidised to form ferric hydroxide, which is precipitated. The figures of Halvorson and Starkey result in an equilibrium product $[Fe^{\cdot\cdot\cdot}][OH']^3$ equal to 6.1 x 10^{-32}, which is larger than the solubility product - 1.1 x 10^{-36} (18). Consequently solution of iron will continue, and corrosion is possible according to the electrochemical theory.

When iron has once begun to rust, the subsequent progress proceeds more quickly even under conditions where bright iron would remain unattacked. Suggestions have been made that the rust acts catalytically as an oxygen carrier (19), and also that the rust is very porous and hygroscopic so that it becomes moist and provides the necessary electrolytic conditions. J.Aston (20) has shown that wet rust is anodic to bare iron, and hence attack takes place immediately below the deposit . The wet rust shields the metal from oxygen and renders it anodic. According to R.J.McKay (21) the rust accelerates the corrosion in two ways, i. oxygen is removed by its reaction with ferrous hydroxide, and ii. iron, which would set up a counter e.m.f. in the oxygen concentration cell, is removed by precipitation.

J.A.N.Friend (22) has suggested a colloidal theory of corrosion in which he expresses the view that iron is passive in distilled water in the absence of a catalyst, and passes into solution only with extreme slowness, owing to traces of electrolytes that are present. The dissolved iron is probably at first present in a more or less completely ionised state as ferrous ions, but is rapidly converted into the sol of ferrous hydroxide. This sol then undergoes oxidation by dissolved oxygen into the sol of a higher hydroxide, ferric hydroxide sol being formed under the most favourable conditions, and probably ferroso-ferric hydroxide sol when the supply of oxygen is limited. The higher hydroxide sol now acts catalytically by oxidising metallic iron with relative rapidity and simultaneously undergoing reduction to a lower hydroxide sol, only to be oxidised again as oxygen from the air diffuses towards it. In effect, the theory of Friend means that the hydrosol of iron hydroxide acts as an oxygen carrier as it passes alternately between the ferrous and ferric states.

Those salts that favour the rusting of iron are supposed to peptise the colloid, whilst those salts that inhibit corrosion are supposed to flocculate the colloid. This theory has not received general acceptance. U.R.Evans (23) considers that corrosion inhibitors act by covering the anodic areas of iron with a protective film. W.G.Whitman and co-workers (24) have shown that the effects of salts on the rate of corrosion do not vary concomitantly with the stability of colloidal iron hydroxide.

The conditions under which corrosion occurs when vapours condense on a metal surface need not necessarily be similar to corrosive conditions in cases of total immersion, even when the surface is aerated. Evans (25) conducted qualitative tests in the presence of fumes of volatile reagents when investigating atmospheric corrosion, and found appreciable attack on most metals when condensation took place. These tests were all done at room temperature, and the liquids employed were very concentrated. E.Anderson (26) expressed the view that the corrosive action of mists and fumes is the same as that of the resultant solutions. However, he carried out no quantitative experiments to obtain verification of this theory. As long as the temperature of corrosive gases is maintained above the dew point, usually no serious corrosion results.

In many cases, the gases which carry the suspended material as a mist or fume may serve to form a protective coating, so that metals and alloys may at times be successfully used in the presence of a mist or fume (26).

The Condensation of Vapours.

W.L.Badger (27) distinguishes four types of condensation of liquids from their vapours.

1. Dropwise condensation is that case where the condensate does not wet the surface of the metal on which the vapour is condensing. Only drops appear, and when large enough, fall off as such.

2. Film-type condensation is that case in which the condensate wets the surface of the condenser.

3. Mixed condensation is a case in which certain areas are not wetted and certain other areas are wetted, i.e. some areas are dropwise and some are film-type.

4. The case occurs where the whole of the surface is not wetted and yet appreciable areas may be blanketted by streams of condensate. In this case the streams of condensate do not have a fixed position but move about across the surface.

The type of condensing that takes place depends on the nature and condition of the surface. Dropwise condensation does not usually occur unless the cooling surface is in some way contaminated by an oily substance. Very smooth or polished surfaces do show a tendency to induce dropwise condensation without the known presence of oil. Clean steam normally condenses in a film on clean surfaces whether rough or smooth. Film-type condensation can occur on very rough or very foul surfaces even if coated with oil (28).

Condensation, even on non-wetted surfaces such as an oily surface, begins at very slight supersaturation. The dewdrops always form at the same active centres which are probably spots on the surface where there are impurities whose angle of contact with water is smaller than that of oil. Condensation on metals begins at very slight supersaturation, but on drying and repeating, it begins above the dewpoint in the case of non-noble metals. This is ascribed to the presence of soluble impurities in the pores of the metal, and may have an important bearing on corrosion (29).

Corrosion under Drops.

The corrosion of iron or steel by a drop of aqueous liquid depends in most cases on electrochemical action between the central, unaerated portions, which become anodic and suffer attack, and the peripheral aerated portions, which become cathodic and in general, remain unattacked. The velocity of attack depends largely on whether the cathodic and anodic products are soluble or not. In the case of pure water, the anodic product, ferrous hydroxide, is perceptibly soluble, and spreading outwards, becomes oxidised at the junction between the aerated and unaerated regions, yielding a brown ring of the nearly insoluble ferric hydroxide, which also extends over the top of the drop as a membrane. These were the conclusions drawn by U.R.Evans (30) who carried out tests on corrosion under drops at room temperatures. U.R.Evans, L.C. Bannister and S.C.Britton have successfully conducted experiments to tap currents from corroding portions of differential aeration cells, and shown that the amount of corrosion is equivalent to the current flowing (31).

Corrosion in Tar Distillation Stills.

According to A.R.Warnes and W.S.Davy (32) corrosion occurs in the mild steel still heads of tar distillation equipment due to the vapours which are given off during the process. The mechanism of the process of corrosion is a complicated one, and they found it difficult to form a theory to fit in with all the conditions that may exist in the still. They were 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, was the chief cause of corrosion. The plates were eaten away at a greater speed at those points where excessive condensation takes place, and this is due, in all probability, to the continuous flow of liquid removing the products of corrosion more rapidly, and thus exposing fresh surface of iron to the attack. The final products into which the corroded iron is converted, appear to be ferrous sulphide and ammonium ferrocyanide. Ammonium thiocyanate occurs in small quantities.

No investigation was made by Warnes and Davy to verify this opinion. It would therefore only be true to state that one or more of the substances mentioned above, or their dissociation products, causes the corrosion. Though distillation of tar products starts at 80°C, the temperature range at which most of the coal tar is distilled, 250°C - 350°C, is very much higher than the temperature at which the experiments recorded in this thesis, were carried out. Also little or no condensation of water vapour takes place, which plays an important role in corrosion by condensing vapours from hot solutions. It is therefore likely that direct attack by the decomposition products is experienced in the tar distillation equipment, and is not of the nature of corrosive attack described in the following pages.

Corrosion in Benzol Plants.

S.E.Whitehead (33) found that corrosion of wrought iron and mild steel in benzol plants only appeared when the gases contained ammonia. He did not, however, attribute the attack to ammonia nor to hydrogen sulphide which also may be present. The analysis of deposits from corroded preheaters always contained a fairly large proportion of cyanogen compounds, which are well known to be highly corrosive.

The investigations that have been carried out on ammonium sulphide vapours indicate that corrosion is not due to hydrogen sulphide in the presence of ammonia. Whitehead supposed that corrosion was due to cyanide compounds that are produced by the reaction between ammonia and carbon disulphide.

$$3CS_2 + 8NH_3 \rightarrow NH_4CNS + (NH_4)_2S_3 + 2NH_4CN + 2H_2S$$

Results that have been obtained in tests with ammonium thiocyanate, go to show that this supposition is probably correct. The advice to eliminate all traces of ammonia from the gas before its entry into the scrubbers, is therefore sound.

SUMMARY OF FINDINGS

The general conclusions arrived at through the research investigation of condensation corrosion described in this thesis, are dealt with in this section.

The corrosion of a metal by condensing vapours can be divided into two types according to the way in which condensation takes place on the metal surface. In the first type of attack, dropwise condensation results in the formation of drop-cells in which each drop of liquid forms a separate electrolytic cell. Corrosion occurs on account of differential aeration. The area just within the outer edge of the drop, to which oxygen has free access, becomes a cathodic area, while the inner portion of the drop, from which oxygen is comparatively excluded, becomes the anodic area. It is an essential of drop cell attack that oxygen be present to provide the necessary electrolytic conditions, so that the exclusion of oxygen prevents corrosion of this nature. The nett result of drop-cell attack is that corrosion takes the form of pitting under the drops.

In the other form of corrosion, direct attack of the whole surface of the metal is effected by condensation of the film-type. In this case, it is not always necessary for oxygen to be present, and corrosion has been observed in its absence. Though film-type condensation was associated with the severest attack, it was also present in the cases of complete freedom from corrosion, and evidently may afford a measure of protection under certain circumstances. Drop-cell attack may be more dangerous from the standpoint of failure of chemical plant, since the penetration may be greater even though the total loss of metal is less than that experienced in some cases of direct attack.

In general, the ammonium ion played little part in the mechanism of corrosive attack, and the governing factor was the anion associated with it. The total corrosion varied from complete protection to extremely high rates of attack.

PRELIMINARY WORK

A certain amount of work was done which provided experience and an insight into the problems and factors that needed attention, in order adequately to fulfil the aims of the investigation. A simple apparatus was set up, and a number of tests were carried out.

First Corrosion Test Apparatus (Plate 1).

The original apparatus employed to examine the corrosion of the mild steel test pieces by the condensing vapours, consisted of a 1 litre flask which contained the solution. This flask was heated and maintained at a constant temperature by a Glascol electric heating jacket controlled through a Powerstat variable transformer. It was thus possible to keep the temperature constant to 1°C. The flask was connected to a corrosion chamber by a glass tube which passed down to the bottom of the corrosion chamber and ended in a horizontal ring with evenly spaced holes around the inside. This ring was covered by a layer of glass beads to even the flow of vapour over the whole cross-section. The part of the glass tube between the flask and the corrosion chamber that was exposed, was lagged with asbestos string to conserve heat and to minimise condensation. This was not altogether effective as a certain amount of condensation always took place during the experiment. The corrosion chamber was a 6½ inch high, 3 inch diameter Pyrex container that was fitted with a large rubber bung at the top. It was kept at an even temperature in a thermostatically controlled waterbath, which was continuously stirred by a motor driven stirrer.

Air was drawn through the solution in the flask and passed into the corrosion chamber where it came in contact

Plate 1. First Corrosion Test Apparatus.

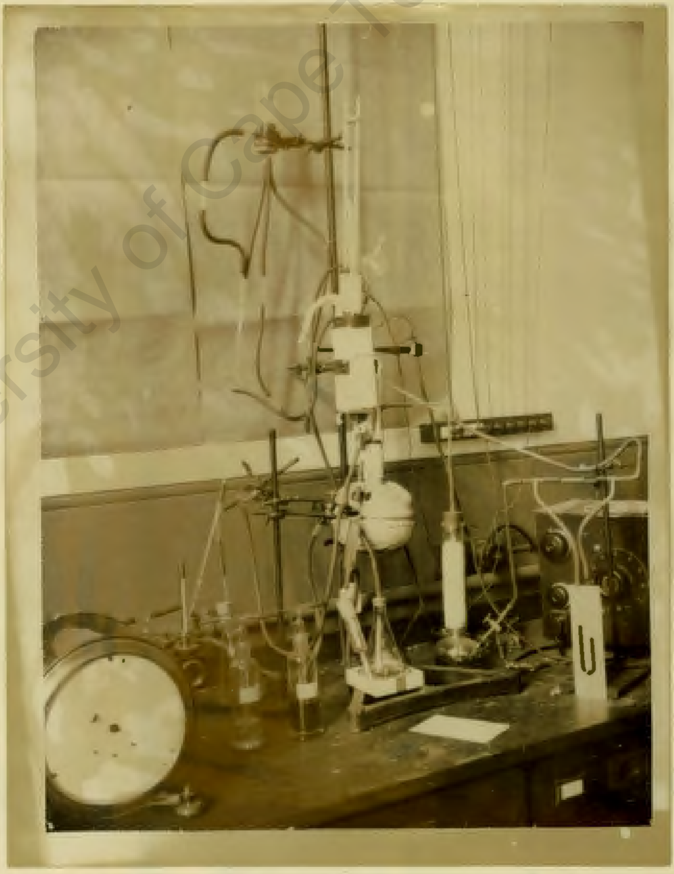


Plate 2. Modified Corrosion Test Apparatus.

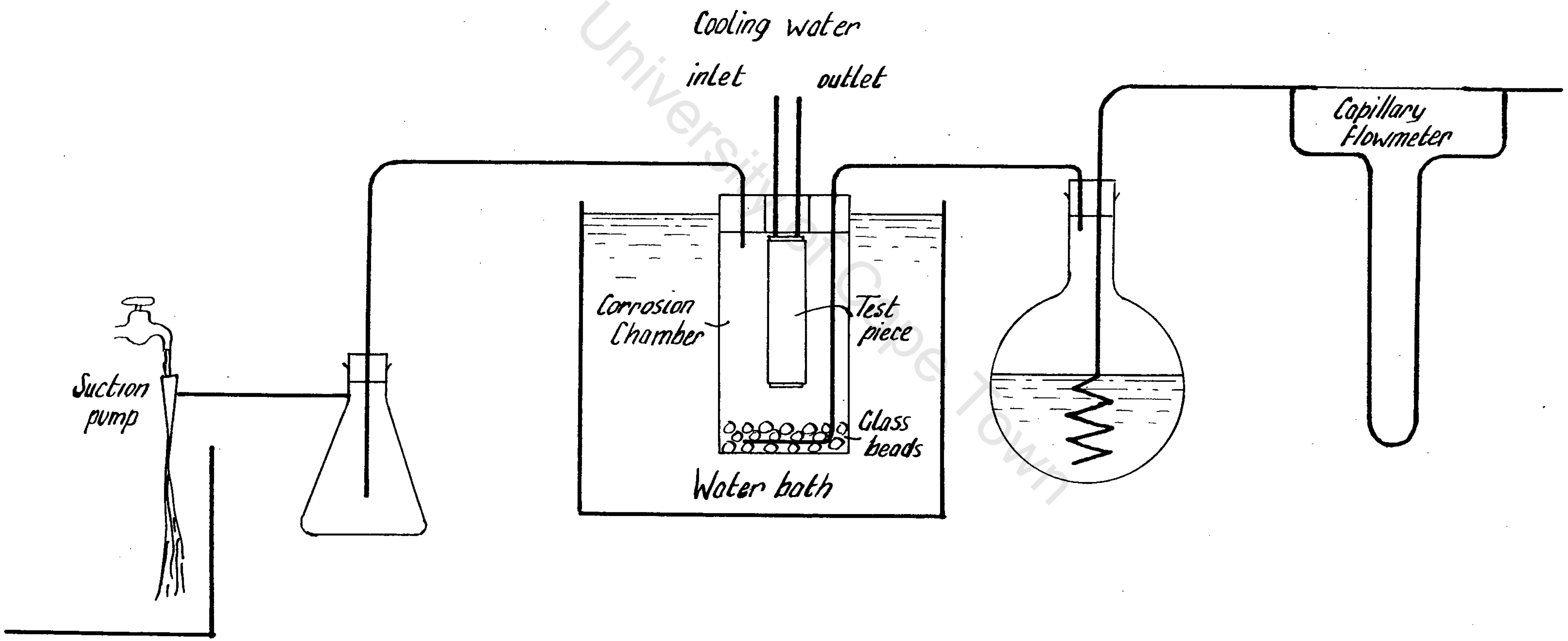


Figure 1. First Corrosion Test Apparatus.

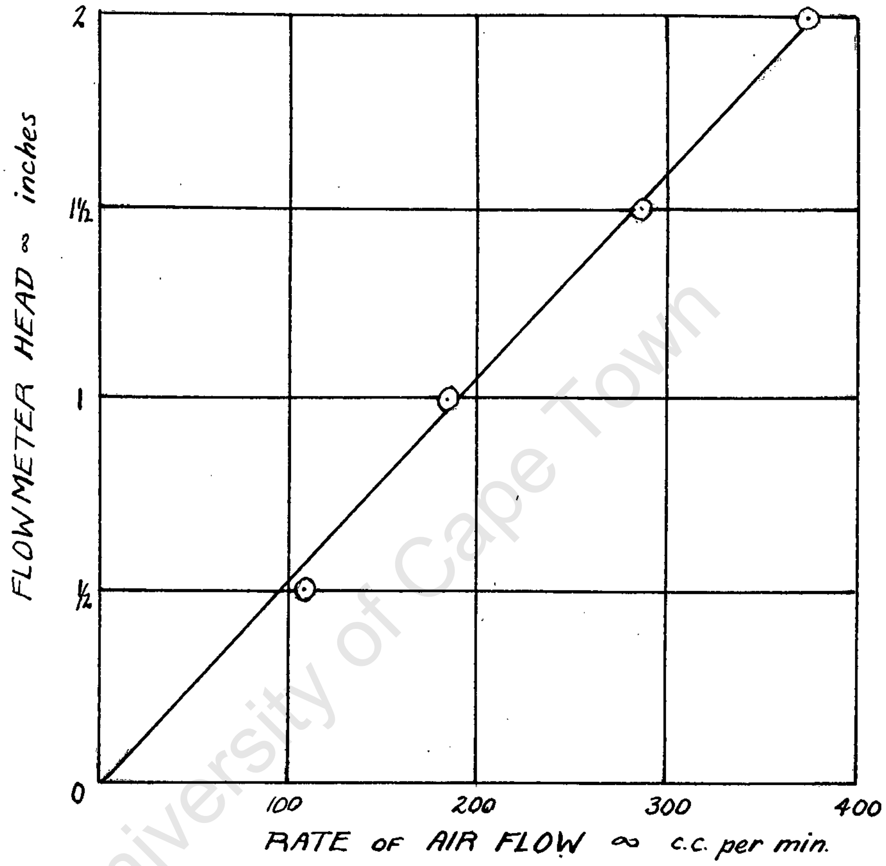


Figure 2. CALIBRATION of FLOWMETER

with the test pieces. The test pieces were $\frac{3}{4}$ inch external diameter, 4 inch long with the walls 1/16 inch thick. They were of mild steel, and were cooled by a stream of water flowing through the inside. This caused the vapours to condense on the outer surface. The air flow was maintained at a steady rate by keeping a constant mamometer head on a capillary flow-meter at the inlet of the apparatus. The capillary flow-meter was graduated by maintaining various constant heads and measuring the rate of flow of air by displacing a definite volume of water from a standard flask and noting the time taken. From these results, a graph was drawn from which the volume rate of flow could be read. (Figure 2)

There were certain drawbacks to this preliminary set-up, which were rectified in the final apparatus.

1. On account of evaporation from the open waterbath, it had to be topped up with water at 80°C from time to time during tests. This meant constant attention, and no tests of long duration could be performed.

2. There was an undesirable amount of condensation in the tube between the flask and the corrosion chamber in spite of the lagging.

3. The condensate from the test pieces collected in the bottom of the corrosion chamber, and blocked the distribution holes. It was overcome by withdrawing condensate periodically though a glass tube. The glass beads, also, had to be taken out and thoroughly washed between each test.

4. The test specimen could not be watched during a test. Hence, the type of condensation and the progress of corrosion could not be seen.

5. The rate of flow of cooling water through the test piece was not constant, though the flow was adjusted to approximately 250 c.c. per minute. This would naturally affect the condensing conditions, and the temperature of the surface of

the specimen would not remain constant.

Corrosion by Water Vapour.

On commencing corrosion tests, it was noted that the cooling water was attacking the inside surface of the test piece. This was greater than the corrosion by the condensing vapour itself; and it was decided to coat the interior surface of the test piece with a protecting material. To do this, a solution of Perspex in amyl acetate was used. The coating was tested for a period of 65 hours by passing cooling water through a specimen having the outer surface protected by a layer of grease; the loss in weight amounted to a quantity of 0.0001 gm per hour. This result is a high figure, and another test for 17 hours gave a figure less than half of this value i.e. 0.00003 gm per hour. For the short test periods, the probable loss is less than the accuracy of the weighing, and for the longer periods, the loss is small enough to be neglected.

A series of tests were carried out with distilled water in the flask. A sufficient number of tests was made to plot a graph of corrosion up to 6 hours duration of time. The longest period had to be limited because the water bath had to be topped up periodically to make up for evaporation losses. The procedure was carefully followed in each experiment, and was as follows.

The condition of the metal surface is very important from the corrosion standpoint, and the amount and even the nature of the attack may be considerably affected by different surface conditions. This is particularly the case in the initial stages of the corrosive attack. A polished surface has the effect of delaying the initiation of attack for a considerable period (34). The specimen was therefore carefully prepared before each test. It was smoothed down with emery cloth, No.0 being the final grade used. A surface was obtained that was smooth but not polished. The last rub was always done by hand, because specimens may be different if the grinding of one has been more vigorous than the other, since isolated masses of oxide pushed down below the surface may vary in such cases, and affect the reproducibility of results. In order to prevent the possible presence of glue from the emery cloth, the test piece was then washed in ethyl alcohol and ether in turn. After drying in a desiccator, it was weighed carefully. The interior surface was coated with a film of Perspex by pouring some solution into the specimen and then pouring it out again. Sufficient adheres to the surface to provide an adequate film of uniform thickness when dried. The specimen is now ready for test.

In the meanwhile, the temperatures in the flask and water bath were raised to 80°C and air was drawn through the system at a manometer head of 1 inch of water which corresponded to a rate of flow of 185 c.c. per minute or 1.7 inches per minute over the specimen surface. Later the water in the manometer was changed to light oil since it evaporated too rapidly. Cooling water was run through the test piece at about 250 c.c. per minute, and it was inserted into the corrosion chamber when steady conditions obtained.

Upon completion of the test period, the test piece was removed and cleaned of all the corrosion product by rubbing with a soft cloth. No other method of removal was deemed necessary as the product was very loose. The Perspex coating was removed by thoroughly washing with acetone. Finally the specimen was washed once more with alcohol and ether; and on drying, it was weighed. The process was repeated until a constant weight was obtained. A large number of expressions or units are used to express the corrosion resistance of materials. As the weight of the specimens was determined in grams, the term adopted to express the amount of corrosion was milligrams per square decimeter. Only whole numbers need generally be used to record corrosion of any practical significance with this term.

Corrosion took the form of pitting, and a yellow-brown corrosion product was formed over the pit holes. In one case a very high result was obtained which, it is believed, was due to surface contamination. The results of the tests were plotted on a graph (Figure 3), which gave a smooth curve and showed an increasing rate of corrosion with time for the period under consideration. In view of the subsequent test results with the final apparatus, it should be noted that all the water vapour corrosion tests were done on the same piece of steel i.e. test piece No.II.

Corrosion by Vapours from Ammonium Thiocyanate Solution.

Reference was made by Nosalevich (35) that, of the constituents of ammoniacal liquors, the most dangerous from a corrosion standpoint is ammonium thiocyanate, particularly on account of possible accumulation. This substance was the first salt to be examined with regard to corrosion by vapours.

Effect of Insoluble Solids in the Solution:

A dilute solution of ammonium thiocyanate was boiled, but it was found that no thiocyanate was carried over in the vapours until a concentration of about 9% in the mother liquor had been reached. On the other hand, when flowers of sulphur was added to a solution - sulphur is present in the residue receiver of the benzole recovery plant - distinct signs of thiocyanate were shown in the distillate when spot-tested with acidified ferric nitrate. Indications were shown in the vapours from a solution with a concentration as low as 0.9% ammonium thiocyanate. Ammonium thiocyanate is apparently vaporised as such, since there was no indication that the compound decomposed in the

Plate 3. Spot Corroded Test Specimen.

x 2

Plate 4. Streaky Corroded Test Specimen.

x 2

vapour phase. The vapours were tested for probable decomposition products - ammonia and hydrogen sulphide - with negative results. It was thought possible that the effect was due to a catalytic reaction. But it was necessary to use a 5 gram quantity of sulphur to procure distillation of thiocyanate, so this theory was ruled out. Other insoluble solids produced the same phenomenon. Chips of porous pot and powdered quartz were found to cause distillation of ammonium thiocyanate at low concentrations.

The effect is dependent on the area of the surface exposed in the solution and not on the total quantity of solid present. Fine chips of porous pot had a greater effect than the same weight of large pieces. There was also a decrease in activity when the same porous pot was used more than once. This led to the suggestion that the slight acidity of the material promoted the rise of vapour pressure of the ammonium thiocyanate. However, investigations by Gell (36) showed that this was probably not the case. The conclusion therefore, is that distillation of the ammonium thiocyanate is brought about by a surface action by the insoluble solid present in the solution. Not all insoluble solids have this reaction, for example, broken glass is inactive; and the exact mechanism of the phenomenon is unknown.

<u>Vapour Corrosion Tests</u>: Seeing that the solution in the residue receiver of the benzole recovery plant contained 2% ammonium thiocyanate, this was the concentration used for the solution in the flask. A quantity of powdered sulphur was added (about 5 grams). Titrations of the solution with N/10 silver nitrate were made before and after each test using ferric nitrate indicator (37). In no case did the concentration alter by more than 0.1%. The mean value during each test was, in general, 2.0%. An endeavour was made to measure the amounts

CORROSION RESULTS IN PRELIMINARY TESTS

Test Piece No.	Duration of Test. hours	Corrosion mgm	Corrosion mgm/dm^2	Condensate on Specimen. c.c./hr.
Distilled water vapours.				
II	1	1.2	2.0	
II	2	2.0	3.3	7.5?
II	4	1.3	2.2	1.7
II	4	3.9	6.6	
II	5	23.2	39.2	
II	5	5.6	9.5	2.0
II	6	7.4	12.5	2.3
2% Ammonium Thiocyanate with Sulphur in suspension.				
IV	1h.10m.	2.1	3.6	
I	2	4.9	8.3	
I	3	12.8	21.6	
II	4	27.4	46.3	
I	5	9.3	15.7	
I	5	23.1	39.0	
III	5	14.8	25.0	
IV	7	20.9	35.4	

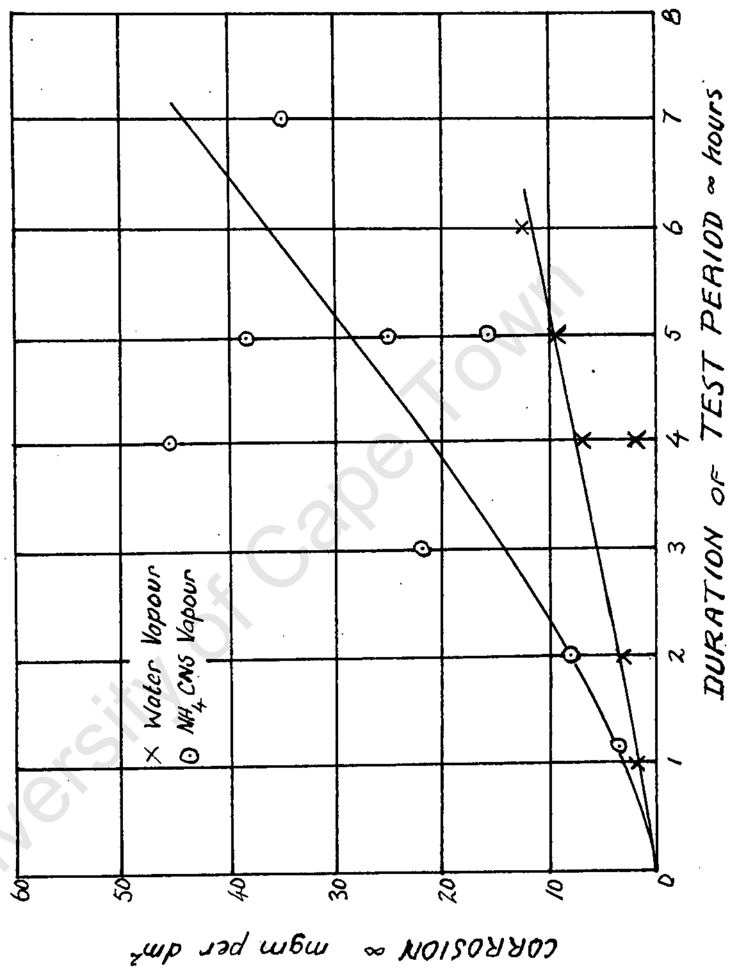


Figure 3. PRELIMINARY CORROSION TESTS

of water vapour passing over during each test by measuring the volume of solution in the flask before and after each test. This was not very accurate on account of the solution that remained in the flask adhering to the sides after it was poured back into a 500 ml. standard measuring flask. From these rough figures it was calculated that about 0.07 gm. ammonium thiocyanate passed over in the vapour per hour under the conditions of test, which were the same as those for water vapour. No attempt was made to absorb the vapours for analysis, though means for that purpose were under consideration.

The first three results fell on a smooth curve which showed a sharp rise in rate of attack. Further tests gave varying results which were much below the curve and did not agree with each other. It was first thought that the low variable results might be due to moisture condensing on the cooling water tubes that were exposed above the test piece. This water would run down and blanket the condensation of further vapour on the specimens themselves, and yield film-type condensation. However, when this fault was corrected, more tests also failed to give results that made any approach to a smooth curve. These tests were made on different test pieces.

An examination of photographs of the specimens showed that the first tests resulted in corrosion in the form of numerous small round pits which were evenly spread over the surface (Plate 3). The later tests showed corrosion in the form of long streaks interposed by uncorroded patches (Plate 4). It was thought that these results were dependent on the type of condensation occurring on the surfaces. The round pitting could probably be due to dropwise condensation; the streaky corrosion may occur with film-type condensation which has streams of condensate flowing down the surface. It was not known why different types of condensation should take place, as the surfaces in each case were identical and had been prepared in the same way.

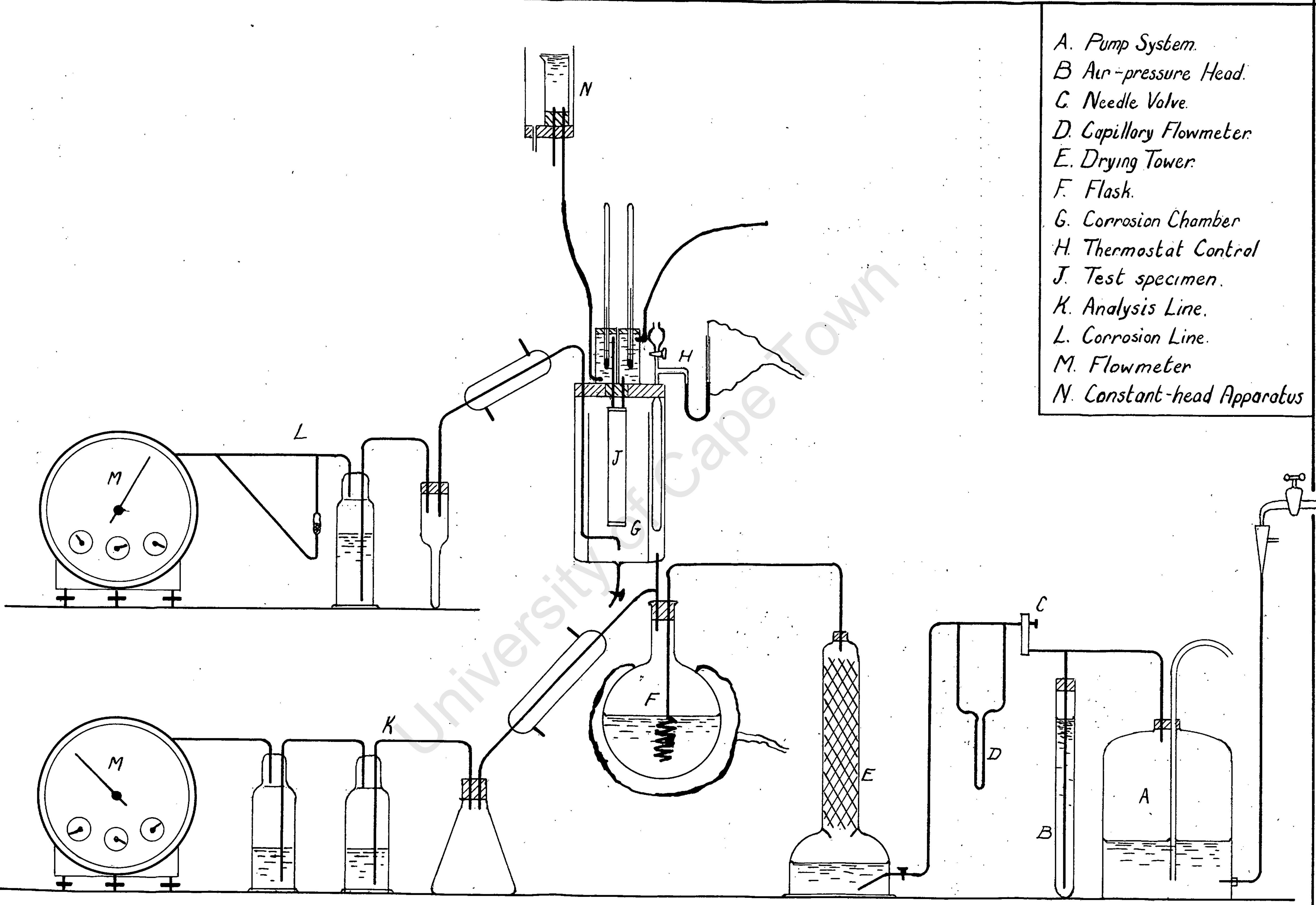
Tests with this apparatus were discontinued, and an improved set-up used.

THE CORROSION TEST APPARATUS

The preliminary test apparatus had a number of disadvantages that have been listed on page 15 of this thesis, and consequently a completely new arrangement was made to overcome these difficulties. Minor alterations were introduced into the first set-up of the new modified apparatus as improvements were found advantageous. The general system is described below, and is illustrated by a diagram. (Figure 4)

Since the mechanical flowmeters that were available were unsuitable for use at pressures other than atmospheric, it was necessary to blow air through the system instead of using suction as in the first apparatus. The water suction pump was converted into a blower by connecting the ejection end to a large 10 litre bottle (A) where the water and air are separated. The water passes up a tube and overflows to the drain; under pressure of the water overflow head, the air is blown through the system. The pressure of the air is controlled by a hydrostatic release head (B), and a constant stream of excess air passes into the atmosphere. The rate of flow of air through the apparatus is regulated with a needle valve to maintain a constant head of 1½ inches on a capillary flowmeter (D) which gave a flow rate of 100 c.c. per minute or 2.3 inches per minute over the test specimen.

The air passes through concentrated sulphuric acid to dry it, then up a tower of caustic soda pellets to remove carbon dioxide and to ensure that it is thoroughly dry (E). The pure air passes through a coil immersed in the solution in the flask (F) that is kept at a constant temperature by a Glascol electrically heated jacket, which can be controlled to within at least 1°C. The air is bubbled through the solution, picks up vapour, and enters the outer corrosion chamber through



— DIAGRAM OF CORROSION APPARATUS —

an annular ring with evenly spaced holes around the inside. The corrosion chamber is lagged with asbestos paper, and regulated in temperature by an air thermostat (H) operating a heating coil that is wound round the chamber. A gap is left in the asbestos lagging for observation of the specimen during test. An air thermostat was used for control because a liquid control did not operate as quickly. Between the flask and the corrosion chamber provision is made for vapour to be drawn off for analysis in an analysis line (K). The hot vapours rise up the outer chamber and then pass down an inner container in which the test piece (J) is placed. Vapour condenses on the test piece and the remaining gas leaves the chamber through an inverted L-piece at the bottom.

The gases for analysis and from the corrosion chamber pass first through a condenser and then through absorption bottles containing appropriate absorbents. The volume passing through each limb is measured by the mechanical flowmeters (M) before leaving the system. Those gases from the corrosion line (L) also pass through a capillary flowmeter which is kept at a constant head.

The flow of cooling water through the test piece is kept constant by the use of a constant head arrangement, which also supplies water for the condensers.

FACTORS ENTERING THE EXPERIMENTS

The conditions under which corrosion is tested, can only be exactly identical if the specimens are all tested at the same time in the same apparatus. One specimen must remain in the apparatus for the whole time of the test, while others are withdrawn at suitable periods for examination. When this system cannot reasonably be carried out, efforts must be made to reproduce the conditions as closely as is possible for each test run. The variables in the corrosion tests with condensing vapours are considered in this section.

Test Specimens.

It is essential for a satisfactory corrosion test, that the sample to be tested should be of a large size to give a result that is sufficiently representative under the conditions of exposure. The size is generally limited, however, by the capacity of the corrosion test apparatus. In practice, the exposed surface of the specimen should not be less than two square inches; and the largest test piece possible for the test apparatus should be used, provided it may be accurately weighed.

In the selection of the size of the specimens used in these tests, only an 18 inch length of $\frac{3}{4}$ inch external diameter mild steel tube was available. The tube was cut into four specimens each 4 inches in length which gave a surface area of over 9 square inches, which is ample for test. The thickness of the walls of the tube was 1/16 of an inch. The type of steel used fell under the number S.A.E. 1095 according to the Society of Automotive Engineers' numbering system, and had a composition:

Carbon	1.08%
Manganese ...	0.47
Silicon	0.04
Sulphur	0.04
Phosphorus ..	0.01

The weight of the specimens varied during the tests, since the preparation for each test necessitated rubbing with emery cloth and a consequent loss in weight. On an average they weighed 55 grams each.

Tests on materials for chemical plants should be carried out on the materials in the state in which they will be used. As will be described later, the test pieces were heat-treated to obtain uniformity for each test. The structure of the metal is altered, and hence probably the rate of attack;

but the lack of fresh material made the treatment necessary.

Temperature.

The effect of temperature on the corrosion of iron in aqueous solutions is not only dependent upon the normal increase in reaction rate due to a rise in temperature, but there is also the retardation of corrosion owing to the decreasing solubility of oxygen in water with rising temperature. A maximum effect will therefore be obtained at some critical temperature when the effect of the decreasing solubility of oxygen is greater than the effect of a rise in temperature on the reaction rate. According to the observations of H.Endo (38), this critical point lies between 60° and 80°C. In Figure 5, the results of H.Endo are plotted on a graph. The tests described in this thesis were carried out at a vapour phase temperature of 80°C. At this temperature, the effect of the decreased solubility of oxygen is dominant, and it is therefore probable that the maximum rate of corrosion has been reached. If this is the case, variations of temperature, even by as much as 2° - 3°, will only have a negligible effect on the amount of corrosion. However, the temperature of the reaction is not the same as the temperature of the vapours, but is controlled by the surface temperature of the metal; and as a consequence, the solubility of oxygen may not yet be the dominating factor.

Both the temperature and the rate of flow of the cooling water within the test specimens play a part in determining the surface temperature of the test pieces. The temperature of the surface in turn determines the amount of condensate as well as the amount of corrosion and the actual temperature of the reaction. The rate of flow of cooling water did not vary by more than 10 c.c. from the set rate of 250 c.c. per minute throughout the tests. Complete condensation of the vapours took place at this rate of flow.

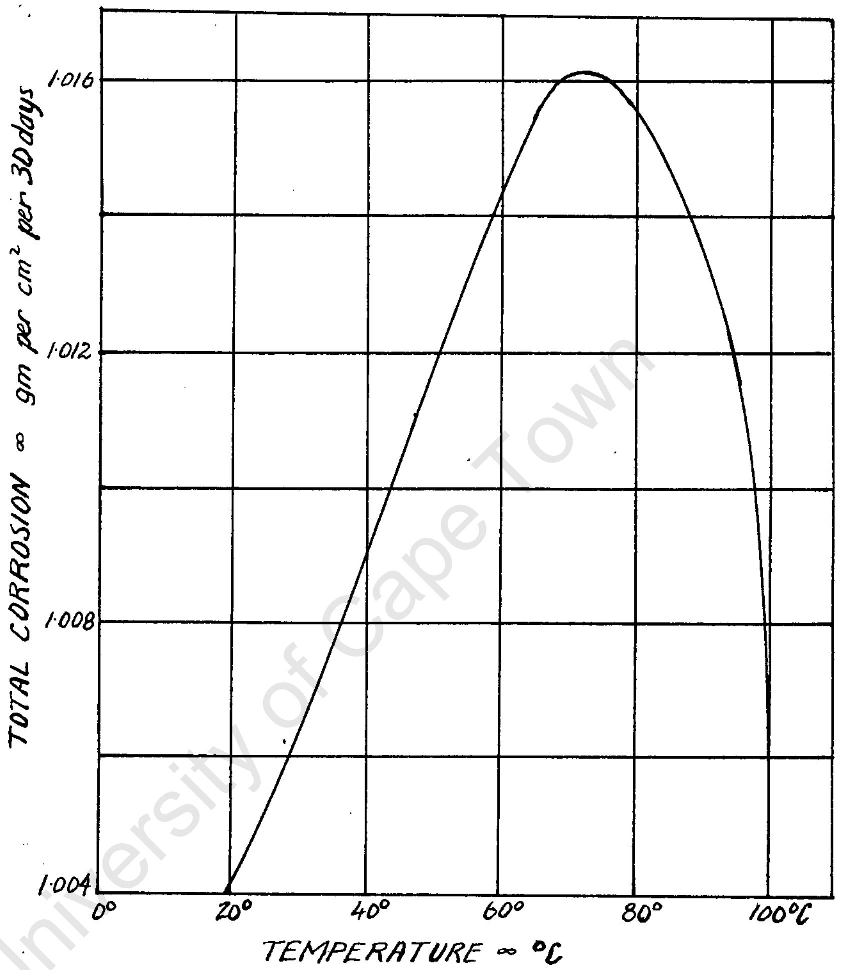


Figure 5. EFFECT of TEMPERATURE on CORROSION

The opinion was held that the variation in temperature of the cooling water between summer and winter had little effect on the corrosive reaction at the surface of the test piece. Calculations were made to determine the respective temperatures of the surface of the test pieces for low winter and high summer cooling water temperatures. Figures were taken from actual test results and calculations appear in Appendix I.

The greatest variation in the temperatures of the cooling waters occurred during tests with distilled water. In this case, corrosion took place at surface temperatures between 72°F (22°C) and 76.5°F (24.7°C). Reference to Figure 5 will show that the error involved for a single reading is negligible. Between 20°C and 60°C there is a difference in corrosion of 1%, i.e. for a variation of 2.7°C the difference in the amount of corrosion is less than one tenth of one percent. This had no effect on the spread of results, the highest surface temperature being found with the lowest result as often as not, and vice versa.

Gas Flow Rate.

The rate of flow of gas was arbitrarily adjusted to give a flow past the test piece estimated to correspond to the rate that vapours would rise from an open vessel containing the solution at the temperature in question. This rate was such that, in practice, only a negligible amount of the vapours did not condense on the surface of the test piece. Usually, complete condensation occurred, which followed an immediate clouding of the metal surface when the specimen was inserted into the apparatus at the beginning of each test.

The rate of flow of gas materially affects the degree of saturation of the vapours. It is doubtful whether complete saturation was ever obtained under the conditions of the experiments. However, the main aim of condensing a sufficient quantity of vapour on the surface was achieved; and the gases must have approached saturation since only a slight lowering of the temperature caused precipitation of moisture in the short tube between the flask and the corrosion chamber.

Temperature Control.

No condensation of vapours should occur before they come in contact with the test piece surface. This necessitates careful temperature control of the vapours after leaving the flask. In the first tests, condensation took place in the tube between the flask and the corrosion chamber, and in the chamber itself. After these parts had been well-lagged and provided with a heating coil controlled by an air-thermostat, no further condensation trouble was experienced and the gases reached the test piece at 80°C.

Concentration of the Solution.

The vapour pressures of the solute and/or the decomposition products depend on the concentration of the solution. Where direct attack takes place, the amount of corrosion is certainly dependent upon the composition of the solution since this determines the concentration of the corrosive agent in the condensate. Where attack is due to drop-cells, this need not necessarily be the case, and the concentration is not of such great practical importance.

In the case of ammonium thiocyanate, the concentration was determined to correspond with that present in the benzole recovery plant (1). In other cases, the concentration was adjusted to yield measurable quantities of gases in the analysis stream. In general, the variation of concentration due to evaporation was of no great importance - 2% ammonium thiocyanate solution only altered by 0.2% during long tests.

CORROSION BY WATER VAPOUR

In corrosion by condensing vapours from a solution, the basic criterion on which the corrosive effect of a dissolved salt is considered, should be the corrosion effected by the solvent. For all the tests in this series, the solvent was distilled water, and consequently it was examined first.

Conditions of Test.

The conditions under which tests were carried out are as follows. The rate of flow of cooling water through the test piece was maintained at between 250 c.c. and 260 c.c. per minute, which gave a rise in temperature of about 0.5°C between the inlet and the outlet. The temperature difference was measured from time to time during tests with thermometers that could be read to 0.01°C by the use of a magnifying lens; and they had been standardised in melting ice for the zero reading and checked against each other at various temperatures. A correction curve was drawn and used to determine the correct difference of the inlet and outlet temperatures of the cooling water.

The hydrostatic head at the oil manometer of the capillary flowmeter that registered the total flow of air through the system, was kept constant at 1.5 inches, while that in the line from the corrosion chamber was regulated at a reading of 1.0 inch on the manometer. Thus constant gas flow conditions were maintained throughout the tests. The air thermostat kept the temperature of the corrosion chamber at a constant 80°C to within 1°C - the same temperature as that of the liquid in the flask. The necessity for maintaining a strict control on the temperature is illustrated by a difficulty that arose at the beginning of corrosion testing.

There was an unaccountable discrepancy between the quantity of vapour condensing in the analysis line and the quantity of condensate collected from the corrosion chamber through the bleed tube provided for the purpose at the bottom. These quantities should be proportional to the volumes of gas flowing past the test piece, which condenses the vapour, and through the analysis line condenser. The higher proportion in the corrosion chamber may have been due to more efficient condensation on the metal specimen, so a glass tube of the same dimensions as the test pieces was placed in the corrosion chamber under the same conditions that were set for normal corrosion tests. It was obvious from the start that more vapour was collecting in the corrosion chamber than in the analysis line, though the volumes passing through the two lines were about the same, i.e. 6.45 litres per hour through the analysis line and 5.7 litres per hour through the corrosion line. Condensate was discovered dropping from the bleed tube of the analysis line which came out vertically at the top of the corrosion chamber in the initial set-up. This accounted for the error.

A well lagged Y-tube was inserted between the flask and the corrosion chamber and the analysis gas was drawn from this point. The discrepancy immediately ceased, and never recurred.

Corrosion Tests.

Great care was taken with the water vapour tests to ensure that the test specimen was thoroughly clean and that the surface was properly prepared. The general procedure of the preliminary tests was followed. At the start of each test it was noticed that the condensation was completely dropwise, and that only when the condensate flowed down the tube did film-type condensation take place on those areas under the stream. Dropwise condensation in this case may be due to the smoothness of the surface as it was certainly in no way oily. Another reason may be that the rate of condensation is very slow, and the normal rules for condensation may not be applicable since they were determined for rapid condensation from boiling solutions. Unlike the preliminary water vapour tests, the corrosion results were very erratic and did not fall on a smooth curve.

Three possible explanations were advanced for the cause of these erratic results.

1. Penetration of hydrogen at the cathodic areas of the corroding metal by diffusion and its possible alloying, may affect the surface properties in subsequent tests. This has been indicated in work on hydrogen overvoltage (39). In order to overcome this possibility of hydrogen absorption, and to obtain uniformity of specimens, the test pieces were to be heated under vacuum at a temperature above 700°C for a suitable length of time.

2. The test pieces themselves may not be uniform. This is a possibility, even though they were all cut from the same length of mild steel tubing that was only itself 18 inches long.

3. The nature of the corrosion may give erratic results. Corrosion in the form of pitting is notorious for unpredictable results in practice.

Procedure for Preparing Test Specimens.

Approaching the problem from the points of view enumerated above, a new procedure was adopted for preparing the specimens for test. The specimen is first rubbed up with No.1 grade emery cloth and then with finer grades until there is a smooth finish free from pit holes; the final rub is made with grade No.FF emery cloth. After an initial treatment in which the specimen is heated at 850°C for six hours, it is heated for one hour at that temperature between each test. Later it was changed to a 4-hour soaking at 850°C between tests. The temperature of the furnace was determined with a thermocouple. The furnace consisted of a 1 inch diameter fused silica tube wound with a 750 watt heating coil and lagged with asbestos. The furnace tube was connected to a water vacuum pump, and during both the soaking and cooling periods the maximum vacuum was maintained. This was necessary to prevent excessive oxidation. After cooling, which took about 40 minutes, the test specimen was removed from the furnace, and the oxide cleaned off by the method of Clarke described below. The test piece was rubbed once more with No.FF emery and given a final rub with grade No.O. The test specimen was then washed in alcohol and ether as before, and was ready for test.

This method was used in an endeavour to drive off dissolved hydrogen from the surface layers of the metal, thus destroying the effect of any hydrogen-iron electrode; and also to make the specimen as uniform as possible. S.J.French and L.Kahlenberg (40) have said that gas-metal electrodes are specific for each particular gas and metal, and are related to the absorbing power of the metal for the gas; also, the combination potential is due both to absorbed gas and to a condensed film of gas on the surface of the metal. Oxygen and hydrogen have the opposite effect to each other.

The grain structure of the metal is considerably altered after a number of heatings in the furnace. The process is comparable to annealing, but as the temperature is below the upper critical point, the test piece is under-annealed. A large grain structure is built up. So much so, that the structure can be seen with the naked eye when a test piece is taken out of the furnace after cooling. A certain amount of oxide scale is formed at each end of the specimen in the furnace, even though it is under vacuum. This scale was removed in the first few instances by cleaning with emery cloth, but a much easier method was found by cleaning it chemically by the method of Clarke.

Chemical Removal of Corrosion Product.

When the tests for the 12-hour and the 18-hour periods were carried out, part of the corrosion product was difficult to remove, and rubbing with a soft cloth was unavailing. It was decided to employ some other means to remove the adherent product. The choice lay between cathodic treatment and a chemical method. Cathodic methods tend to give low values for corrosion, while chemical methods give correspondingly high results. Cathodic treatment entails electrolysis for 10 to 30 minutes with the test specimen as the cathode in a suitable electrolyte. A quicker and more convenient method is the chemical process employed by S.G.Clarke (41). This was the method adopted for all tests.

Concentrated hydrochloric acid is an effective solvent for rust, and it may be used for the quantitative de-rusting of steel if there is present: (a) a suitable inhibitor to prevent attack on the steel at the pores or denuded areas in the rust coating; (b) a reducing agent to reduce ferric chloride formed by the dissolving rust. A method has been devised in which the rusted steel is immersed in a vigorously stirred solution of the following composition:

Conc. hydrochloric acid	100 parts
Antimonious oxide, Sb_2O_3	2 parts
Stannous chloride crystals	5 parts

A test piece was cleaned from all rust, then the surface was rubbed with emery cloth, followed by the usual washing in alcohol and ether. The interior was coated with a film of Perspex laquer inthe usual manner. When this specimen was immersed in the above solution with vigorous stirring for 5 minutes, the loss in weight amounted to 1.5 mgm. A series of tests were carried out which showed that the loss in weight was nearly proportional to time. Results are given in the table below.

Time	Loss in Weight
30 sec.	0.2 mgm
1 min.	0.4 mgm
2 min.	0.7 mgm
5 min.	1.5 mgm

For the longer tests with a very large amount of corrosion product adhering to the surface of the metal, the time of immersion in the de-rusting solution was between 40 and 50 seconds. Hence the maximum error that is incurred for the severest corrosion is never more than 0.3 mgm. For those tests where there was scarcely any corrosion product, the immersion time was generally not more than 10 seconds, and usually amounted to a mere dip in the solution. Hence in these cases, the error in the result would seldom exceed 0.1 mgm. These errors are probably on the high side, since most of the time of immersion is spent in removing the corrosion product and the solution is not in contact with the metal until this is accomplished.

Corrections for this factor in the experiments were applied.

Tests with Heat-treated Specimens.

After the heat-treatment of the test specimens was introduced, the results of the tests improved considerably. The figures for different test pieces were of the same magnitude, and from the results that have been plotted on a graph, it is clear that there is no decided difference between the test specimens when they have been treated in the identical manner. Heat-treating the test pieces has therefore been successful in this direction. The corrosion values obtained, however, do not lie close together, but are spaced in a band that gets wider as the test period increases.

Mathematical Analysis of Test Results.

Statistical analysis methods were applied to the values obtained in the tests on account of the considerable deviations from the mean that were found. The mathematical theory of errors was used to determine which results were unacceptable. In order to reject results, recourse must be made to the Null Hypothesis, which serves as a general basis upon which to act. The Null Hypothesis states:- When a reading has a residual greater than a value with a definite ratio to the probable deviation of a single reading, the result may be regarded as a mistake. The ratio depends on the number of observations that were made. A residual is the difference between a reading and the arithmetic mean of a set of readings. A mistake is a result that, due to some experimental error, has a value that cannot be accepted as being a true value for the test, and is consequently rejected. Sherwood and Reed (42) advocate the rejection of values with the deviation from the mean greater than five times the average deviation. This simple rule is supposed to be adequate for most ordinary work. On the other hand, W.N.Bond (43) recommends a more exact rule known as Chauvenet's Criterion, as a guide for the rejection of an observation. Chauvenet's Criterion states that a reading may be rejected when

$$0.304 \frac{1}{r}\int_0^k e^{-0.227\frac{x^2}{r^2}}\,dx > \frac{2n-1}{2n}$$

where r = probable deviation

$x = kr$ = largest error, i.e. error of the suspect reading.

n = number of observations.

(See Appendix II)

Hence, when it was found that a value obtained in a test could be due to a mistake, that value was rejected. In the case of the 18-hour tests, the first tests on specimens No.I and No.IV were carried out after only three or four hours heat-treatment in the vacuum furnace, which probably explains why the values

CORROSION BY DISTILLED WATER VAPOURS AT 80°C

Test Piece Number	Duration of Test hours	Total Corrosion Observed mgm	Total Corrosion Corrected mgm	Corrosion mgm/dm^2	Points of Attack.	Condensate on Test Piece. c.c./hour	Heat cal/min	Rate of Gas Flow. cm/min
III	2:00	4.0	4.0	6.75		1.0	130	9.2
II	4:00	3.4	3.4	5.7		1.5	137	9.3
I	6:00	12.7	12.7	21.4		1.8	130	8.5

Results below are for heat-treated specimens.

Test Piece Number	Duration of Test hours	Total Corrosion Observed mgm	Total Corrosion Corrected mgm	Corrosion mgm/dm^2	Points of Attack.	Condensate on Test Piece. c.c./hour	Heat cal/min	Rate of Gas Flow. cm/min
I	2:00	0.5	0.5	0.8	2250	1.7	129	10.6
II	2:00	0.9	0.9	1.5	2300	2.3	133	10.3
II	2:00	2.1	2.1	3.5		1.5	122	9.7
I	4:00	2.0	2.0	3.4	2120	1.4	132	8.5
II	4:00	3.7	3.7	6.2	2100	2.0	134	9.1
II	4:00	2.9	2.9	4.9		2.3	143	9.7
II	4:00	4.6	4.6	7.7		1.3	119	8.7
I	6:00	2.4	2.4	4.05		2.5	143	9.9
I	6:00	3.6	3.6	6.1	3700	1.7	128	10.2
II	6:00	0.9	0.9	1.5	1410	2.1	137	8.9
II	6:00	4.7	4.7	7.9	3350	1.9	131	11.1
II	6:00	6.5	6.5	10.9	3520	1.2	124	9.0
II	6:00	5.5	5.5	9.3		1.4	115	10.0
II	6:00	6.5	6.5	10.9	3900	1.0	118	8.6
III	6:00	4.0	4.0	6.8		1.4	116	8.7
II	9:00	9.3	9.3	15.7	4000	1.2	120	9.0
II	9:00	9.3	9.3	15.7	4400	1.4	116	9.0
II	9:00	7.0	7.0	11.9	4000	1.1	120	8.9
II	9:00	7.0	7.0	11.9	4030	1.3	117	8.9
II	9:00	10.3	10.3	17.4	3600	1.3	118	9.1
III	9:00	10.0	10.0	16.0		1.5	117	8.9
I	12:00	11.2	11.1	18.7	2620	1.2	126	9.5
II	12:00	7.4	7.4	12.5	2050	1.3	130	9.6
II	12:00	12.2	12.1	20.4	4220	1.9	130	10.7
II	12:00	11.3	11.2	18.9	3580	1.1	121	8.3
II	12:00	12.2	12.1	20.4	3700	1.2	131	8.1
III	12:00	11.7	11.6	19.7		1.3	112	7.7
I	18:00	2.8	2.8	4.7	3000	2.8	134	10.1
I	18:00	22.4	22.2	37.4	3550	2.1	129	10.4
I	18:00	15.7	15.5	26.1	4000	2.5	133	9.3
I	18:00	26.6	26.4	44.5	4320	1.7	130	9.4
I"	18:00	12.4	12.2	20.6	4020	4.8	143	25.4
II"	18:00	21.2	21.0	35.4	3900	4.2	148	20.9
II	18:00	16.7	16.5	27.8	4300	1.7	131	10.7
II	18:00	16.3	16.1	27.1	4150	2.5	133	11.6
II	18:00	32.9	32.7	55.1		1.4	130	9.1
II	18:00	19.4	19.2	32.4		2.3	131	9.0
II	18:00	18.3	18.1	30.6	4130	1.3	131	8.8
II	18:00	15.1	14.9	25.2	4050	1.5	130	12.4
II	18:00	10.1	9.9	16.7	2110	1.7	120	10.2
II	18:00	15.2	15.0	25.3	3960	1.8	133	12.6
II	18:00	19.4	19.2	32.4	3500	1.3	120	8.6
II	18:00	18.9	18.7	31.6	3720	1.2	120	8.6
IV	18:00	26.0	25.8	43.5		1.9	131	9.5
IV	18:00	26.4	26.2	44.2		1.6	126	9.7
IV	18:00	22.6	22.4	37.8	3950	1.3	127	8.7
IV	18:00	13.5	13.3	22.5	3360	1.3	124	8.3

" indicates that the gas flow was doubled.

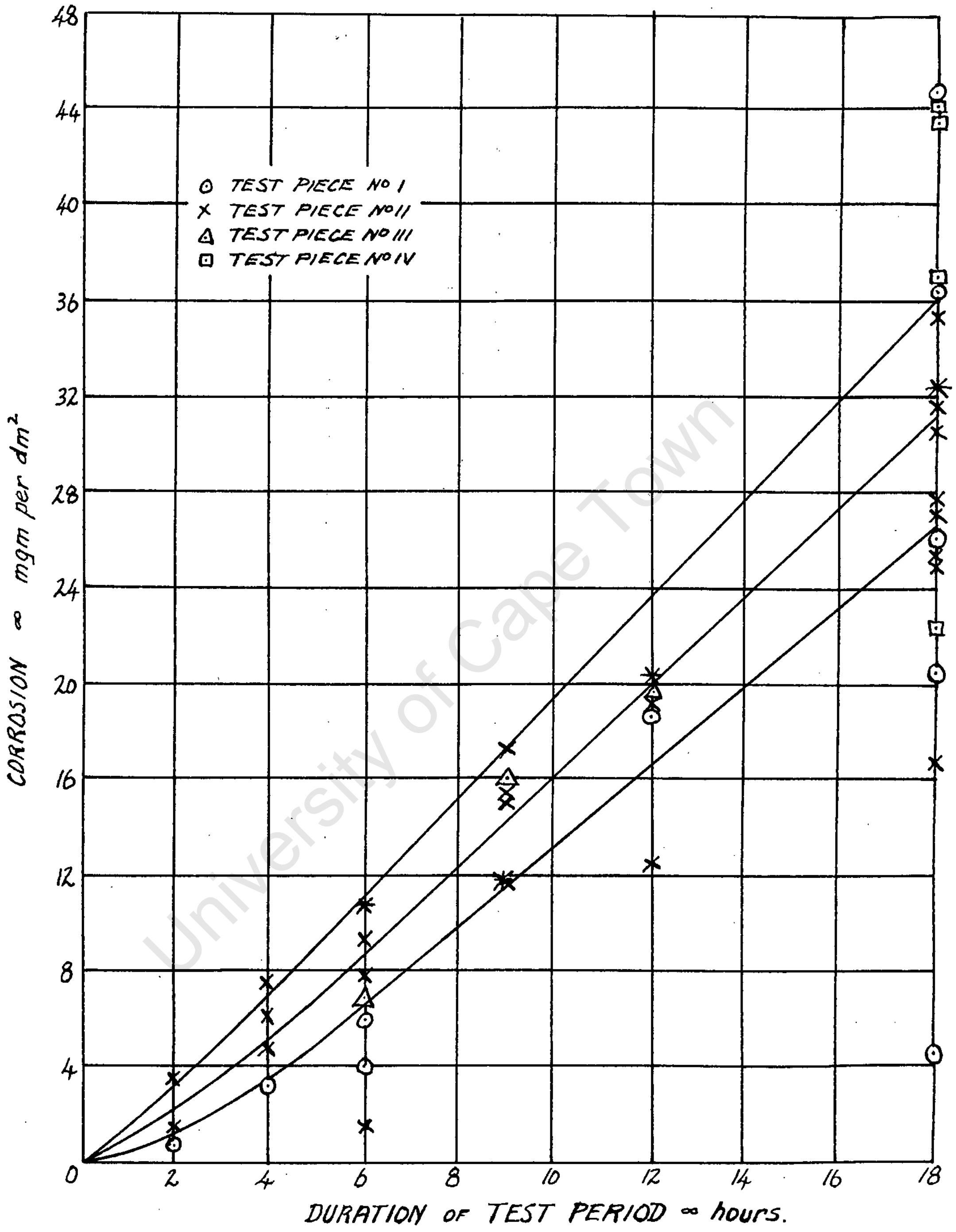


Figure 6. CORROSION by WATER VAPOURS.

deviated so much from the results of the rest of the tests. The other results were obtained after heat-treatment for over ten hours. (see page 39)

Application of Theory of Errors.

Symbols used: Residual v
Average deviation .... e
Standard deviation ... s (for a single result)
Standard error .... S (for arithmetic mean)
Probable deviation ... $r = ks$
Number of results .... n

The value of k is taken from a table (Appendix III)(44).

$$s = \pm\sqrt{\frac{\Sigma v^2}{(n-1)}}$$

$$S = \pm\sqrt{\frac{\Sigma v^2}{n(n-1)}}$$

$$e = \frac{\Sigma |v|}{\sqrt{n(n-1)}}$$

4-hour Corrosion Tests.

No.	Result mgm/dm^2	v	v^2
I	3.4	-2.2	4.84
II	6.3	0.6	0.36
II	4.9	-0.7	0.49
II	7.7	2.1	4.41
	22.2	5.6	10.1

Arithmetic mean (A.M.) = 5.6 $\quad n = 4$

$$S = \pm\sqrt{\frac{10.1}{4 \times 3}} = \pm 0.92 \qquad e = \pm\frac{5.6}{\sqrt{4 \times 3}} = \pm 1.62$$

$$s = \pm\sqrt{\frac{10.1}{3}} = \pm 1.84 \qquad r = \pm 0.766 \times 1.84 = \pm 1.41$$

The determination of the confidence limits ($\pm L$) between which the true value of the mean lies, is given by the equation:

$$\pm L = \pm t\left(\frac{s}{\sqrt{n}}\right)$$

where t is known as Student's t (45). These are the limits within which the mean of any other set of n readings will fall with reasonable accuracy. It is usually accepted that if the result is right 19 out of 20 times (i.e. 95% confidence), there is reasonable accuracy.

For a confidence of 95% and when n is 4, the value of Student's t is 2.78 (from tables).

$$\pm L = \pm \frac{2.78 \times 1.84}{\sqrt{4}} = \pm 2.56$$

Limits of corrosion mean = 5.6 ± 2.56

6-hour Corrosion Tests.

No.	Result mgm/dm^2	v	v^2
II	1.5	-6.5	
I	4.05	-3.9	15.2
I	6.1	-1.9	3.6
II	7.9	-0.1	0.01
II	10.9	2.9	8.2
II	9.3	1.3	1.7
II	10.9	2.9	8.2
III	6.8	-1.2	1.4
	56.0	14.2	38.3

A.M. = 8.0 n = 7

$$S = \pm\sqrt{\frac{38.3}{7 \times 6}} = \pm 0.96 \qquad e = \pm\frac{14.2}{\sqrt{7 \times 6}} = \pm 2.19$$

$$s = \pm\sqrt{\frac{38.3}{6}} = \pm 2.52 \qquad r = \pm 0.718 \times 2.52 = \pm 1.81$$

For a confidence of 95%,

$$\pm L = \pm \frac{2.37 \times 2.52}{\sqrt{7}} = \pm 2.26$$

Limits of corrosion mean = 8.0 ± 2.26

The value 1.5 is rejected because it is a mistake according to Chauvenet's Criterion, being 2.9 times the probable deviation of a single reading (r). There is an unusually low number of points of attack, and the surface must have been contaminated. The point 4.05 lies below the lower band limit and the probable error. Its value is just acceptable by Chauvenet's Criterion; but interpolation shows that the arithmetic mean should be higher. If the value 4.05 is ignored, the arithmetic mean is raised sufficiently to fall on the interpolated curve. The confidence limits are at the same time adjusted to suit the curve. The new values are given below.

No.	Result mgm/dm^2	v	v^2
I	4.05	-4.6	
I	6.1	-2.6	6.76
II	7.9	-0.8	0.64
II	10.9	2.2	4.84
II	9.3	0.6	0.36
II	10.9	2.2	4.84
III	6.8	-1.9	3.61
	51.9	10.3	21.05

A.M. = 8.65 $\qquad$ n = 6

$$S = \pm\sqrt{\frac{21.05}{6 \times 5}} = \pm 0.84 \qquad \sigma = \pm \frac{10.3}{\sqrt{6 \times 5}} = \pm 1.88$$

$$s = \pm\sqrt{\frac{21.05}{5}} = \pm 2.05 \qquad r = \pm 0.728 \times 2.05 = \pm 1.49$$

With the new values the point 4.05 may be rejected as a mistake according to Chauvenet's Criterion. It is 3.1 times r. Now for a confidence of 95%,

$$\pm L = \pm \frac{2.45 \times 2.05}{6} = \pm 2.05$$

Limits of corrosion mean = 8.65 ± 2.05

<u>9-hour Corrosion Tests.</u>

No.	Result mgm/dm^2	v	v^2
II	15.7	0.8	0.64
II	15.7	0.8	0.64
II	11.9	-3.0	9.0
II	11.9	-3.0	9.0
II	17.4	2.5	6.25
III	16.9	2.0	4.0
	89.5	12.1	29.5

A.M. = 14.9 $\qquad$ n = 6

$$S = \pm\sqrt{\frac{29.5}{6 \times 5}} = \pm 0.99 \qquad \sigma = \pm \frac{12.1}{\sqrt{6 \times 5}} = \pm 2.21$$

$$s = \pm\sqrt{\frac{29.5}{5}} = \pm 2.43 \qquad r = \pm 0.728 \times 2.43 = \pm 1.77$$

For a confidence of 95%,

$$\pm L = \pm \frac{2.45 \times 2.43}{\sqrt{6}} = \pm 2.43$$

Limits of corrosion mean = 14.9 ± 2.43

<u>12-hour Corrosion Tests.</u>

No.	Result mgm/dm^2	v	v^2
~~II~~	~~12.5~~	~~-7.1~~	
I	18.7	-0.9	0.81
II	20.4	0.8	0.64
II	18.9	-0.7	0.49
II	20.4	0.8	0.64
III	19.7	0.1	0.01
	98.1	3.3	2.59

A.M. = 19.6 $\qquad$ n = 5

$$S = \pm\sqrt{\frac{2.59}{5 \times 4}} = \pm 0.36 \qquad \sigma = \pm \frac{3.3}{\sqrt{5 \times 4}} = \pm 0.74$$

$$s = \pm\sqrt{\frac{2.59}{4}} = \pm 0.80 \qquad r = \pm 0.740 \times 0.80 = \pm 0.60$$

The value 12.5 is rejected by Chauvenet's Criterion. The residual is 11.8 times r.

For a confidence of 95%,

$$\pm L = \pm \frac{2.57 \times 0.80}{\sqrt{5}} = \pm 0.96$$

Limits of corrosion mean = 19.6 ± 0.96

18-hour Corrosion Tests.

No.	Result mgm/dm^2	v	v^2
I	4.7	26.5	
II	55.1	23.9	
I	37.4	6.2	38.5
I	26.1	-5.1	26.0
I	44.5	13.3	177.0
I	20.6	-11.2	125.5
II	35.4	4.2	17.8
II	27.8	-3.4	11.6
II	27.1	-4.1	16.8
II	32.4	1.2	1.4
II	30.6	-0.6	0.4
II	25.2	-6.0	36.0
II	16.7	-14.5	210.0
II	25.3	-5.9	34.8
II	32.4	1.2	1.4
II	31.6	0.4	0.2
IV	43.5	12.3	151.0
IV	44.2	13.0	169.0
IV	37.8	6.6	43.5
IV	22.5	-8.7	75.6
	561.1	117.9	1136.5

A.M. = 31.2 n = 18

$$S = \pm\sqrt{\frac{1136.5}{18 \times 17}} = \pm 1.93 \qquad e = \pm\frac{117.9}{\sqrt{18 \times 17}} = \pm 6.75$$

$$s = \pm\sqrt{\frac{1136.5}{17}} = \pm 9.40 \qquad r = \pm 0.700 \times 9.40 = \pm 6.58$$

For a confidence of 95%,

$$\pm L = \pm\frac{2.10 \times 9.40}{\sqrt{18}} = \pm 4.66$$

Limits of corrosion mean = 31.2 ± 4.66

The values 4.7 and 55.1 are rejected according to Chauvenet's Criterion, since the residuals are greater than 3.3 times the probable deviation of a single reading i.e. ± 6.58.

Points of Attack.

The number of points of attack on each specimen were counted from the photographs, which were taken after each test run. This is a simpler and easier method than counting the actual number of points on the specimen itself. A clear strip of photographic film, with the emulsion removed, was marked off with an area corresponding to an area on the photograph of one sixteenth of the total area of the test piece surface, i.e. one quarter of the circumference by one quarter of the height. The strip of film was placed over the photograph of the corroded specimen, and the number of points of attack in the marked area was counted; the count was multiplied by sixteen to get the total number on the whole surface area of the test specimen.

The method is, of course, subject to error. But, as the photographs of the corroded specimens were taken where the corrosion was as nearly average as could be judged by eye, the results of the counts were accurate to within 5%. Those counts which were compared with counts from the specimens themselves, checked to within 100 points of attack for test pieces with from 2,000 to 3,000 points of attack.

The number of points of attack (see Figure 7) increases with time until 9 hours of corrosion has passed, after which the number of points normally remains constant to all practical purposes. When the test results were abnormally low, a correspondingly low number of points of attack were counted. The number of points was not, however, markedly proportional to the total corrosion. The points of attack are probably formed very rapidly at the commencement of the test; the rate of formation decreases after a short interval and by the time 9 hours is reached, the rate of increase in points of attack is practically zero. After this, corrosion only proceeds at the points already formed and increases by enlargement of the corrosion areas, which spread across the metal surface until

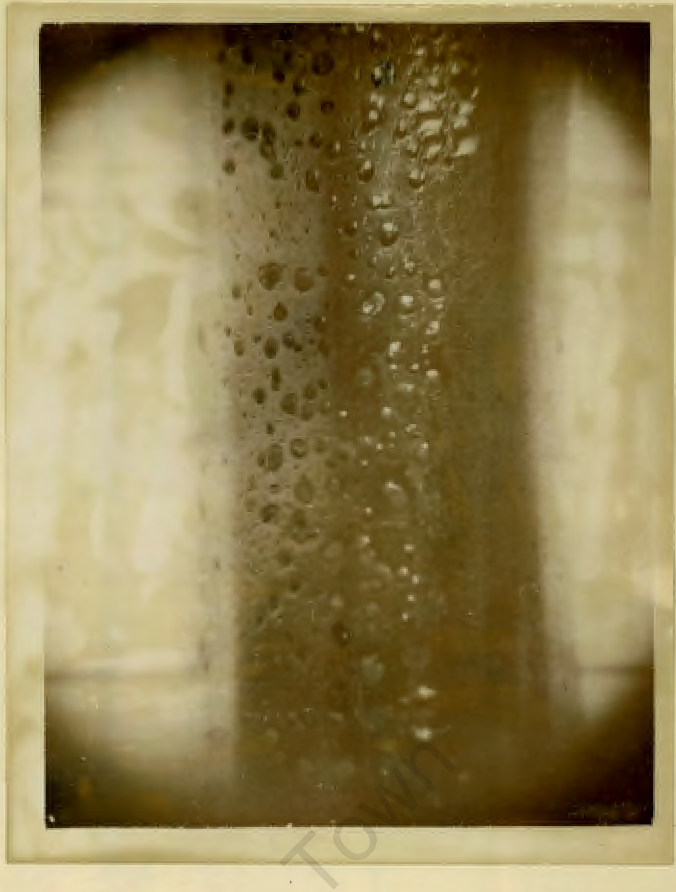


Plate 5. Drop Corrosion.
X 2

Plate 6. Enlarged Corrosion Area.
x 2

fairly large areas may be covered by a single continuous layer of corrosion product (Plate 6).

Mechanism of Attack.

The pitting that takes place as a result of the condensation of water vapour on the surface of mild steel must be regarded as caused by a number of separate cells operating at each point of attack. Where the points of attack are close together, they may eventually unite when the corrosion product has grown to such an extent that both points are covered by the same layer of rust. Evidence goes to show that corrosion occurs under separate drops, and hence each drop condensing on an unattacked surface has the potentiality of initiating a new point of attack. That they do not all give rise to attack, may be due to the possibility that the metal grains do not have the same activity on all faces of the crystal structure. The more active points are attacked, whereas the less active or passive points remain unchanged. Each drop under which corrosion occurs, must be considered as a complete and separate corrosion cell in itself.

U.R.Evans (30) has made observations of corrosion under drops at room temperature in the presence of air. The following is an extract from his paper regarding corrosion under drops of distilled water.

"A crinkly brown ring (brown on the outside, dark green on the inside) occurs all round the drop very close to the edge, and a thin brown membrane extends over the top of the drop; inside this membrane there is a narrow ring of liquid, below which the metal is quite unattacked. Within the ring the steel is distinctly corroded; the ground of the metal is also covered with a loose deposit, green below and brown above.

"The probable explanation is as follows. Close to the edge of the drop where oxygen has direct access to the

Plate 7. Point of Corrosion Attack.
x 160

Plate 8. Corrosion Pit Hole.
x 160

metal, the direct production of an oxide film occurs, which, being formed in situ, is protective; before it has reached a thickness sufficient to show the first interference tint, this film ceases to grow further. Naturally the protected iron is cathodic towards the iron in the centre of the drop, to which oxygen does not diffuse so readily. Therefore anodic attack will proceed everywhere except just around the margin of the drop, and this attack will produce ferrous hydroxide. Where the ferrous hydroxide comes in contact with diffusing oxygen, it is oxidised first to the intermediate oxide and then to the brown ferric hydroxide. These compounds are much less soluble and will appear as a precipitate, and since they are formed at an appreciable distance from the metal, they are not protective or closely adherent. A large quantity is formed close to the surface of the metal and by its formation helps to absorb diffusing oxygen and thus to keep the surface below it anodic.

A similar effect was noticed with regard to the corrosion on the test pieces. The corrosion spots, when sufficiently large to be satisfactorily examined, showed rings of orange-brown corrosion product surrounding areas of darker brown. They had the shape of small volcanic craters.

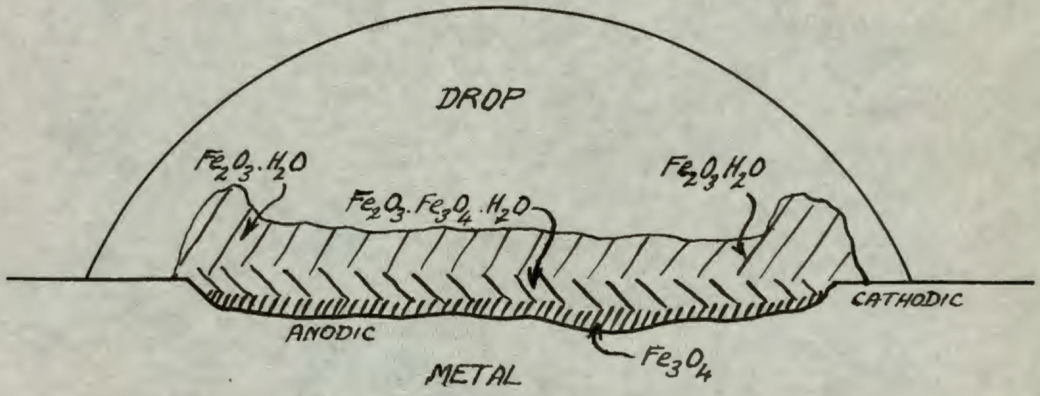


Figure 8. DIAGRAM of DROP-CELL

The corrosion product in immediate contact with the metal was nearly black in colour and adhered fairly strongly to the surface. It was impossible to remove by rubbing, so it had to be dissolved by chemical means.

In this case, the mechanism of corrosion does not follow the explanation of U.R.Evans exactly, possibly due to the effect of temperature. It has been shown on page 4 that ferrous hydroxide is present in solution and is not precipitated. Instead, it is oxidised to ferric hydroxide via the intermediate green hydroxide, and is precipitated as yellow rust in a ring just within the drop and also over the central anode area. This yellow rust is probably a hydrated oxide, $Fe_2O_3.H_2O$, rather than ferric hydroxide, $Fe(OH)_3$ (45). The rust effectively screens the anode area and decreases the access of oxygen to the hydroxide below. Consequently a lower hydrated oxide, possibly represented by the formula $Fe_2O_3.Fe_3O_4.H_2O$, is precipitated below the outer layers, and a black anhydrous magnetite, Fe_3O_4, is formed at the metal surface to which it adheres very firmly. There is therefore a progressive increase in oxygen content in the corrosion product from the metal outwards (see Figure 8). A photographic record of the progress of drop-cell corrosion will be given in the section on Drop Tests, in which tests, a drop of solution is placed on a steel specimen and the process of corrosion is observed.

Alteration of Metal Grain Structure.

After heat-treatment of the test pieces had been in operation for some time, it was noticed than bands had appeared at both ends of the test pieces, when they were removed from the pickling bath to remove oxide scale formed in the vacuum furnace. These bands were about 1/2 inch wide all round the specimens at each end, and appeared lighter in colour than the rest of the test piece (Plate 9). There was

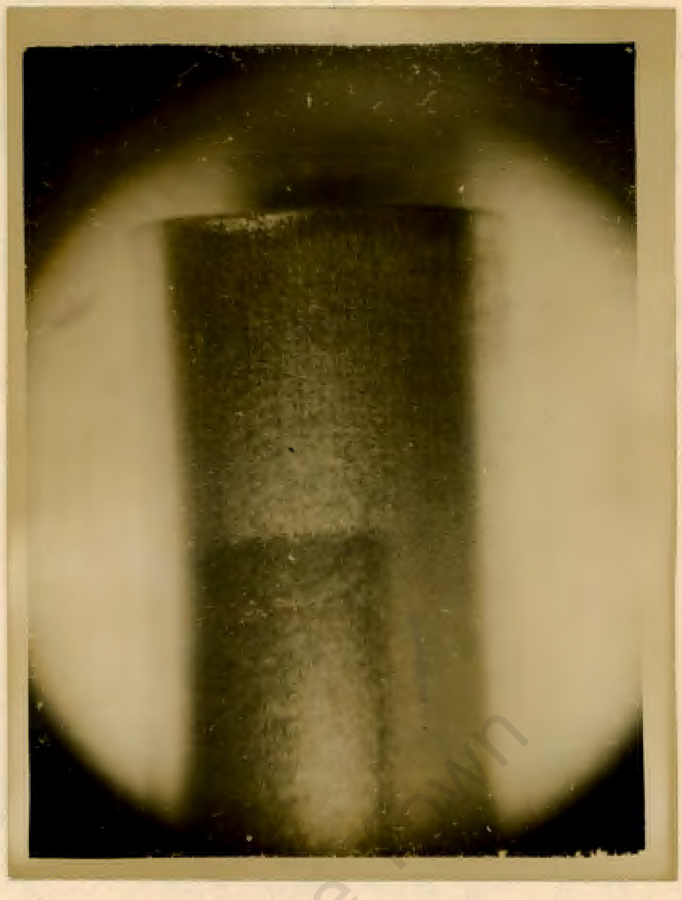


Plate 9. Band at End of Heat-treated Test Specimen.
x 2

Plate 10. Showing Banded Attack.
x 2

Plate 11. Fine-Grained Structure.
X 2

Plate 12. Coarse-Grained Structure.
X 2

a sharp line of demarcation between the band and the rest of the specimen. At the same time, a difference was seen in the corrosion occurring at the ends and on the main portion of the test specimen. At the ends there were a large number of small points of attack which were close together, whereas the remainder of the specimen was attacked at larger spots more widely spaced. Also there was a fairly sharp distinction between the two forms of attack with the dividing line about 1/2 inch from each end (Plate 10).

An examination of the pickled surface under a microscope showed that the structure of the metal was not uniform. At each end there was a much finer grain than at the middle of the specimen, where the grain was quite large and could in fact be seen with the naked eye. A specimen that was pickled in dilute nitric acid clearly brought out the difference in grain structure. This difference is shown in photographs (Plates 11 and 12).

An experiment was carried out on a specimen that had not yet been heat-treated. After heating in the vacuum furnace for four hours, the first signs of grain enlargement appeared at the middle of the test specimen. This grain enlargement grew more pronounced as further heat-treatment was carried out; the enlarged structure spread from the middle outwards towards the ends. It was not until twelve hours treatment that any definite signs of band formation appeared, when a band was noticed at one end only. However, after a further three hours heating, another band was shown at the other end, and the bands were more definite.

The test piece was then placed so that one end only was in the heated part of the furnace where it would be hottest. After two hours there was no change, but when it had been heated for another three hours, the band had disappeared and the grain was enlarged right to the end. For subsequent corrosion tests the specimens were first given a heat-treatment for twelve hours or longer to enlarge the whole structure.

No really satisfactory explanation has been found, but the following is a suggestion to account for the difference in structure. The middle section of the test piece, when in the furnace, was at the hottest part and the temperature rose here to a higher degree than at the ends which were cooled by radiation along the furnace tube. The temperature given by a thermocouple was 850°C, but it is possible that the temperature may have been even higher than this at times. At temperatures just above the critical line, the structure of steel consists of very small austenitic crystals, but at higher temperatures some of these grow at the expense of the others. Thus at the ends, which are just at or above the critical point, the structure is fine grained; while in the middle, the grains grow on soaking at the higher temperature. This does not however, explain why there should be such a sharp line of demarcation between the two structures, as it would be expected that the change in structure would be gradual and according to the temperature gradient.

It was noted that, though there were more points of attack on the fine grain sections of the test specimens, the corrosion was more concentrated and intense at the points on the large grain section. It is probable therefore, that the total corrosion for both sections was the same; but the pit holes in the large grain structure were deeper than in the fine grain, hence the larger the grain the deeper the penetration for any time period under the same conditions, and a large grain structure is more likely to fail when corrosion is by pitting than a close grained structure.

Observations that have been reported on the effect of grain size on the corrosion of metals are sometimes conflicting. The evidence is, however, often complicated by the simultaneous presence of other factors in the experiments.

S.W.Smith (46) considered that a small grain size favoured attack, whereas J.P.Sparrow (47) and S.Whyte (48) claimed that a fine structure resists attack better than does a coarse structure. G.D.Bengough and R.May (49) said that the effect of grain size was small, but that corrosion is less with a small grain structure than with a large one. J.H.Whitely and A.F.Hallimond (50) decided that there was no difference in the attack on annealed iron having widely differing grain sizes.

It is probable, therefore, that the grain size is not of very great importance; but nevertheless, for comparative tests, it is wise to use samples that have similar grain structures.

CORROSION BY VAPOURS FROM AMMONIUM HYDROXIDE SOLUTION.

In order to perform corrosion tests using a solute that is normally gaseous and which has consequently a high vapour pressure, it is necessary to select a solution for the flask that will give a vapour that does not contain excessive quantities of the gas at the temperature of the test. While it may be possible to absorb and measure high concentrations of a gas like ammonia, it requires a large amount of absorbent, and the concentrations of the reagents employed in the estimations must also be high. This may be entirely unnecessary if lower concentrations of corrosive gas can be used with the same effect. It is reasonable to start investigations with solutions with which one normally works. This was the policy that was adopted to determine the concentrations of the solutions that were used in the corrosion tests, unless other considerations made the use of specific solutions advisable.

Tables were consulted to discover a solution that had a vapour pressure of ammonia at 80°C that could be measured with a reasonable accuracy by absorption in acid. Although exact figures could not be obtained, it was estimated that a 0.2N solution would be suitable. Such a solution was prepared and placed in the flask.

In the absorption bottles of the analysis and corrosion lines, 2N sulphuric acid was used to absorb the ammonia that passed through the system. At the end of the test the acid was added to the condensate collected in the analysis line before the estimation of the total ammonia in the gas stream. The absorbent was neutralised with sodium hydroxide solution and excess added. Determination of the ammonia was accomplished by distillation into standard acid, the excess of which was titrated with 0.1N sodium hydroxide.

Only one test of two hours duration was run for the condensing vapour corrosion by ammonia. This was because there was complete protection, and not even the attack by distilled water was experienced. A drop test in which a drop of ammonia solution was placed on the flat prepared surface of a piece of steel, also showed no corrosion. This result was not surprising on account of the well-known passivity of steel in alkaline solutions. Whitman, Russell and Altieri (51) and U.R.Evans (52) have pointed out that the behaviour of a metal to different solutions seems to be determined very largely by the solubility of its oxides in the liquid in question, and this strongly supports the view that passivity is due to an obstructive oxide film that has failed to dissolve. The protection is therefore attributed to a thin film of ferrous hydroxide or oxide which is insoluble at the high pH of the condensed ammoniacal vapours (see pages 3 and 4).

In all these tests the air is freed from carbon dioxide before passing it through the hot solution in the flask: according to J.W.Shipley and co-workers (53) iron will not dissolve in purified water free from carbon dioxide until the pH falls below the value of 9.4. F.N.Speller (54)(see Figure 9) has also classified waters in terms of their acidity:- (a) Alkaline waters have a pH greater than 10, and corrosion is slow, normally due to the depression of the solubility of the oxide film; (b) Neutral waters have a pH between 10 and 4.3, and corrosion takes place in the presence of oxygen; (c) Acidic waters, having a pH below 4.3, rapidly corrode iron with the liberation of hydrogen, even in the absence of the depolariser oxygen.

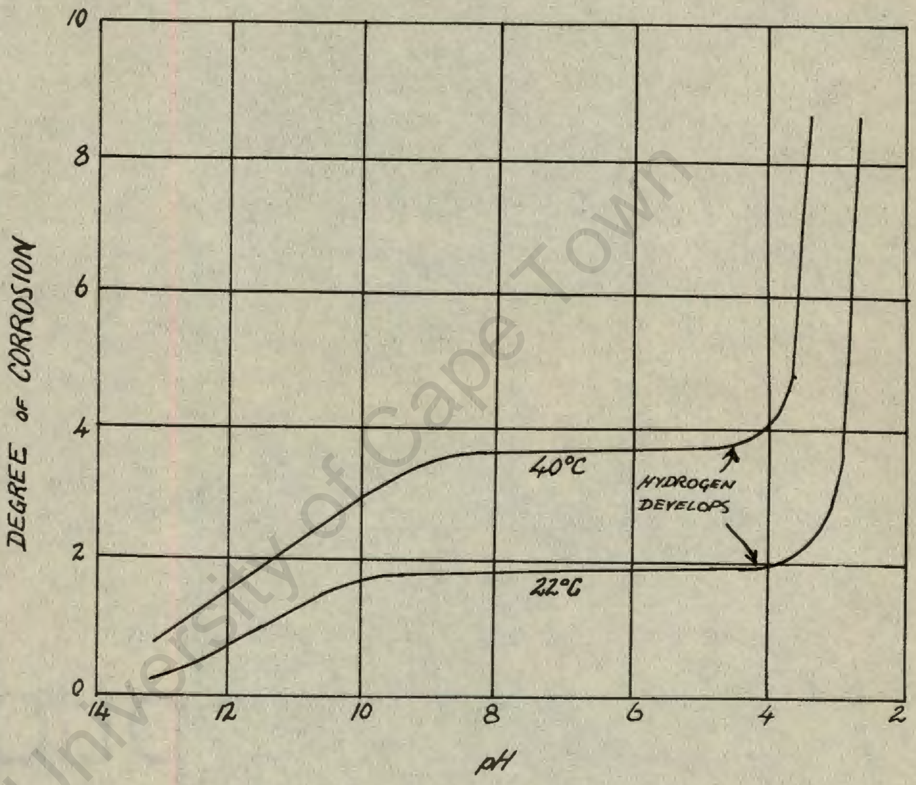


Figure 9. EFFECT of pH on CORROSION

CORROSION BY VAPOURS FROM AMMONIUM THIOCYANATE SOLUTION

Tests were carried out to investigate the corrosion process and the corrosion curve of mild steel by condensing vapours from a solution of ammonium thiocyanate. As in the preliminary tests, a 2% solution was used, since it is the concentration present in the residue receivers of the benzole recovery plant. Porous pot was added to the flask containing the solution in order to promote the vaporisation of the salt. This is more convenient than the use of sulphur which has the same effect, because sulphur has a tendency to stick to the side of the flask and is difficult to remove. The concentration of ammonium thiocyanate was determined before and after each test with 0.1N silver nitrate. The variation in concentration for the 15-hour tests was between 0.2 and 0.3 per cent.

Estimations of thiocyanate were also made on the condensates from the test pieces and in the analysis line. N/760 silver nitrate was used in this case, which is equivalent to 0.1 mgm ammonium thiocyanate per c.c. Only very small quantities of thiocyanate were detected from time to time in the condensate from the test pieces. In many instances no indication of thiocyanate was found at all. From the analysis line, there were larger quantities of thiocyanate, the concentration in the distillate being about 8 parts per million. In case any thiocyanate was not condensed with the vapour and passed on, a solution of ferric nitrate indicator was placed in a wash-bottle after the condensate receiver. During the whole series of tests no positive indication was observed.

The attack on the test specimens was very marked, and brown spots of corrosion product were seen after only five minutes exposure to the corrosive vapours. The penetration was not apparently as deep as might be expected when compared with that of distilled water with the same total corrosion. This must be on account of the larger areas that were attacked by the ammonium thiocyanate vapours. The attack was most pronounced at the top of the specimens where there was most condensation. Corrosion was entirely of the drop-cell pitting type which can be seen in photographs taken after a 4-hour test (Plates 13 and 14). After a time, large drops of condensate started at the top and ran down the tube to drop off at the bottom. Corrosion then took the form of streaks along the edges of the condensate stream (Plate 15). When the stream passed over points of attack, they were stifled and scarcely grew in size (Plate 16).

The growth of a drop-cell is illustrated by photographic plates (Plates 17, 18, 19 and 20). At the start, the corrosion product completely covers the corrosion area. As the bulk of the product increases however, it begins to split up until finally it totally disintegrates and is washed away, revealing a black spot of fairly adherent oxide. The 15-hour corrosion spot photograph (Plate 20) shows the disruption just before the corrosion product is washed away.

The corrosion curve for the vapours from the 2% solution of ammonium thiocyanate shows a very rapid rate at the beginning of the attack. This rate was 10 times that for water vapour. The rate of attack was not maintained; and it began to decrease progressively as time passed. The curve shows the possibility of being asymptotic to a certain corrosive level (Figure 10, page 67).

In an endeavour to reach the asymptote, means were considered to step up the corrosion rate. The only method that did not alter the conditions of the test was to

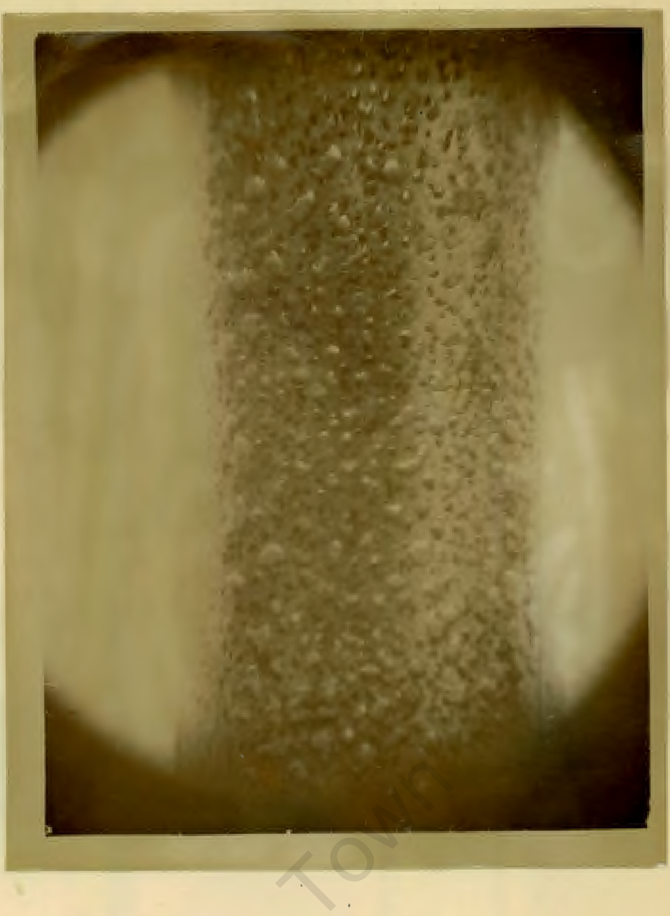


Plate 13. Corrosion by Drop-cell Attack.
x 2

Plate 14. Corrosion Pit Holes.
x 2

Plate 17. 2-hour Corrosion Spot.
× 160

Plate 18. 4-hour Corrosion Spot.
× 160

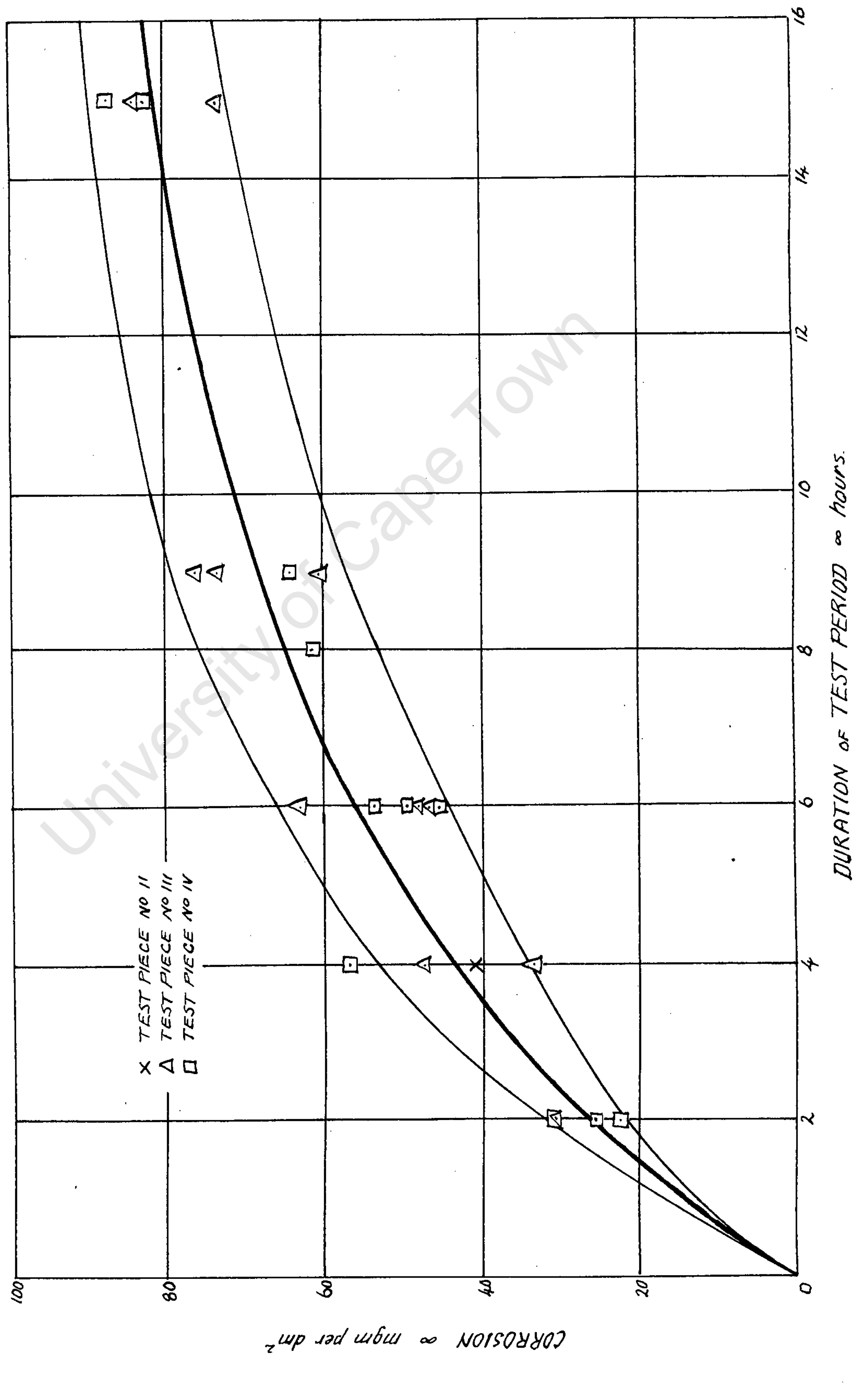
CORROSION BY AMMONIUM THIOCYANATE VAPOURS AT 80°C

Test Piece Number	Duration of Test hours	Total Corrosion Observed mgm	Total Corrosion Corrected mgm	Corrosion mgm/dm^2	Points of Attack.	Gas Rate of Flow. cm/min	Cooling Water Temperature °C	Condensate on Test Piece. c.c./hour	NH_4CNS in Condensate p.p.m.	Heat cal/min
III	2:00	18.0	17.9	30.2	7600	8.6	19.63	0.5	16	118
IV	2:00	13.2	13.1	22.0	4770	11.5	19.97	2.0	8	129
IV	2:00	18.0	17.9	30.2	5270	10.8	19.84	1.0	20	126
IV	4:00	34.2	34.0	57.3	7550	8.9	19.40	1.0	10	121
II	4:00	24.6	24.4	41.1	4440	8.6	19.37	2.5	6	125
III	4:00	28.2	28.0	47.2	4610	8.7	19.81	2.0	7	129
III	4:00	20.2	20.0	33.7	3880	8.4	18.56	2.1	9	131
IV	6:00	31.8	31.6	53.3	4500	9.4	20.10	1.2	6	123
III	6:00	37.5	37.3	63.0	4500	9.1	19.80	1.1	5	124
III	6:00	28.5	28.3	47.7		9.1	19.48	0.6	6	111
IV	6:00	27.2	27.0	45.6	3000	9.5	20.29	1.1	5	124
IV	6:00	29.3	29.1	49.0	5400	7.9	19.84	1.1	6	118
IV	8:00	36.4	36.2	61.0	5390	7.7	18.34	2.7	6	140
III	9:00	44.0	43.8	73.8	3240	8.6	19.13	1.3	7	118
IV	9:00	38.2	38.0	64.1	3840	8.5	20.04	1.7	9	125
III	9:00	45.5	45.3	76.3	5120	8.3	19.96	1.2	6	115
III	9:00	35.8	35.6	60.1		7.1	18.12	1.7	6	130
IV	15:00	51.8	51.6	87.1	4250	8.0	18.67	2.4	3	137
III	15:00	43.6	43.4	73.2		5.0	18.94	1.4	10	150
IV	15:00	49.0	48.8	82.2	3840	6.9	18.67	1.5	8	137
III	15:00	49.7	49.5	83.3	3840	6.7	17.27	1.9	5	133
Corrosion in nitrogen medium.										
IV	6:00	0.7	0.6	1.0	nil	9.3	18.57	3.0	4	132
Corrosion using 5% solution instead of 2% solution.										
IV	2:00	15.0	14.9	25.0	4300	8.8	17.63	1.5	31	131
III	6:00	27.6	27.4	46.2	4320	9.3	17.95	3.0	8	127

CORROSION BY AMMONIUM THIOCYANATE VAPOURS AT 80°C

Test Piece Number	Duration of Test hours	Total Corrosion Observed mgm	Total Corrosion Corrected mgm	Corrosion mgm/dm^2	Points of Attack.	Gas Rate of Flow. cm/min	Cooling Water Temperature °C	Condensate on Test Piece. c.c./hour	NH_4CNS in Condensate p.p.m.	Heat cal/min
III	2:00	18.0	17.9	30.2	7600	8.6	19.63	0.5	16	118
IV	2:00	13.2	13.1	22.0	4770	11.5	19.97	2.0	8	129
IV	2:00	18.0	17.9	30.2	5270	10.8	19.84	1.0	20	126
IV	4:00	34.2	34.0	57.3	7550	8.9	19.40	1.0	10	121
II	4:00	24.6	24.4	41.1	4440	8.6	19.37	2.5	6	125
III	4:00	28.2	28.0	47.2	4610	8.7	19.81	2.0	7	129
III	4:00	20.2	20.0	33.7	3880	8.4	18.56	2.1	9	131
IV	6:00	31.8	31.6	53.3	4500	9.4	20.10	1.2	6	123
III	6:00	37.5	37.3	63.0	4500	9.1	19.80	1.1	5	124
III	6:00	28.5	28.3	47.7		9.1	19.48	0.6	6	111
IV	6:00	27.2	27.0	45.6	3000	9.5	20.29	1.1	5	124
IV	6:00	29.3	29.1	49.0	5400	7.9	19.84	1.1	6	118
IV	8:00	36.4	36.2	61.0	5390	7.7	18.34	2.7	6	140
III	9:00	44.0	43.8	73.8	3240	8.6	19.13	1.3	7	118
IV	9:00	38.2	38.0	64.1	3840	8.5	20.04	1.7	9	125
III	9:00	45.5	45.3	76.3	5120	8.3	19.96	1.2	6	115
III	9:00	35.8	35.6	60.1		7.1	18.12	1.7	6	130
IV	15:00	51.8	51.6	87.1	4250	8.0	18.67	2.4	3	137
III	15:00	43.6	43.4	73.2		5.0	18.94	1.4	10	150
IV	15:00	49.0	48.8	82.2	3840	6.9	18.67	1.5	8	137
III	15:00	49.7	49.5	83.3	3840	6.7	17.27	1.9	5	133
Corrosion in nitrogen medium.										
IV	6:00	0.7	0.6	1.0	nil	9.3	18.57	3.0	4	132
Corrosion using 5% solution instead of 2% solution.										
IV	2:00	15.0	14.9	25.0	4300	8.8	17.63	1.5	31	131
III	6:00	27.6	27.4	46.2	4320	9.3	17.95	3.0	8	127

Figure 10. CORROSION by VAPOURS from SOLUTIONS of AMMONIUM THIOCYANATE.



increase the concentration of the ammonium thiocyanate in the solution and hence in the vapours. The concentration in the flask was increased to 5%, and tests were run. Both the points obtained for vapours from the 5% solution fell within the range of values for vapours for 2% solutions. The concentration of ammonium thiocyanate in the analysis line condensate increased by about three times. In the condensate collected from the test piece, the concentration also rose to measurable amounts. Hence it shows that this increase in solution concentration, while it raises the vapour pressure, has no effect on the corrosion itself; and only small amounts of ammonium thiocyanate in the vapours will raise the corrosion considerably from that of pure water.

Mathematical Analysis of Test Results.

For symbols used, see page 41.

2-hour Corrosion Tests.

No.	Result mgm/dm^2	v	v^2
III	30.2	3.3	10.9
IV	22.0	-4.9	24.0
IV	30.2	3.3	10.9
IV	25.0	-1.9	3.9
	107.4	13.4	49.4

A.M. = 26.9 n = 4

All these results are acceptable according to Chauvenet's Criterion.

$$S = \pm\sqrt{\frac{49.4}{4 \times 3}} = \pm 2.02 \qquad e = \pm\frac{13.4}{\sqrt{4 \times 3}} = \pm 3.97$$

$$s = \pm\sqrt{\frac{49.4}{3}} = \pm 4.05 \qquad r = \pm 0.766 \times 4.05 = \pm 3.10$$

For a confidence of 95%,

$$\pm L = \pm\frac{2.78 \times 4.05}{\sqrt{4}} = \pm 5.64$$

Limits of corrosion mean = 26.9 ± 5.64

4-hour Corrosion Tests.

No.	Result mgm/dm^2	v	v^2
II	41.1	-3.7	13.7
III	47.2	2.4	5.8
III	33.7	-11.1	123.2
IV	57.3	12.5	156.3
	179.3	29.7	299.0

A.M. = 44.8 n = 4

$S = \pm\sqrt{\frac{299.0}{4 \times 3}} = \pm 4.99$ $e = \pm\frac{29.7}{\sqrt{4 \times 3}} = \pm 8.58$

$s = \pm\sqrt{\frac{299.0}{3}} = \pm 9.98$ $r = \pm 0.766 \times 9.98 = \pm 7.65$

For a confidence of 95%,

$$\pm L = \pm\frac{2.78 \times 9.98}{\sqrt{4}} = \pm 13.9$$

Limits of corrosion mean = 44.8 ± 13.9

The arithmetic mean and the limits calculated above do not fit the interpolated curves from the other test period calculations. Taking the interpolated values, we have:

Limits of corrosion mean = 43.5 ± 9.5

For these limits,

$$\text{Student's } t = \pm\frac{9.5 \times \sqrt{4}}{9.98} = \pm 2.0$$

This is equivalent to a confidence of 88.4%.

No values may be rejected according to Chauvenet's Criterion.

6-hour Corrosion Tests.

No.	Result mgm/dm^2	v	v^2
IV	53.3	1.6	2.6
III	63.0	11.3	128.0
III	47.7	-4.0	16.0
IV	45.6	-6.1	37.1
IV	49.0	-2.7	7.3
	258.6	25.7	191.0

A.M. = 51.7 n = 5

$S = \pm\sqrt{\frac{191.0}{5 \times 4}} = \pm 3.09$ $e = \pm\frac{25.7}{\sqrt{5 \times 4}} = \pm 5.75$

$s = \pm\sqrt{\frac{191.0}{4}} = \pm 6.90$ $r = \pm 0.740 \times 6.90 = \pm 5.10$

For a confidence of 95%,

$$\pm L = \pm\frac{2.57 \times 6.90}{\sqrt{5}} = \pm 7.94$$

Limits of corrosion mean = 51.7 ± 7.94

but the number actually decreased after the first two hours. It is probable that the greater corrosive nature of the ammonium thiocyanate vapours induces a greater number of corrosion cells than in the case of distilled water vapour, and that these are formed more rapidly. Once the maximum number is reached for the particular specimen, the corrosion cells increase in size and many unite together with a consequent reduction in the total number.

Action of Ammonium Thiocyanate Solution on Steel.

A drop test (page 114) on a 5% solution of ammonium thiocyanate resulted in a sulphide corrosion product, whereas the attack by condensate yielded oxides. Hence it is necessary to use actual condensate to get a clear picture of the nature of possible corrosive attack by condensing vapours. The concentration of soluble compounds in a drop may have a considerable effect on the corrosion and even change its nature altogether.

Consequently a large drop of actual condensate was used in a further drop test. After an hour, a ring of orange-brown corrosion product had formed, not at the surface, but slightly away from the edge and inside the drop, thus leaving a clear outer area all round the edge. The area within the ring of corrosion product was also clear; but after six hours, it was noticed that the inner surface had coated over with the orange-brown corrosion product. The outer ring could be described as a wall, since it was comparatively narrow and high. After this, the corrosion product did not increase very markedly in bulk, and further attack must have been stifled by the covering layer. When the corroded spot was examined, a greyish stain was apparent below the bulk of the product, but not to the extent of the black deposit of sulphide under the 5% drop.

These observations follow the apparent pattern of corrosion by condensing vapours from the ammonium thiocyanate solutions. It is clear that the attack must be in the nature of an electrolytic cell through differential aeration. When a drop forms on the surface of the specimen, it grows in size until its own weight causes it to flow down the tube and drop off at the bottom. A stream of liquid is formed which acts like a very elongated drop. The unattacked area around a drop just inside the outer edge or along the edge of a stream of downward flowing condensate, is the aerated portion to which oxygen is freely available by diffusion. It is consequently the cathode in the differential aeration cell. The inner part is not as freely aerated, since diffusion is not as free, and thus becomes the anode. The actual nature of the part played by ammonium thiocyanate is not yet clear, but will be dealt with later. At the junction of the anodic and cathodic areas, iron appears to be precipitated as oxide, which later spreads over the surface of the anodic area to block the free passage of ions and stifle the attack. This would explain the decreasing rate of attack noticed in the condensation tests.

Condensation Corrosion in the Absence of Oxygen.

An effort was made to determine the role played by oxygen in the corrosion attack by ammonium thiocyanate vapours.

All the oxygen in the corrosion apparatus was washed out by passing nitrogen through the system for thirty minutes. A 2% solution of ammonium thiocyanate was again used in the flask; nitrogen was bubbled through the solution held at 90°C to replace any dissolved oxygen. As the test piece was being placed in the corrosion chamber, gas was allowed to escape, thus assuring that no oxygen would enter even at the start of the test.

Condensation took place on the test piece immediately in the form of small droplets; but after thirty minutes no corrosion could be seen, showing that the attack had been markedly reduced, since with oxygen, attack occurred after only five minutes. The total corrosion for six hours was 0.7 mgm, which is negligible compared to the other results. There were some small black spots on the surface, but no signs of oxide product.

Both the condensate in the analysis line and that collected from the test specimen had the same concentration of ammonium thiocyanate, which corresponded to that which was normally obtained in the analysis line using air and a 2% solution. This obviously shows that ammonium thiocyanate vapour did not react nor was it dissociated on the metal surface.

The conclusion reached, is that the vapours - water as well as ammonium thiocyanate, since no attack was registered at all - do not corrode mild steel in the absence of oxygen. It is confirmed that the attack must therefore be due to a reaction involving differential aeration. The vaporisation of ammonium thiocyanate is not due to any reaction with oxygen with subsequent recombination on condensation.

Combination Tests.

It was recognised that there might be a reaction between the corrosion products and ammonium thiocyanate. If the ammonium thiocyanate does not enter into a direct corrosion attack on the steel, the acceleration of corrosion must be due to a reaction with the initial corrosion product resulting from the attack by water vapour itself. A test specimen was therefore corroded, first in air-water vapour and followed by exposure to vapours from ammonium thiocyanate solution in an atmosphere of nitrogen.

The water vapour attack was carried out for a 6-hour period, at the end of which the corrosion appeared to be normal. Without removing the test piece, the distilled water was poured out, hot thiocyanate solution was substituted, and the test continued. Nitrogen was passed through the system to drive out oxygen, and the ammonium thiocyanate solution was saturated with nitrogen before starting the second stage of the test. The specimen was exposed to the vapours from the solution through which nitrogen was passed for a further 6-hour period. The orange-brown corrosion product from the water vapour attack had turned black in colour and was reduced in apparent bulk at the conclusion of the test period.

The corrosion result (39.0 mgm/dm^2) was much higher than that for six hours corrosion by water vapour (9.3 mgm/dm^2). Also, there was a decrease in the concentration of ammonium thiocyanate in the condensate from the test piece, which was not, however, as much as in the presence of oxygen. This result demonstrates that in the absence of oxygen, for example under a covering of corrosion product, ammonium thiocyanate can still react, provided a corrosion cell has already been formed. There is at the same time, a change in the nature of the corrosion product. The dark product under the covering of the main corrosion product in the 15-hour tests was produced in this manner. The continued activity of the corrosion cell may be due to a differential hydrogen cell. Hydrogen, absorbed on the anodic area during corrosion under aerated conditions, may still maintain the electrolytic conditions necessary for corrosion.

A mixture of iron filings and ferric hydroxide, the probable corrosion product, was warmed with a dilute solution of ammonium thiocyanate, while a slow stream of nitrogen was bubbled through the liquid. The brown hydroxide, orange in dilute solutions, darkened and finally turned black. A test for sulphide gave a negative result, and it was taken that a reduction had taken place to form a lower oxide.

Following similar lines to the preceding combination test, a test was carried out in which the specimen was first exposed to ammonium thiocyanate vapours in nitrogen, and then to water vapour alone, both for six hour periods.

In this case the corrosion by thiocyanate vapour in nitrogen again took the form of black spots or stains on the metal surface. The water vapour corrosion developed normal orange-brown spots and the total corrosion was just 16.9 mgm/dm^2, which is slightly below the water vapour curve at 12 hours. The attack did not appear to be out of the ordinary.

Theory of Corrosion Attack.

The following theory has been developed to explain the phenomena which have occurred in the tests.

On condensing upon the surface of the steel, each droplet of solution forms a separate differential aeration cell. The outer rim of the drop, to which oxygen has greater access, is the cathode, while the anode of the cell is the inner, less aerated portion of metal. When a number of drops coalesce to form a larger drop, it will run down the specimen leaving a stream behind. Corrosion still proceeds by differential aeration. In this case the cathode is situated just within the edge of the stream, and the anode is down the middle. Oxygen acts as a cathode depolariser, and a current is set up within the metal, electrons passing from the anode to the cathode.

At the cathode, alkaline conditions are experienced and the solution of the oxide film is depressed

$$\frac{1}{2} O_2 + H_2O + 2e \longrightarrow 2 OH'$$

At the anode, iron passes into solution as ferrous ions. Ammonium thiocyanate is more highly ionised tha pure water, and the solution of iron is assisted by the presence of thiocyanate ions, which form the colourless ferrou thiocyanate with the iron.

$$Fe + 2H^{\cdot} \longrightarrow Fe^{\cdot\cdot} + H_2$$

$$2NH_4CNS \longrightarrow 2NH_4^{\cdot} + 2CNS'$$

When ferrous thiocyanate meets the cathodic solution, the hydroxide reacts with it to yield ferrous hydroxide, which is immediately oxidised by dissolved oxygen; and the boundary between the anode and cathode areas is marked by a precipitate of ferric hydroxide. In like manner, ferric hydroxide is precipitated over the anodic area in the centre.

In this process, ammonium thiocyanate promotes the corrosive attack by increasing the conductivity of the condensate. Only a small concentration of thiocyanate will raise the rate of attack three or four times the rate for distilled water.

Eventually the corrosion product gets so thick that it stifles the anode area, and corrosion proceeds as in the absence of oxygen. Such attack produces a black deposit, which is attributed to the partial oxidation of ferrous hydroxide to an intermediate hydroxide or to anhydrous magnetite (55).

$$6Fe(OH)_2 + O_2 \longrightarrow 2Fe_3O_4 + 6H_2O$$

The black product is closely adherent, and attack diminishes as it is formed. This may be seen from the corrosion curve, which shows a rapid attack at first, and a decreasing rate as time passes. (Figure 10)

CORROSION BY CONDENSING VAPOURS

FROM SOLUTIONS OF AMMONIUM SULPHIDES

It has been claimed that the corrosion in benzol plants (33) was not due to either ammonia or hydrogen sulphide. It has already been shown that ammonia by itself affords complete protection to steel when in condensing vapours; corrosion when hydrogen sulphide is also present is considered in this section.

The use of ammonium sulphide as the corroding agent raises problems not encountered with ammonium thiocyanate. Ammonium thiocyanate is a stable solid, while ammonium sulphide cannot be prepared in the solid state from aqueous solutions because it dissociates very readily into ammonia and hydrogen sulphide; but it is obtained as a colourless crystalline compound from a mixture of the two gases kept at about -18°C. At higher temperatures it decomposes. At atmospheric pressure no combination takes place above 32.5°C even in solution, for at this temperature the total pressure of the ammonia and hydrogen sulphide is 760 mm.Hg. (56). The problem therefore was to lower the vapour pressure, not to raise it as in the case of thiocyanate.

A system was devised for the analysis of the vapours that were given off from the solution in the flask. No absorbents were known which do not react with either ammonia or hydrogen sulphide, that can be used to estimate moisture. Acidic reagents like phosphorus pentoxide, react with ammonia; basic absorbents like lime react with hydrogen sulphide. Even Calcium chloride combines with ammonia to produce an addition product $CaCl_2.8NH_3$. Finally exact accuracy was sacrificed, and the moisture in the gas stream was measured by passing it through a condenser and measuring the volume condensed during the period of test. The uncondensed gases then passed into a standard solution of iodine in 2N sulphuric acid. Ammonia is absorbed by the sulphuric acid; hydrogen sulphide reacts with the iodine and sulphur is precipitated. Since iodine is volatile, a further wash bottle was used containing standard sodium thiosulphate, which took up any volatilised iodine coming from the previous absorption bottle. The error in using iodine with a thiosulphate trap is not more than 0.2 ml. in the titration (57). At the end of the test, the total quantities of gases were estimated by combining the condensate and the contents of both wash bottles. Titration of the unused iodine with standard sodium thiosulphate firstly, gave the hydrogen sulphide content by difference. Then excess sodium hydroxide solution was added, and the mixture boiled for the ammonia to distil into a flask containing an excess of standard hydrochloric acid. The titration of this excess with standard alkali once all the ammonia was driven over, gave the ammonia content of the gases also by difference. From these values, the partial pressures were calculated.

The first solution used in the flask for a corrosion test was a polysulphide of ammonia, as it was believed that this would be more stable than the sulphide, and hence give slighter vapour pressures. Sulphur was shaken up with an 8% stock solution of ammonium sulphide until no more would dissolve. The solution changed colour from yellow to a very dark ruby red. This solution was then diluted four times to give an approximately 2% solution. Sulphur was precipitated, and at the same time the colour changed to an orange red. This solution was used in a trial run to determine the constitution of its vapours.

The result of the trial run at 80°C gave a hydrogen sulphide figure of 48.2 mgm/litre of air or a partial pressure of about 130 mm.Hg. It was thought that this was a rather high concentration, so the solution in the flask was diluted a further ten times. A trial run was made on this solution, and the hydrogen sulphide amounted to less than half the above proportion. The diluted solution was used in the corrosion tests.

A very rough method was used in order to determine the approximate composition of the polysulphide solutions. 100 gm of the 8% ammonium sulphide solution was taken and sulphur added until no more could be seen to dissolve. The resultant solution was filtered and weighed. The increase in weight gave the quantity of sulphur dissolved to form polysulphide. Calculation showed the probable constitution to be $(NH_4)_2S_7$.

$$\underset{68}{(NH_4)_2S} + (x - 1)\underset{32}{S} \longrightarrow (NH_4)_2S_x$$

Let n be the mole fraction of ammonium sulphide involved.

$$\begin{aligned} n.32(x - 1) &= 20.0 \\ n.68 &= 8.0 \\ (x - 1) &= \frac{20.0 \times 68}{32 \times 8.0} \\ &= 5.3 \\ x &= 6.3 \end{aligned}$$

The sulphur precipitated when this solution was diluted to the solution used in the tests, was filtered off and weighed. Calculation gives the formula for the polysulphide in the diluted solution. On diluting 12.5 ml. concentrated solution to 500 ml., 1.0 gm of sulphur was precipitated.

$$(NH_4)_2S_{6.3} \longrightarrow (NH_4)_2S_x + (6.3 - x)\ S$$

12.5 ml. concentrated solution contains 1.0 gm $(NH_4)_2S$.

$$\begin{aligned} \frac{(6.3 - x)\ 32}{68} &= \frac{1}{1} \\ (6.3 - x) &= \frac{68}{32} \\ &= 2.1 \\ x &= 4.2 \end{aligned}$$

i.e. polysulphide in diluted solution is probably - $(NH_4)_2S_4$.

Sulphide Vapour Corrosion.

For corrosion tests, the corrosion line was also built up to cope with the analysis of the gases for hydrogen sulphide and ammonia. A condenser was provided to condense excess moisture that passed the test piece. Then followed a wash bottle containing 2N sulphuric acid to absorb ammonia; and a standard solution of iodine was placed in the same wash bottle to absorb hydrogen sulphide. The total concentration in the gas stream was so high, that all the iodine was used during the test run. Hence the procedure followed in the analysis line, where the rate of gas flow was much lower, could not be used. At the moment that the iodine was titrated by the hydrogen sulphide in the gas, the total volume was read on the flowmeter, and the hydrogen sulphide concentration could be calculated. A final wash bottle containing a concentrated solution of iodine was used to prevent the escape of hydrogen sulphide after the standard solution had been used up.

With very dilute polysulphide solution in the flask, a 2-hour test was run. No corrosion was visible when the test piece was removed, nor was there any loss in weight of the test piece. This no-corrosion result was confirmed by running a 6-hour test, which resulted in a total loss in weight of only 0.5 mgm/dm^2, which is lower than that for the test using nitrogen and ammonium thiocyanate. In the 6-hour test there was a uniform discolouration over the whole surface of the test piece. The condensate from the specimen had the light yellow colour of ammonium sulphide.

When the 6-hour test was started, it was noticed that, though droplets formed immediately the specimen was inserted, the condensate spread rapidly over the surface to give a uniform film of liquid. A drop test was carried out, and the drop also spread till it covered more than double the original area. No corrosion occurred in the drop test. When the very concentrated solution of ammonium sulphide was dropped on the surface of the piece of steel, it spread very rapidly.

Following these results, a test was run using a 0.5% solution of ammonium sulphide in the flask. The same procedure was carried out to determine the vapour composition as for the polysulphide tests. Once more, there was no corrosion of the test piece and the metal remained in its original clean state. Condensation was again of the film-type; and the condensate had the yellow colour of ammonium sulphide, though with a strong smell of ammonia.

The results show that the vapours from solutions of ammonium sulphides have a protective effect from the corrosion standpoint. Even the normal corrosion expected from water vapour alone does not occur. The protection must be afforded by the concentrations of ammonia that are present in the vapour. L.G.Metcalf (58) has found that the acidic solution of hydrogen sulphide in water causes rapid corrosion of iron either in the absence or presence of oxygen forming black insoluble ferrous sulphide, and resulting in serious pitting around the sulphide particles. E.Q.Camp (59) and E.Q.Camp and C.Phillips (60) have discussed the severe corrosion of equipment caused by hydrogen sulphide in the operation of an oil refinery. They consider that both oxygen and water are accelerators of hydrogen sulphide corrosion, and that both must be present before appreciable attack can occur. It is common practice in the petroleum industry to inject ammonia into distillation units for the control of corrosion by hydrochloric acid, and it is probable that a similar action takes place in the case of hydrogen sulphide corrosion. The ammoniacal concentration in the condensate protects the steel by depressing the solution of the thin oxide film that is present. Another protective aid is thought to be caused by the type of condensation. As the droplets of condensate spread, they joined together to form a film over the surface. Corrosion is thus prevented by blanketting the formation of differential aeration drop-cells, that are normally associated with dropwise condensation. A similar effect had been noticed when streams formed during the thiocyanate attack. Those points of attack within the body of the stream were stifled and ceased to play any marked part in the corrosion process.

CORROSION BY CONDENSING VAPOURS FROM SOLUTIONS OF AMMONIUM SULPHITES.

The tests on the vapours from the solutions of the ammonium sulphites, produced a type of corrosion that had not been encountered previously in these tests. The attack was direct and varied in intensity according to the composition of the solution and the resulting vapours. At one end of the vapour composition series, almost complete, if not complete, protection was experienced, while at the other end, the attack was extremely vigorous.

A stock solution of ammonium sulphite (22°Bè) was taken and diluted to give an approximately 10% solution. A trial run was made to determine the composition of the vapours given off at 80°C. This is done by sealing off all outlets and passing the vapours through the analysis line only.

The method for the analysis of the vapours in the gas stream from the solution, was similar to that used for the ammonium sulphide vapours. It was a modification of the method of Johnstone (61). A condenser was used to condense the moisture into a tube that was weighed before and after each test, thus determining the water content of the vapours. After each run, the condensate was added to a wash bottle which contained a standard solution of iodine and dilute 2N sulphuric acid. Sulphur dioxide reacts with the iodine, while ammonia is absorbed in the sulphuric acid. A further wash bottle was included to catch any iodine vapours coming from the first wash bottle, in standard sodium thiosulphate. The contents of this wash bottle were also combined with the iodine solution before titrating the excess iodine with more standard thiosulphate to estimate the sulphur dioxide content by difference.

Excess sodium hydroxide solution was added; the contents of the flask were boiled, and ammonia was distilled into an excess of standard hydrochloric acid. Titration of the surplus enabled the ammonia content of the vapours to be estimated.

Condensation Corrosion Tests.

Corrosion tests were then carried out with this solution which was found to have a measurable gas constitution. The corrosion line was fitted out in the same way as the analysis line to enable an estimation to be made of the gases after leaving the corrosion chamber.

At the start of the test the test piece clouded over and droplets were formed which spread to form larger drops. Attack took place in large patches and not under individual drops. Apparently the attack was direct and did not take the form of electrolytic corrosion by drop-cells.

When the test piece was examined after the test (Plates 21 and 22), it was covered by large areas of a black deposit of ferrous sulphide with an overlayer of brown oxide. The brown layer was blotchy, and had gaps through which black deposit could be seen. The results of the first two 2-hour tests were in very close agreement, which suggests that the attack is nearly uniform, and not due to a variable number of separate cells.

It was found necessary to use fresh solution in the flask after every few tests, as the total corrosion dropped and there was a change in the nature of the corrosion to that more like drop-cell attack. At first, this was attributed to the oxidation of the sulphite to the sulphate by the oxygen of the air bubbling through the solution. Hydroquinone, and later stannous chloride, were added as inhibitors of oxidation,

Plate 21. Sulphur Dioxide Type
of Corrosion.
x 2

Plate 22. Corroded Metal Surface.
x 2

but there was little effect in preventing the diminution of corrosion in subsequent tests. The effect was finally traced to the alteration in the vapour pressures of the gases as the solution composition changed.

When tests were carried out with solutions prepared from a fresh bottle of ammonium sulphite out of stock, no corrosion of the test specimen took place whatsoever. This remarkable result was explained when it was seen that the vapours had altered in composition. The concentration of ammonia had risen from 1.04 mgm/litre (0.62 mm.Hg.) to 15.7 mgm/litre (14 mm.Hg.), while the sulphur dioxide concentration decreased from 3.74 mgm/litre (0.59 mm.Hg.) to 0.24 mgm/litre (0.06 mm.Hg.). Thus, in effect, the specimens were attacked by vapours with an entirely different gas composition and containing an excess of ammonia, whereas, previously, there had been a slight excess of sulphur dioxide. It is therefore probable that the practice of adding ammonia to the vapours containing sulphur dioxide in benzol treatment plants(57), should be effective in preventing corrosion, provided that the dosage is maintained continuously and is not interrupted for any length of time during the operation of the plant. In such a case the sulphur dioxide attack would take place vigorously, and might nullify the beneficial effect of the addition of ammonia.

An analysis of the new stock solution showed that it was ammonium sulphite with an excess of ammonium ion. Very likely, the first bottle had altered in composition on standing for a number of years after being opened. The ammonia probably evaporated until a balance was set up with equal partial pressures of ammonia and sulphur dioxide, after which the ammonia and sulphur dioxide would come off in constant proportions. This theory is substantiated by the

Plate 23. Showing white Ferrous Sulphite
on Test Specimen.
x 2

figures obtained for the partial pressures. Since the vapour pressure is governed by the number of molecules of gas present, and though the vapour pressures of the two gases may be equal, the equivalence of sulphur dioxide is greater than that of ammonia, and provides an excess of sulphurous acid on condensation to react with the mild steel test pieces.

An effort was made to reproduce the previous corrosion results by converting the second solution to the first before carrying out a test. Sulphur dioxide was passed through a freshly made (approximately 10%) solution (A) until it was saturated and gas was given off when it was shaken. This new solution (B) was then heated to 80°C to obtain saturated conditions at that temperature, and after cooling, an analysis was made which gave the following figures:

Equivalents of SO_2 per 100 ml. - 0.3540
Equivalents of NH_3 per 100 ml. - 0.1530
Concentration of NH_4HSO_3 - 15%

There was an excess of sulphur dioxide.

A 2-hour corrosion test was run using solution (B) in the flask. Corrosion occurred immediately, and was characterised by a black deposit of ferrous sulphide (62) covering the surface of the specimen. Towards the end of the run, the deposit appeared to frost over, when it became coated with a white layer (Plate 23). The corrosion product was very thick, hard and tenacious. Underneath, the metal showed that it had been attacked uniformly and very vigorously, for the grains stood out prominently. The corrosion result was very high, over 1.2 gm being lost in the two hours of the test. In the receiver for collecting the condensate from the test specimen, a white-coloured salt separated out. Upon heating, it decomposed to yield a brown iron oxide. It had a reducing action on iodine; it was only slightly soluble in water, but dissolved when sulphur dioxide was passed through the liquid.

Thus the salt exhibited the properties of ferrous sulphite.

In this test, the sulphur dioxide concentration in the gas stream was very large. So large was it, that the usual method of estimation of the gases was not carried out, but direct determination in the analysing line was used. Starch indicator was added to the iodine absorbent, and the volume noted on the gasmeter when it was titrated by sulphur dioxide. From this figure, the concentration was calculated. It was not a very accurate method of estimation, but for the high proportion of sulphur dioxide compared with other figures, it was regarded as being sufficiently true.

Theory of Corrosion Attack.

Corrosion is so vigorous that it is probable that direct attack takes place. This deduction is confirmed by drop tests that were carried out on the condensate from a typical run, the original solution and a solution of sulphurous acid. In each case, the formation of the black corrosion product was immediate, and the drops showed a tendency to spread, which would result in film formation under condensing conditions and prevent electrolytic attack by drop-cells. Also, in contrast to the cases of drop-cell attack, no corrosion spots were noticed and the attack was uniform over the surface. The substances detected in the corrosion product that adhered to the metal were ferrous sulphide, ferric hydroxide and ferrous sulphite, while the condensate collected from the test specimen consisted of brown ferric hydroxide dissolved in an acidic solution of ferrous sulphite and sulphate (62).

The mechanism of attack is deduced to be as follows:- The iron dissolves in the acidic condensate to yield a solution of ferrous sulphite.

$$Fe + 2H^{\cdot} + SO_3^{''} \longrightarrow Fe^{\cdot\cdot} + SO_3^{''} + H_2$$

Atomic iron is a strong reducing agent, even stronger than hydrogen; and it reduces the ferrous sulphite to ferrous sulphide close to the metal surface (63). At the same time, ferrous hydroxide is produced and converted to ferric hydroxide by oxygen of the air.

$$3Fe + FeSO_3 + 3H_2O \longrightarrow FeS + 3Fe(OH)_2$$

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3$$

As the coating of sulphide gets thicker, less contact is made between ferrous sulphite and iron atoms, so that it is no longer converted to sulphide, but is precipitated over the surface when the solution becomes supersaturated. Ferrous sulphite is also oxidised by oxygen to sulphate which is found dissolved in the condensate.

<u>Corrosion and Vapour Composition.</u>

The results that were obtained, indicated that the corrosion of the test specimens by condensing vapours depended upon the proportion of ammonia and sulphur dioxide in the vapour, and hence upon the constitution of the solution in the flask.

A series of tests was then carried out to determine to what extent this was the case. Tests of two hours duration were run using solutions in the flask of varying proportions of ammonium and sulphite ions in order to evolve different compositions of ammonia and sulphur dioxide. Tables are drawn up (page 91), that list the relationship between the solution constitution, the composition of the vapours and the corrosion. It may be seen that the vapour composition does not bear a definite relation to the composition of the solution; but corrosion is influenced by the amount of sulphur dioxide in the vapours. Graphs of corrosion against concentration of sulphur dioxide in the condensate (Figures 10 and 11)

Figure 11. CORROSION by VAPOURS from SOLUTIONS of AMMONIUM SULPHITES.

(2-hour tests)

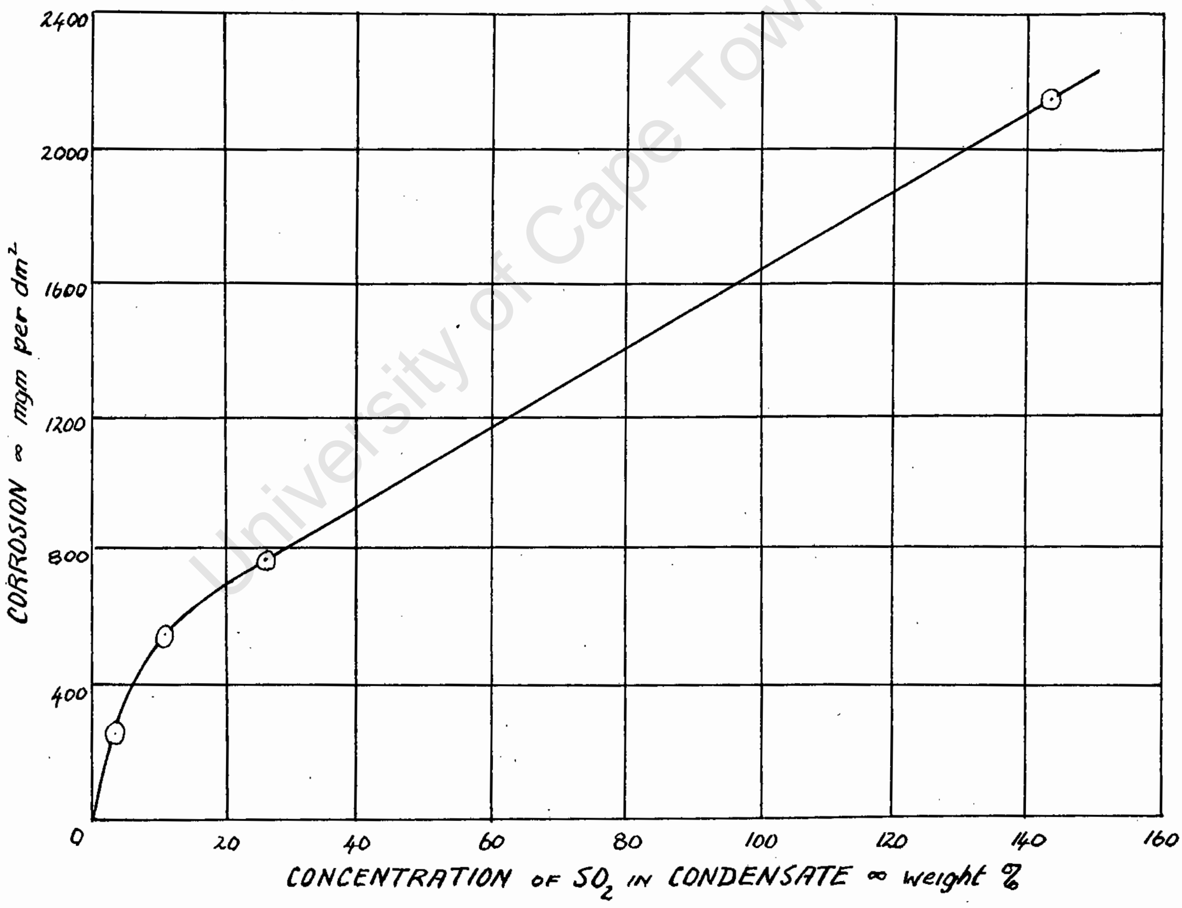
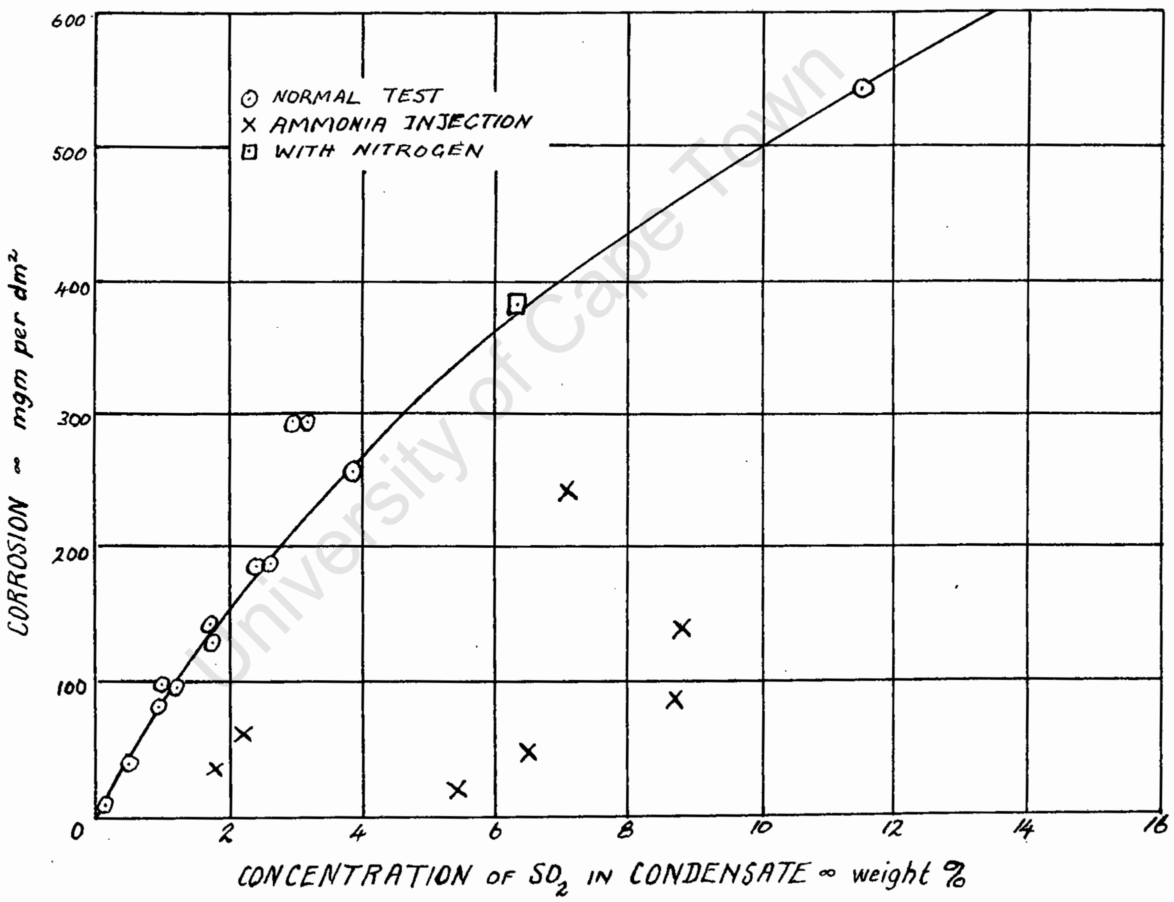


Figure 12. CORROSION by VAPOURS from SOLUTIONS of AMMONIUM SULPHITES.

(2-hour tests)



were drawn, which fitted the points obtained from the tests very closely with the exception of two results, one of which was undoubtedly an experimental error, since difficulty was experienced in getting an even flow of gases through the apparatus. The corroding gases went through the corrosion chamber in a series of spurts. The closeness of the experimental points to the curve, is a definite indication that attack was uniform and direct. The rate of attack was very rapid up to a concentration of about 10% sulphur dioxide in the condensate on the test piece. Then the rate decreased to a constant value.

These results pointed to the conclusion that corrosion by the vapours from solutions containing ammonia and sulphur dioxide (or ammonium sulphite - bisulphite solutions) was in some way governed by the sulphur dioxide concentration in the condensate on the test piece. The lower rate of attack at the higher concentrations was probably due to the protection afforded by the corrosion products. The results did not appear to be materially affected by the ammonia except perhaps at the lower concentrations of sulphur dioxide, when the ammonia content was very dominant. Certainty could not be reached on the last supposition, however, because the partial pressures do depend on the solution composition. When the ammonia partial pressure is high, the sulphur dioxide partial pressure is low, and vice versa. It is not possible to get both concentrations high at the same time directly from ammonia - sulphur dioxide solutions. Consequently, it was planned to run ordinary tests with a solution yielding a high sulphur dioxide figure, and to introduce ammonia into the gas phase directly.

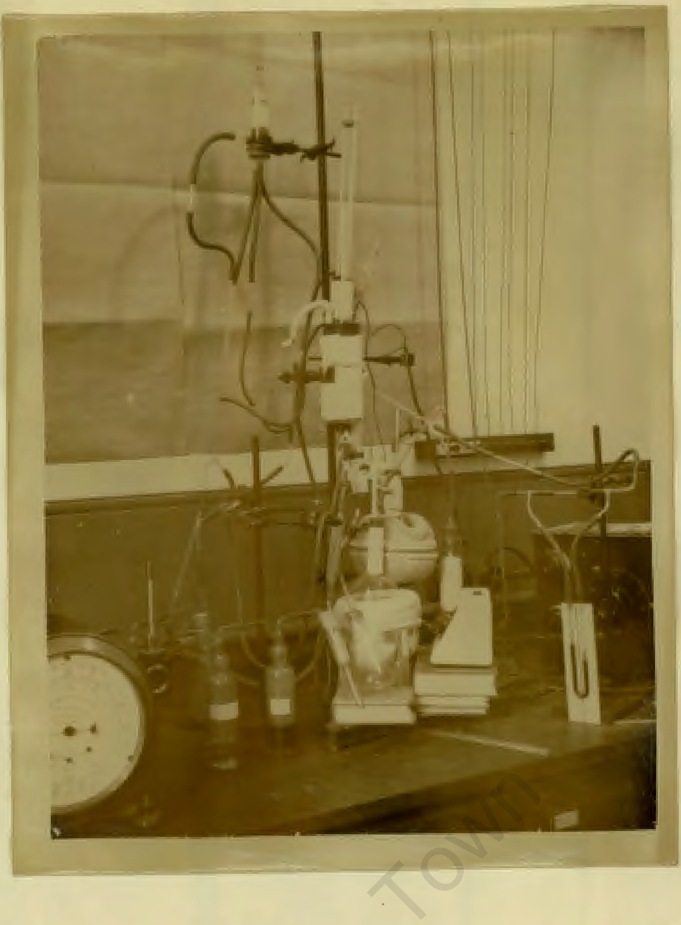


Plate 24. Ammonia Injection Apparatus.

Plate 25. Close-up of Modification.

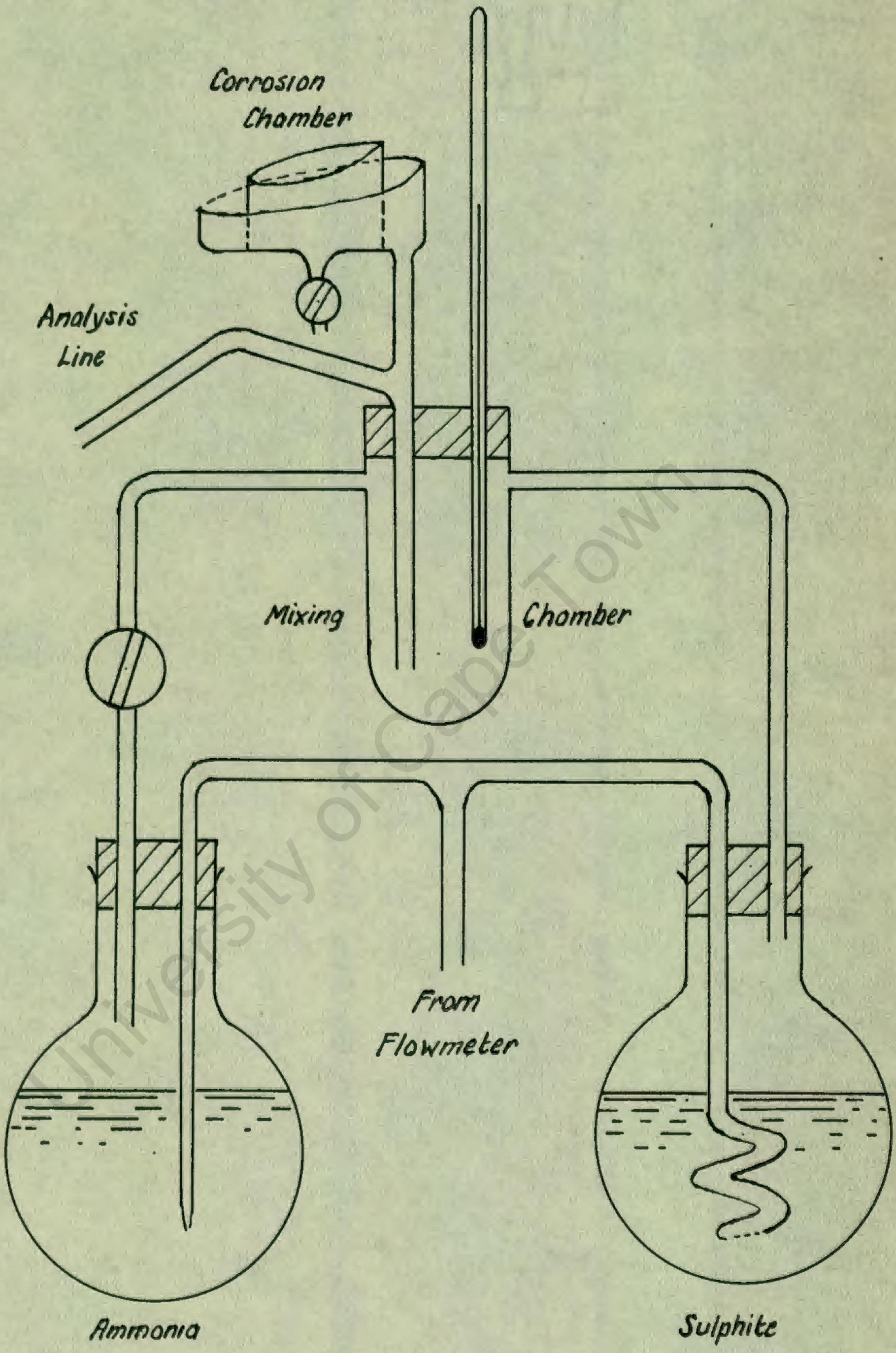


Figure 13. **DIAGRAM of AMMONIA INJECTION MODIFICATION.**

Ammonia Injection Tests.

In order to have high concentrations of both gases in the vapours, the apparatus was modified (Figure 13, Plates 24 and 25). Air was bubbled through a solution of ammonia, kept at 80°C by means of a Simmerstat heating mantle. The concentration of the ammonium hydroxide was varied for different test runs, in order to alter the amount of ammonia injected into the gas stream. Immediately after the ammonium sulphite - bisulphite solution flask, a mixing tube was fitted, into which the two gas streams entered at right angles to each other, were mixed, and passed into the corrosion chamber. The mixing tube was kept at a temperature well above 80°C by heating with a small gas jet, to prevent condensation taking place.

During a trial run to estimate the vapour composition, the ammonia and sulphur dioxide formed a fume of ammonium sulphite, which was not totally absorbed in the analysis line. However, when an additional wash bottle containing acid - iodine absorbent was included in the system, it proved to be adequate in removing all the fumes before the last wash bottle.

After consulting tables for the vapour pressure of ammonia solutions at 80°C, a 0.05N solution was used in the ammonium hydroxide flask for the first corrosion test. Corrosion did take place, though attack was no longer uniform over the whole surface, but occurred in fairly large patches; and there was a change in the nature of the corrosion product, which consisted mostly of ferric hydroxide with small amounts of ferrous sulphide. The condensate from the test piece contained ferrous sulphite, ferrous sulphate, and a greenish hydroxide precipitate in ammonium hydroxide solution. The corrosion result was reduced to about a third of the corrosion for a corresponding concentration of sulphur dioxide in the condensate without ammonia injection.

The ammonia solution was diluted to one half of its concentration; and another 2-hour test was run. This time, corrosion was rapid and of the straight sulphur dioxide type with the production of a black ferrous sulphide deposit. The total corrosion was, however, also cut down, but not by such a great amount as in the first test. Results of tests appear in the table on page 91 and are plotted on Figure 12.

After further tests with various concentrations of ammonia and sulphur dioxide, it became clear that the nature of the corrosion could be divided into two types according to the corrosion product formed. The first, with lesser amounts of ammonia injected, was similar to normal sulphur dioxide attack, with perhaps more ferric hydroxide being formed. The other occurred in the presence of greater amounts of ammonia, and resulted in little or no formation of ferrous sulphide. In this case, the increased proportion of ammonium hydroxide in the condensate, reduces the acidity of the solution, the solubility of the oxide film, and hence, the ease with which iron passes into solution. The iron that does dissolve, enters the solution as ferrous ions, ferrous hydroxide being the main product, and is immediately precipitated as ferric hydroxide in the presence of dissolved oxygen. Amounts of sulphite may be converted to sulphide in the usual manner; but, as the concentration of hydroxide increases, this tendency gets less, and oxidation to sulphate is more often the case.

Protection Against Corrosion.

Since the introduction of ammonia into the gas phase does not afford complete protection from attack, it is suggested that a more effective and convenient method of corrosion prevention, is to add ammonia to the mother liquor until the vapour pressure of sulphur dioxide is so reduced, that corrosion is overcome. The possibility of this method was demonstrated by running an ammonia injection test with a fairly high sulphur dioxide concentration in the vapours. The corrosion figure was 59.8 mgm/dm^2. The ammonia gas was then bubbled through the solution for two hours; and followed by a straight test, which had a negligible sulphur dioxide figure and the corrosion was reduced to 0.17 mgm/dm^2. It is pointed out, however, that prevention of corrosion is only effected by adding a sufficient quantity of ammonia to the mother liquor, and if insufficient is added, corrosion may be scarcely affected so that the injection of this amount of ammonia into the gas would be more beneficial in the reduction of total attack.

Vapour Pressures.

H.F.Johnstone (61) measured the partial vapour pressures over a range of concentrations of ammonia and relative concentrations of sulphur dioxide in solutions of the ammonia-sulphur dioxide-water system. Formulae were derived to express the partial pressures:-

$$p_{NH_3} = \frac{N.C(C - S)}{2S - C} \quad \text{and} \quad p_{SO_2} = \frac{M.(2S - C)}{C - S}$$

where C is the concentration of ammonia in moles per 100 moles of water and S is the concentration of sulphur dioxide. The values of the constants N and M, are given by $\log M = 5.865 - 2369/T$ and $\log N = 13.680 - 4987/T$, where T is the absolute temperature in $^{\circ}$K. The partial pressure of water follows Raoult's Law. Johnstone's measured results were reasonably, though not strictly, in accordance with these formulae.

The figures obtained for the vapour pressures of ammonia and sulphur dioxide from ammonium sulphite - bisulphite vapours in the corrosion tests showed a very great divergence from the formulae. The measured values vary between a fairly close agreement and over 3,000 times the calculated figures. Concern was felt over this discrepancy and an explanation was sought.

It is pointed out that under certain circumstances, the formulae give negative values for the vapour pressures. This is a physical impossibility. The circumstances are: (1) when the concentration of ammonia (C) is greater than twice the concentration of sulphur dioxide (S), and (2) when the concentration of sulphur dioxide is greater than the concentration of ammonia. When the concentrations are equal, $p_{SO_2} = \infty$ and $p_{NH_3} = 0$. The answer therefore lies in the relative concentrations of ammonia and sulphur dioxide, and the formulae only apply when the relative concentrations are nearly equal and when C is greater than S. All Johnstone's results fall in this category, and the ammonia and sulphur dioxide have concentrations with a slight excess of ammonia.

Johnstone's formulae do not, therefore, apply to the values encountered in the corrosion experiments, and there is no reason to suspect that either are in error.

Some typical results:-

C NH_3/100 H_2O	S SO_2/100 H_2O	Calculated		Measured	
		p_{NH_3}	p_{SO_2}	p_{NH_3}	p_{SO_2}
Examples from corrosion tests:					
4.28	0.58	-1.84	0.38	9.7	0.06
2.42	1.36	3.00	0.01	0.10	1.17
2.76	3.19	-0.12	-4.35	0.10	973
With nitrogen					
2.53	1.09	-3.78	0.01	0.08	3.75
Examples from Johnstone's work:					
22.36	15.71	14.5	2.7	11.6	2.9
22.28	20.35	1.3	51.4	2.0	38.6
5.869	4.274	3.1	1.0	4.0	1.1

CORROSION BY CONDENSING
VAPOURS
FROM SOLUTIONS OF AMMONIUM NITRATE.

A drop test, using distillate from a solution of ammonium nitrate, showed that corrosion by condensing vapours from ammonium nitrate solutions could be expected to take place by drop-cell attack, and that attack would in all probability be quite intense. A series of corrosion tests was therefore started, to determine the corrosion curve and the process of attack by condensing vapours.

Although a number of workers have investigated the vapour pressures of water above solutions of ammonium nitrate, all their determinations were carried out on concentrated solutions, and no estimation of the partial pressures of the other constituents of the vapours was attempted. V.A.Klevke (64) states that there is almost no decomposition of ammonium nitrate during evaporation of its solutions at atmospheric or reduced pressure. As has been seen in the case of ammonium thiocyanate vapours, even very small amounts of dissolved compound in a condensate may have a great effect on the corrosion reaction, and hence the amount of decomposition that does take place in solutions of ammonium nitrate may be of importance in the corrosive action. When solid ammonium nitrate is heated, it normally decomposes to form N_2O and water starting at 170°C; but with extremely careful heating, a great part of it may be split up, undecomposed, into NH_3 and HNO_3, when it shows the phenomenon of sublimation by condensing again on cooler portions of the vessel (65). It is therefore thought most likely that decomposition of ammonium nitrate does not take place at the temperature of the solution in the tests; but it is split up in the vapours from the solution as NH_3 and HNO_3. This supposition is borne out by the alkaline nature of the condensate. If the ammonium nitrate decomposed, the vapour condensate would be acidic, on account of dissolved nitrous oxide. Further confirmation is received from the observations of Klevke and Kaskina (66) who found that ammonia had a higher vapour pressure than nitric acid over solutions containing 55% - 85% of ammonium nitrate.

Corrosion Tests.

To begin with, a 5% solution of ammonium nitrate was used in a trial run, to determine the vapour proportions at 80°C. The system that was devised to absorb and estimate the vapour constituents, was also used in the analysis and corrosion lines during corrosion tests. Moisture was once again condensed and run into a tube, that was weighed to get the water content. The gases were then bubbled through a standard solution of hydrochloric acid. Both ammonia and nitric acid are absorbed in this solution on account of their great solubility. Since ammonia has a higher vapour pressure than nitric acid over solutions of ammonium nitrate, the excess of free ammonia was found by titration of the unreacted acid with standard alkali. Then an excess of sodium hydroxide was added, and the total ammonia determined by distillation into standard acid. The difference between these two values gives the concentration of nitric acid in the vapours.

It was found in this test, that the concentrations of ammonia and nitric acid in the vapours were rather on the low side, so it was deemed advisable to increase the solution concentration to 10% before carrying out corrosion tests. Unfortunately, when this was done, it resulted in the clogging of the delivery end of the spiral tube for bubbling air through the solution. As the hot air bubbled out of the holes, solution was evaporated inside the end of the tube, and had

Plate 26. Pitting Attack by Vapours of
Ammonium Nitrate.
x 2

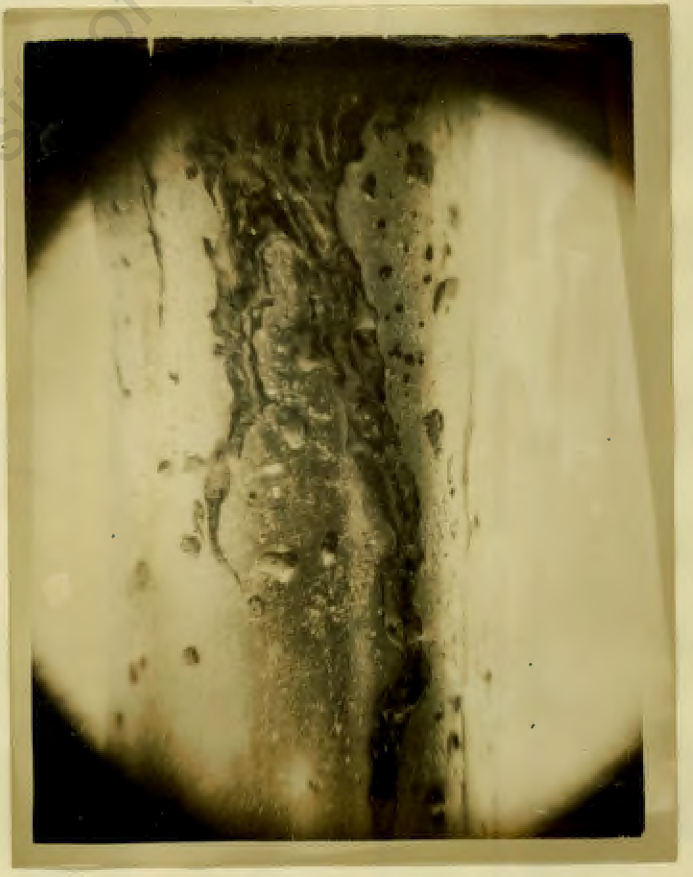


Plate 27. Spreading Corrosion Streak.
x 2

no time to redissolve before a new coating was deposited. Thus the layer of ammonium nitrate was built up until eventually the gas flow was restricted and stopped. The deposited salt could be redissolved very rapidly by stopping the flow for a moment and allowing the solution to wash back into the tube. This method may have been suitable for the short period tests; but it was realised that it would be hazardous to leave the apparatus unattended for more than an hour at a time. Consequently the solution was brought back to 5% concentration.

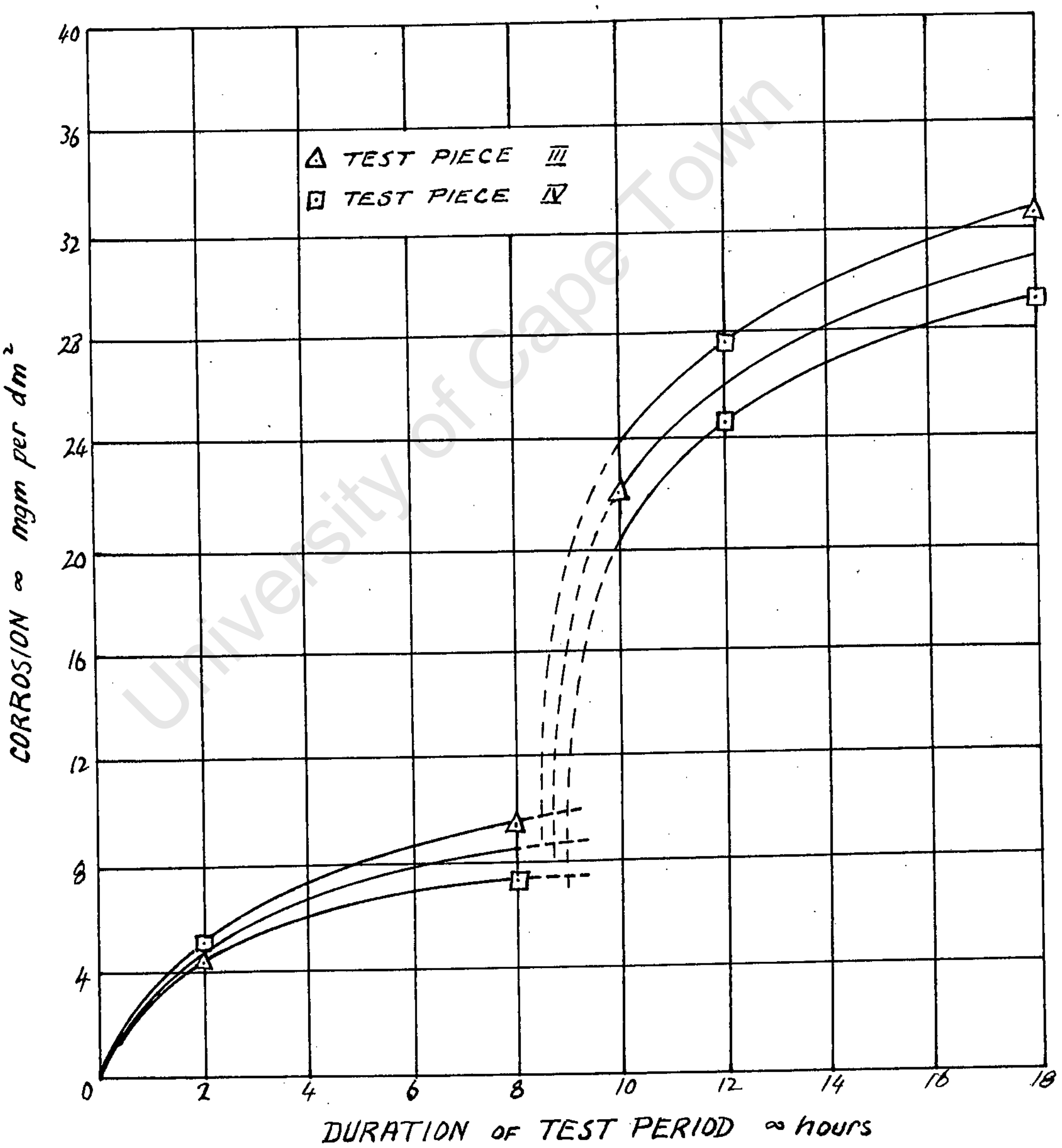
At the commencement of tests, the condensation on the test piece surface seemed to be a mixture of dropwise and film-type; and it appeared at first that the ammonia had afforded complete protection to the steel. But corrosion was slow in starting, and only a very few spots on the metal surface were attacked. Doubts were raised because the drop tests had indicated that the attack should most likely be intense. A sample of condensate was then used for another drop test, and the results were identical with the observations of the original test. Corrosion tests were continued, and it became plain that attack was indeed intense at those spots where cells had developed. The penetration was much greater than for corresponding corrosion results for distilled water. Attack was due to drop-cells (Plate 26), and the corrosion deposits over the pit holes consisted mainly of ferric hydroxide. The condensate was distinctly alkaline. As corrosion progressed, the corroded areas near the top of the specimen grew in size until the product spread into broad streaks (Plate 27). In the tests for the longer periods, some of the corrosion product was washed down into the condensate receiver, where it appeared as a precipitate in the alkaline solution.

The corrosion graph showed a rapid rise in corrosion to begin with; the total corrosion was much above the

CORROSION BY VAPOURS FROM AMMONIUM NITRATE SOLUTION AT 80°C

Test Piece Number	Duration of Test hours	Total Corrosion		Corrosion	Points of Attack	Condensate on Test Piece c.c./hour	Cooling Water Temperature °C	Heat	Rate of Gas Flow cm/min
		Observed mgm	Corrected mgm	mgm/dm^2				cal/min	
IV	2:00	2.9	2.9	4.9	102	1.6	16.02	80	8.4
III	2:00	2.6	2.6	4.4	175	1.7	17.05	99	9.6
IV	8:00	4.4	4.4	7.4	172	1.3	16.27	103	8.0
III	8:00	5.6	5.6	9.4	170	1.4	16.65	89	7.3
III	10:00	13.2	13.1	22.0	500	1.6	16.82	100	9.3
IV	12:00	14.7	14.6	24.6	-	1.8	17.16	102	7.9
III	12:00	16.5	16.4	27.6	530	1.7	-	102	7.7
IV	18:00	17.4	17.3	29.1	545	2.1	17.01	101	8.3
III	18:00	19.3	19.2	32.4	594	2.2	16.85	103	8.8

Figure 14. CORROSION by VAPOURS from SOLUTIONS of AMMONIUM NITRATE



attack for water vapour, though the number of points of attack were only about 100 against 2300 for water vapour attack. The rate of attack decreased rapidly, and not much more corrosion had taken place at eight hours. After about nine hours however, there was another very sharp rise in corrosion rate, which again slowed down till the total corrosion was nearly the same as that for water vapour at eighteen hours. Since the number of points of attack at this stage, was about 560 for ammonium nitrate vapour and 3500 for water vapour corrosion, the penetration for ammonium nitrate must be in the neighbourhood of six times as deep as for water vapour. The curve appears to follow a similar course to that of the corrosion of aluminium by the atmosphere (67), and thus a periodic breakdown and build up of a protective coating must take place in some manner.

Mechanism of Attack.

It is concluded that the following process takes place during attack by the vapours from solutions of ammonium nitrate. Because the vapour contains an excess of ammonia, there is a strong tendency for the condensate to maintain the thin protective oxide film associated with high pH's. Consequently, attack does not begin very readily, nor does it cover a large area with a great number of drop-cells. In any case, there is also the tendency of an ammoniacal condensate to spread over the surface in a film. But because the total ammonia content is so low, this tendency does not prevail, and condensation is almost completely dropwise. Nevertheless, when a large amount of condensate has formed, there is an easier production of wide streams of condensate, which may tend to blanket drop-cell corrosion.

H.T.J.Ellingham (68) reached the conclusion that in attack by solutions of nitric acid, the cathodic reaction consists in its reduction to form nitrous acid, provided that the reaction

$$HNO_3 + 2H \longrightarrow HNO_2 + H_2O$$

proceeds at a sufficient rate to remove the atomic hydrogen produced by the reaction

$$H^{\cdot} + e \longrightarrow H.$$

Nitric acid corrosion of iron takes place only at concentrations below 65%; at higher concentrations iron becomes passive. M. Smialkowski (69)(70) has described the intercrystalline cracks that occur on highly stressed sections and around rivet and bolt holes in the presence of nitrates. D.D.Cubicciotti and W.M.Boyer (71) found that both nitrate and an acidic cation were necessary for stress corrosion to occur. Nitrates act as cathodic depolarisers and, according to E.Müller (72), permit corrosion in the absence of oxygen. Being oxidising agents, they also inhibit the anodic reaction.

Under conditions of condensing vapours, the corrosion is concentrated at the weak points of an otherwise protective film of oxide. Since these points represent only a minute fraction of the total area, a very slight attack will represent a very high anodic current density with the consequence that the penetration will be largely increased. A study of the process of corrosion in a drop test assists in the development of the theory of attack by condensed vapour, but it is not strictly applicable since the cathodic areas are proportionally much greater.

At the weak points of the oxide film - the anode areas - ferrous hydroxide is dissolved in the ammonium salt, which, in solution, has a pH low enough to permit solution of the hydroxide. But as the ferrous ions come in contact with oxygen in the condensate, they are oxidised to ferric ions and ferric hydroxide is precipitated over the point of attack. The precipitate cover prevents oxygen from reaching the anode area to rebuild the protective oxide film, and attack takes place by differential aeration. As the deposit gets thicker, the mobility of the ions is retarded and the corrosion rate gets less. Between eight and nine hours exposure, a sudden spreading of the corroded area takes place accompanied by further breakdown of the oxide film, and the rate of attack once more increases rapidly. In due course, it also gets less when the corroded areas become coated with a sufficiently thick layer of product to reduce the attack.

DROP TESTS.

The drop test is an important auxiliary to the study of corrosion by condensing vapours. In the first place, it affords great assistance in determining the probability or improbability of attack. It also indicates what type of corrosive attack is to be expected, whether drop-cell corrosion or direct uniform attack; and provides an essential guide for the determination of the nature of the corrosive process. It is a very simple test and may be used with advantage when testing to eliminate poor materials from a corrosion standpoint, and especially when a search is being made for suitable metals or alloys for use under condensing vapour conditions.

The procedure that was followed in the drop tests conducted in the laboratory, is as follows. A flat piece of mild steel was smoothed down, first with a file, and then the usual series of grades of emery cloth until grade No.0 was used for the final rub. The surface was then washed with ethyl alcohol, followed by ether, and the metal allowed to dry in a desiccator. A large drop was formed on the prepared metal surface by allowing two drops of the corroding solution to flow from a pipette. A plastic ring was placed round this drop and the whole covered by a microscope slide through which the progress of attack could be observed. The enclosure was made airtight by coating the top and bottom surfaces of the plastic ring with tap grease, in order to keep out the dust and prevent evaporation from the drops. The plastic ring and the glass cover were removed from time to time in order that the process of the corrosive action might be closely observed and a record made on a photograph. The camera was fitted with a special lens of 1.5 inch focal length for a close-up picture. The test may be applied with a number of corrosive solutions at the same time, but each drop must then be covered separately.

The pattern of the corrosive processes revealed in the drop tests, without exception, closely followed the apparent mechanism of the attack in the condensing vapour tests. When no corrosion took place during a drop test, usually accompanied by the spreading of the drop, there was complete protection in the vapour corrosion tests; when drop-cell attack was experienced in the condensation experiments, so also did the drop tests reveal an attack of an electrolytic nature within the drop; and when the attack was direct and uniform for conditions of condensing vapour, the drop test showed that the solution had a tendency to spread over the metal surface to form a film, which attacked the material directly. Hence the drop test is a simple preliminary test that provides the information whether corrosion is a probability or not in condensing vapours. Further, the actual condensation attack takes place under conditions of constantly changing liquid corrosive, which makes the following of the progress and process of attack very difficult and inadequate. The drop test permits a close study of the whole process, and enables a permanent record of each step to be made by means of photographs.

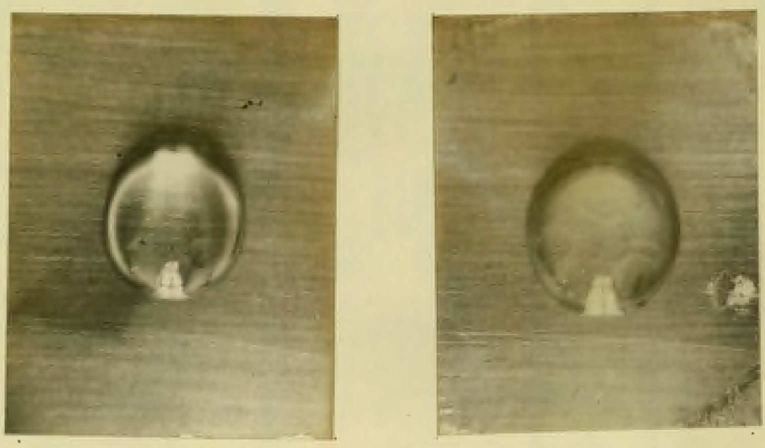
In the following pages a number of drop tests will be described; and theories for the mechanisms of the reactions concerned, will be submitted. When of consequence and where possible, photographic evidence of the progress of attack will accompany the text.

<u>Distilled Water</u>.

A full description is given on page 48 of a drop test on distilled water carried out by U.R.Evans. However, only the final state of the drop-cell is described, and an account of the progress of attack will be given here.

DISTILLED WATER DROP TEST

Plate 28.



a. Start of Test. b. After 2 hours.

c. After 8 hours. d. After 24 hours.

Plate 28a shows the drop at the start of the test. After about an hour, a thin line of corrosion product could be seen in a ring just inside the edge of the drop in contact with the metal. Between this ring and the outer edge was a narrow band of unattacked metal all round the ring. On the inside of the ring, no corrosion product was visible, but after two hours (Plate 28b), this area was covered by a very thin almost transparent layer of a yellowish-green product. By the end of eight hours (Plate 28c), the central corrosion product was quite pronounced and had changed to an orange-brown colour. The ring of corrosion product had also developed, and had become a low "wall" just inside the edge of the drop. The outer circle of metal was still unattacked. At twenty-four hours, the corrosion product had increased in bulk, and a very slight skin had formed over the surface of the drop.

The development of the corrosive attack confirms the theory expressed by Evans. The thin line of corrosion product is formed after the formation of the two electrolytic areas by the diffusion of oxygen to the cathode. Where the cathodic area joins the anodic centre, ferric hydroxide is precipitated in a ring. Later, diffusion of oxygen from the upper surfaces of the drop, precipitates, first the greeny hydroxide intermediate between ferric and ferrous hydroxides, and finally, the brown ferric hydroxide itself, over the anode area in the centre of the drop. This precipitate assists in preventing the access of oxygen to the anode area.

The nature of the corrosion that was shown in the drop test agreed with the findings in the experiments on condensation corrosion by water vapour, in which pitting took place due to drop-cells. The drop of distilled water in the drop test showed no tendency to spread, and condensation was similarly dropwise.

Ammonium Hydroxide.

A drop test carried out on a dilute solution of ammonium hydroxide showed that there was complete protection of the surface under the drop, and the metal was still bright after twenty-four hours exposure. This result was expected in view of the fact that the oxides of iron are insoluble in ammonium hydroxide solution, and consequently the metal surface remains passive and protected by an oxide film. The drop held together, but no differential aeration cell could be formed due to the total passivity of the surface. The condensation corrosion was also zero for the same reason.

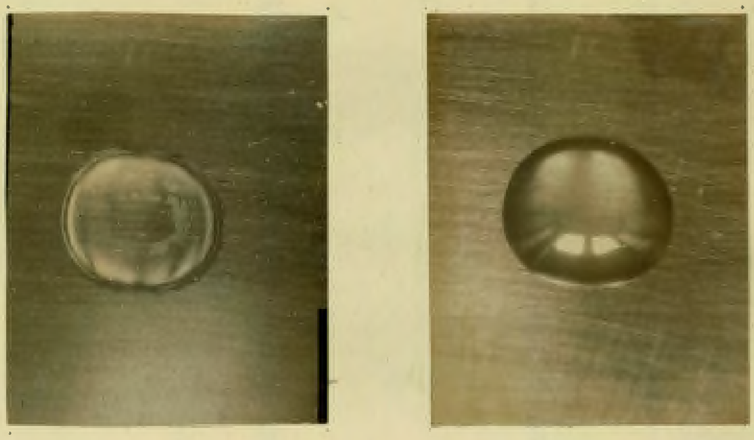
5% Ammonium Thiocyanate.

A drop test was carried out using a 5% solution of ammonium thiocyanate. The original aim of this test was to discover the nature of the condensation attack, but it was soon seen that the two mechanisms were quite different. Subsequently a drop of actual condensate was used in a test to determine the correct process of thiocyanate vapour corrosion. This experience demonstrates the importance of using test liquids that are representative of the actual corroding media found in practice. A difference in concentration of dissolved substance may completely change the corrosion picture.

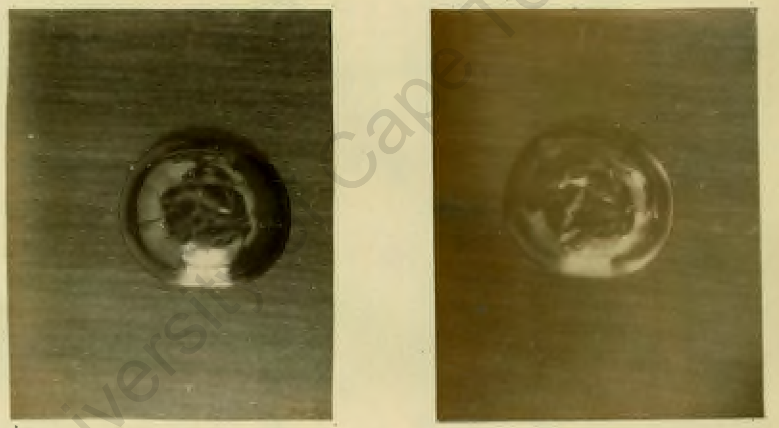
Following the usual procedure, a drop of solution was placed on the prepared surface of the steel specimen (Plate 29a). After an hour, a reddish-brown transparent film was noticed round the edge of the drop in contact with the metal (Plate 29b). This film slowly mounted upwards until it had totally covered the whole outer surface of the drop of ammonium thiocyanate at one and a half hours after application. By the end of a two hour period, the top of the membrane had begun

DROP TEST
with
5% AMMONIUM THIOCYANATE

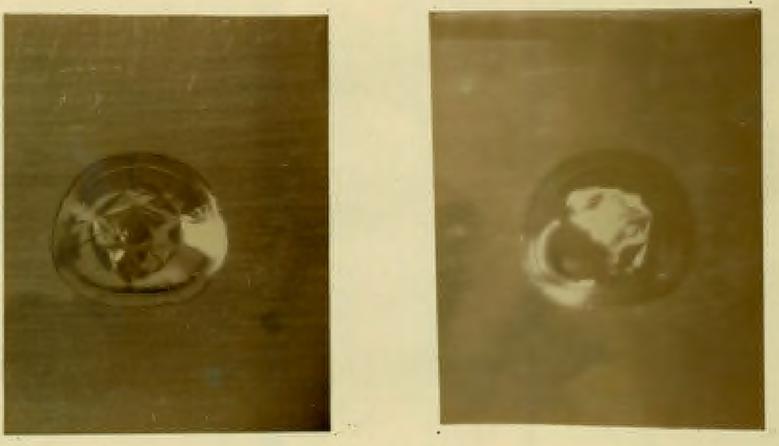
Plate 29.



a. Start of Test. b. After 1 hour.



c. After 2 hours. d. After 3 hours.



e. After 6 hours. f. After 24 hours.

to form a wrinkle (Plate 29c). The skin was still thin enough to be transparent, and the surface of the metal under the drop could be seen to be unattacked and still bright. The membrane grew thicker and the wrinkle on the top more pronounced. At six hours the drop darkened considerably; and the metal was no longer visible through the crust. After fifteen hours, the wrinkled membrane had begun to split up on the top. As it split, further film was formed over the newly exposed surface.

After twenty-four hours exposure, the drop was examined. The membrane was broken into glassy flakes, and the drop underneath examined. The liquid was colourless, but the metal was covered by a black deposit, and it is considered that this black deposit started to be formed at the darkening that was observed after six hours.

The attack is divided into two stages: the first stage involves the formation of a skin over the surface of the drop; the second stage is the formation of a black deposit on the metal surface below the drop.

Stage 1 takes place when ferrous ions pass into solution in the ammonium salt solution. These ions are not precipitated, as ferrous hydroxide is soluble in solutions of ammonium salts, but they migrate to the surface of the drop, and come in contact with an abundance of oxygen at the surface. Here they are oxidised, and ferric hydroxide is precipitated in the form of a glassy film, first round the edges and then upwards over the drop as the ions rise from the metal surface. When the membrane covers the whole liquid surface, oxygen is cut off from diffusion into the drop and all traces are soon used up. Stage 2 of the corrosion then takes place.

In the absence of oxygen, the thiocyanate is reduced by atomic iron at the surface of contact between the metal and the solution. A black precipitate of ferrous sulphide is formed, which coats the metal surface. The corrosion proceeds in this manner until all the thiocyanate has reacted. In effect:

$$Fe + CNS' \longrightarrow FeS + CN'$$

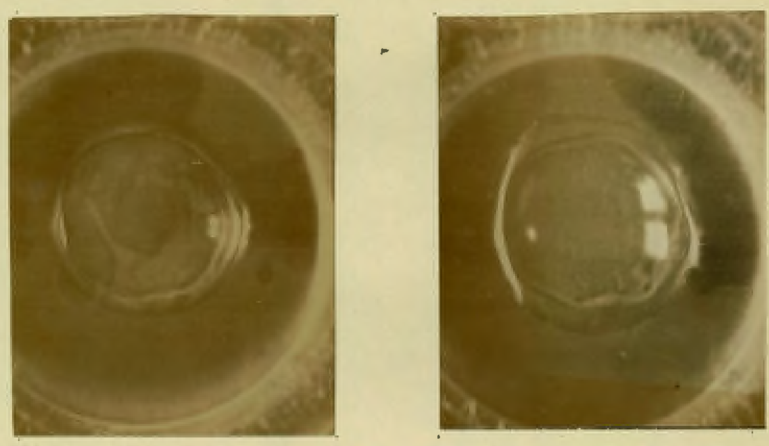
Ammonium Thiocyanate Condensate.

The nature of the corrosive attack in the drop test with condensate from the analysis line of the condensation corrosion apparatus, was entirely different from the test described above. This time the mechanism was apparently identical to the process which caused the attack in the condensation tests, since the corrosion products were the same in both cases.

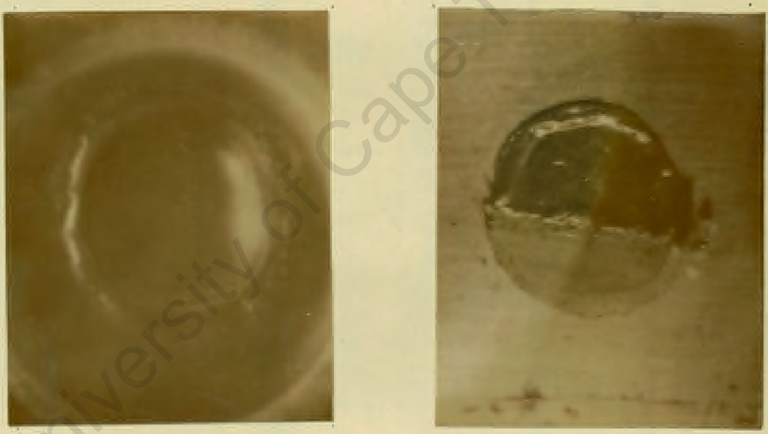
A large drop of condensate was placed on the surface of the steel, and the progress of attack was followed in the usual manner. The drop showed no tendency to spread and covered the same area throughout the experiment. After an hour, a ring of corrosion product had been deposited just inside the outer edge of the drop (Plate 30a), leaving an unattacked area between it and the line of contact between the metal and the edge. At first, the area enclosed within the ring of corrosion product was clear, but after a while a thin yellowish-green gelatinous product appeared over the surface. The colour darkened as it grew thicker, and at six hours, the corrosion product covering the inner area was orange-brown in colour (Plate 30b). There was no further change in the nature of the corrosion products; and after twenty-four hours (Plate 30c), the only difference was that the bulk had increased. Underneath the product, the metal had a grey stain (Plate 30d) which showed a ring below the part above which the first corrosion product formed.

DROP TEST
with
AMMONIUM THIOCYANATE CONDENSATE.

Plate 30.



a. After 1 hour.　　b. After 6 hours.



c. After 24 hours.　　d. Corrosion Product.

The following mechanism of corrosion by condensed drops of ammonium thiocyanate vapours on a steel surface, is the pattern of all cases of attack by differential aeration drop-cells. Figure 15 shows the directions of flow of the anions, the cations and the electrons within the drop-cell system.

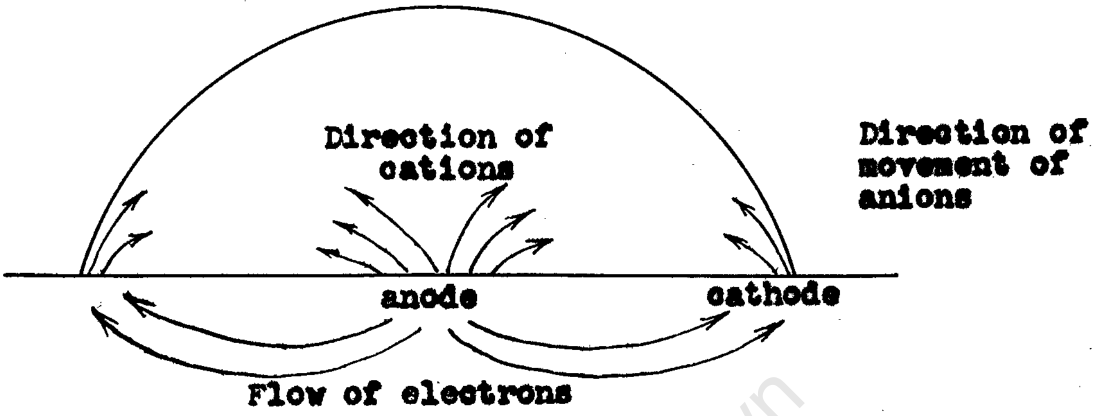


Figure 15. Flow Pattern for Electrons, Cations and Anions.

After a drop of condensate has formed on the surface of the steel, and when oxygen is present, the oxygen diffuses into the liquid and forms an oxygen electrode just within the drop. This area becomes the cathode in the differential aeration cell, while the inner portion is the anode. According to G.D.Bengough, U.R.Evans, T.P.Hoar, and F.Wormwell (73), the oxygen is first absorbed into the iron, and then reacts with a hydrogen ion to yield a hydroxyl ion, which, together with another hydroxyl ion from the ionisation of water, gives two hydroxyl ions.

$$\text{H-OH} + \text{O} + 2e \longrightarrow 2\text{OH}'$$

In this way, oxygen acts as a depolariser in the cathodic reaction and prevents the formation of hydrogen at the more noble electrode.

At the interior of the drop, to which oxygen has little access, an exchange of electrons takes place between hydrogen ions and atoms of iron. The iron passes into solution and the hydrogen ions are discharged.

$$Fe + 2H^{\cdot} \longrightarrow Fe^{\cdot\cdot} + 2H$$

The hydrogen atoms that are produced, may follow either of two courses:- (1) they may unite to form hydrogen gas, or (2) they may be occluded on the surface of the metal. In the later case, which probably takes place, a hydrogen electrode is formed when the atomic hydrogen diffuses into the metal. R.T.Effinger, M.L.Renquist, A.Wachter and J.G.Wilson (74) have stated that a high concentration of atomic hydrogen exists on the corroding surface, and that from this surface it may diffuse into the steel. For hydrogen to diffuse into the metal, (1) there must be a high concentration of atomic hydrogen on the surface, and this normally occurs because of the continued activity of the corrosion cell, and (2) the association of atoms to molecules must not occur at the metal surface which must actively promote the acceptance of hydrogen atoms.

Differential aeration therefore results in an oxygen electrode - hydrogen electrode system with a potential difference depending upon the temperature and the partial pressure of oxygen for each condensed solution.

At the anode area within the drop, iron passes into solution as ferrous ions. In distilled water the ferrous ions are present as hydroxide in solution, but in the case of a dissolved electrolyte which is more highly ionised, such as ammonium thiocyanate, they exist in solution as an ionised salt e.g. ferrous thiocyanate. The complete anode reaction may be represented by the following equation:-

$$Fe + 2H^{\cdot} + 2OH' + 2NH_3^{\cdot} + 2CNS' \longrightarrow Fe^{\cdot\cdot} + 2CNS' + 2NH_3^{\cdot} + 2OH' + 2H$$

At the junction of the anodic and cathodic solutions, the alkaline cathodic solution causes the deposition of iron by reacting with ferrous thiocyanate to yield ferrous hydroxide which is immediately oxidised by dissolved oxygen to ferric hydroxide and precipitated. In like manner, ferric hydroxide is precipitated above the anodic area in the centre. In this process, the dissolved salt - ammonium thiocyanate - promotes the corrosive attack by increasing the conductivity of the condensate.

Eventually the corrosion product gets so thick over the anodic area, that it prevents the free access of oxygen and the corrosive process is modified. A black deposit is produced instead of the initial brown ferric hydroxide. This is attributed to the incomplete oxidation of ferrous hydroxide and an intermediate hydroxide or anhydrous magnetite is produced.

$$6Fe(OH)_2 + O_2 \longrightarrow 2Fe_3O_4 + 6H_2O$$

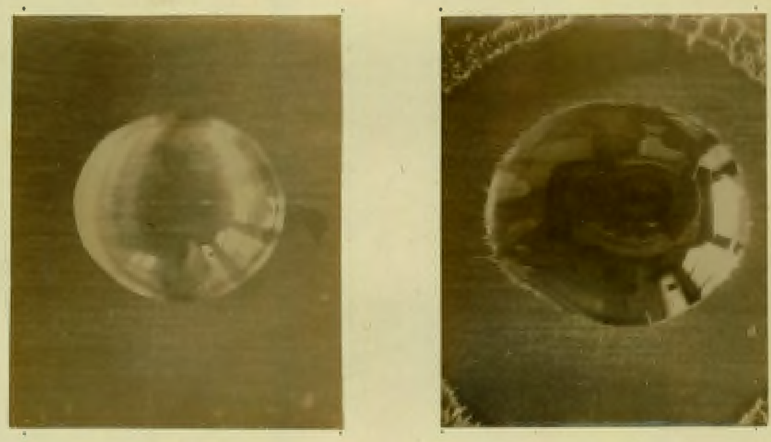
Ammonium Sulphite Solution.

A test solution of ammonium sulphite was used in a normal drop test. Immediately the first drop of solution was allowed to fall on the surface of the steel, the drop began to spread, and this was increased when the second drop was added. It was not long before the metal surface beneath the drop took on a greyish stain, which soon developed into a black deposit of corrosion product (Plate 31b). The supernatant drop remained clear and colourless for a considerable time; but after three hours, a thin film could be seen forming over the surface. This film grew in thickness until it hid the surface beneath the drop from sight. By the end of a seven hour period, the top of the membrane had formed a large wrinkle (Plate 31d). No decided change was apparent after this. The membrane was broken up into brown transparent flakes, and the solution below it was still clear, though the black deposit had grown in bulk.

Following is the suggested mechanism of attack. Due to the rapid spreading of the drop over the metal surface, and to the vigour of attack, no corrosion cell is formed and corrosive action is direct. Iron passes into solution as

DROP TEST
with
AMMONIUM SULPHITE SOLUTION.

Plate 31.



a. Start of Test. b. After 1 hour.

c. After 3 hours. d. After 7 hours.

ferrous sulphite by reaction with sulphurous acid.

$$Fe + 2H^{\cdot} + SO_3^{''} \longrightarrow Fe^{\cdot\cdot} + SO_3^{''} + H_2$$

The ferrous sulphite is then reduced to ferrous sulphide by atomic iron close to the metal surface, and is precipitated as a black deposit.

$$3Fe + FeSO_3 + 3H_2O \longrightarrow FeS + 3Fe(OH)_2$$

The reduction of a sulphite to a sulphide is an unexpected reaction, since sulphurous acid and sulphites are themselves reducing agents. However atomic iron is even more powerful, and consequently is capable of performing the reduction. The possibility of the reaction has been demonstrated elsewhere (63).

Ferrous hydroxide is soluble in the drop of solution, and produces more ferrous sulphite. This is reduced in like manner, and the process continues until all the sulphite has been converted to sulphide, after which, ferrous hydroxide migrates to the surface of the liquid. Here it is oxidised and yields the brown transparent skin of ferric hydroxide.

Ammonium Sulphite Condensate.

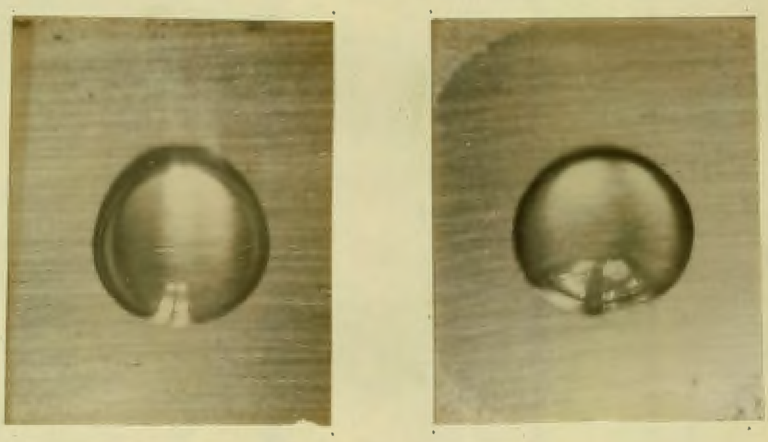
Drop tests showed that the process of attack was different for different condensates, that were collected during corrosion test runs. For condensate with a lower sulphur dioxide content, the corrosion was sluggish and the end products of corrosion were slightly different to those appearing in the drop test with a solution of higher sulphite concentration. In the latter case, attack was very rapid.

Condensate with Lower Sulphur Dioxide Content.

The condensate used in the test came from vapour with constituent vapour pressures, sulphur dioxide - 0.59 mm.Hg. ammonia - 0.14 mm.Hg., and water - 282 mm.Hg., which yielded a condensate containing 0.8% sulphur dioxide by weight. The drop of condensate on the flat steel surface showed no tendency

DROP TEST
with
LOW SULPHITE CONDENSATE.

Plate 32.



a. Start of Test. b. After 1 hour.

c. After 2 hours. d. After 5 hours.

e. After 7 hours. f. After 24 hours.

to spread over the surface once it had settled on the metal. After an hour (Plate 32b), a black deposit was seen at the edge of contact of the solution and the metal. This deposit gradually spread inwards until there was a thin deposit over the whole metal surface under the drop (Plate 32c). At five hours exposure (Plate 32d), the black deposit had become brown at the edge of contact, and this also spread inwards until the black deposit was completely hidden by the brown overlayer. At the same time (Plate 32e), a very thin colourless film formed at the surface of the drop, which developed, as previous membranes had done, until after twenty-four hours it was very wrinkled on the top (Plate 32f).

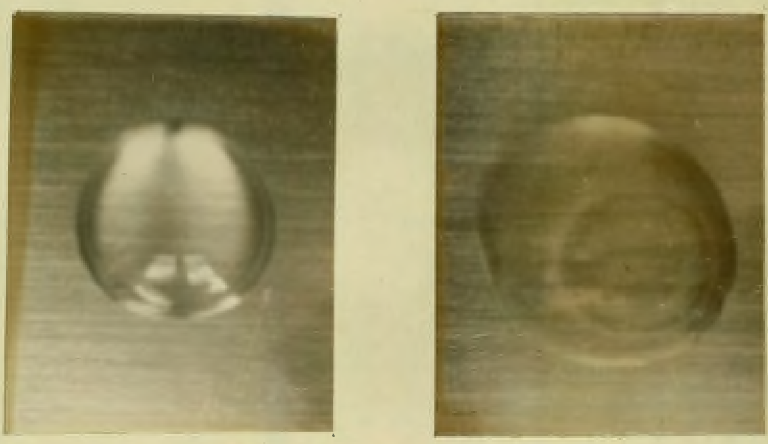
The mechanism of the above attack is believed to be as follows. The deposition of ferrous sulphide from the condensate containing sulphite (or sulphur dioxide) in solution follows the process that has been dealt with before. However, there is only a limited amount of sulphur dioxide in this condensate, and consequently it is used up very soon in the reaction. When this stage has been completed, a new process begins. The solution is now totally ammoniacal, and hence there is a tendency to form a thin hydroxide or oxide film over the metal surface. This film formation is prevented by the presence of sulphide, and the ferrous hydroxide in the solution (formed during the reduction of sulphite to sulphide), is oxidised by dissolved oxygen and precipitated above the sulphide. It is also precipitated as ferric hydroxide in a film over the surface of the drop, thus raising a barrier to the solution of oxygen and bringing corrosion to a standstill.

Condensate with High Sulphur Dioxide Content.

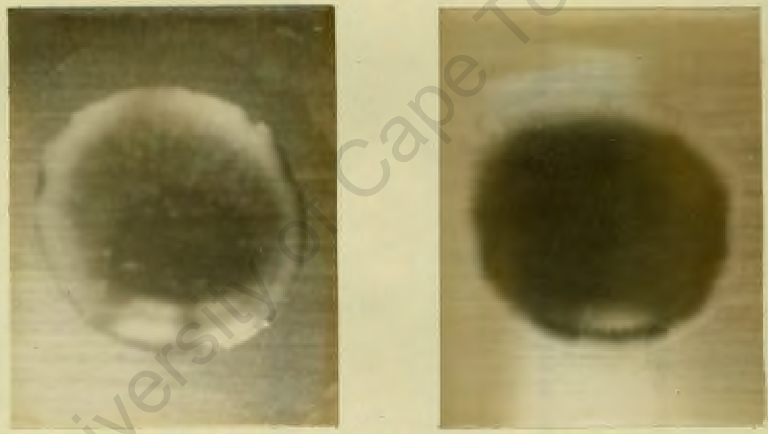
The condensate used in this test came from vapour with the composition: sulphur dioxide - 2.70 mm.Hg., ammonia - 0.27 mm.Hg., and water - 280 mm.Hg. This gave a condensate

DROP TEST
with
HIGH SULPHITE CONDENSATE

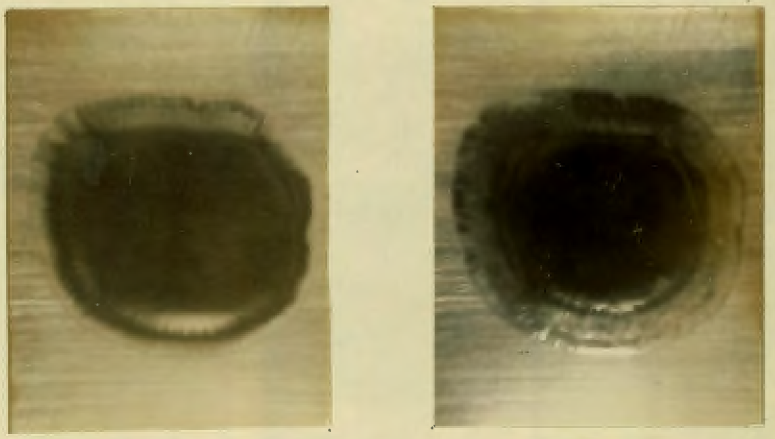
Plate 33.



a. Start of Test. b. After 20 seconds.



c. After 30 seconds. d. After 2 minutes.



e. After 12 minutes. f. After 30 minutes.

of 3.6% sulphur dioxide by weight. Like a sulphurous acid solution, the condensate attacks the metal very readily. Attack took place vigorously in a matter of seconds when a drop was allowed to fall on the prepared steel surface. The drop spread rapidly, and even the first photograph (Plate 33a) does not show the original area. It is possible to see the original size of the drop in Plate 33b, which was taken after twenty seconds. It appears as a light ring within the drop, and the photograph also shows the first darkening of the surface due to corrosion. After thirty seconds (Plate 33c), the majority of the surface under the drop was covered by a deposit, but the original area could be still distinguished. By two minutes the surface was completely black (Plate 33d). At a test exposure of twelve minutes (Plate 33e), the usual membrane was seen to have formed round the edges of the drop, and after thirty minutes it had risen over the drop surface (Plate 33f).

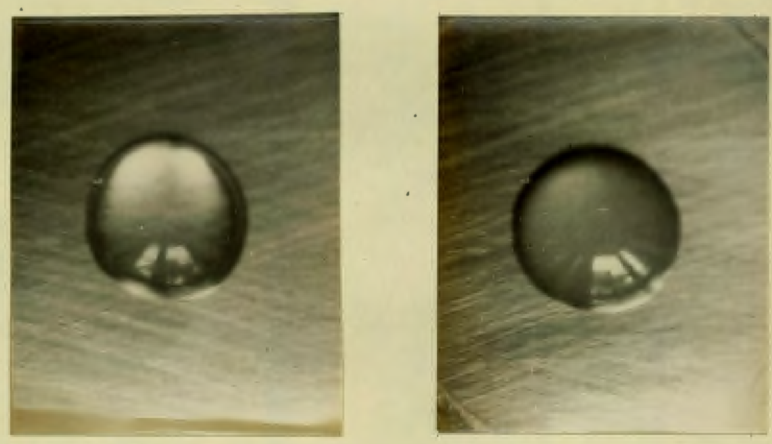
The corrosion follows the familiar pattern for sulphite attack that has been described on page 121. The corrosion occurs over a larger area than the original area of the drop, because the dissolved gases lower the surface tension of the liquid, and hence the angle of contact which causes the drop to spread (75).

Ammonium Nitrate Solution.

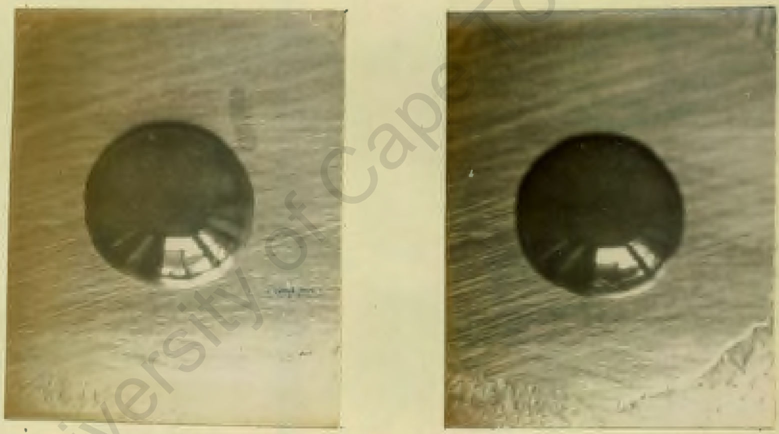
A 5% solution of ammonium nitrate was used in a normal drop test. No tendency to spread was shown, and the drop covered the same area throughout the test. Attack took place directly and there was no sign of an electrolytic cell. After ten minutes, the first signs of corrosive attack appeared; a brownish coloured deposit was formed at the edge of contact between the solution and the steel. The deposit began to spread inwards. At thirty minutes, it was seen that the remainder of the surface under the drop was coated with a green

DROP TEST
with
AMMONIUM NITRATE SOLUTION

Plate 34.



a. Start of Test. b. After 30 minutes.



c. After 8 hours. d. After 24 hours.

gelatinous product (Plate 34b), which darkened in colour until it had changed to a uniform brown in less than eight hours (Plate 34c). After twenty-four hours (Plate 34d), a skin had formed over the surface, and an examination of the corrosion product revealed that there was a black coating on the metal beneath the layer of brown.

The attack is believed to take place in the following manner. The thin oxide film, that is associated with the protective action of ammonium hydroxide, is soluble in ammonium nitrate on account of the hydrolysis of the salt which results in an acidic solution. Iron then passes into solution as ferrous ions while hydrogen ions are discharged.

$$Fe + 2H^{\cdot} \longrightarrow Fe^{\cdot\cdot} + 2H$$

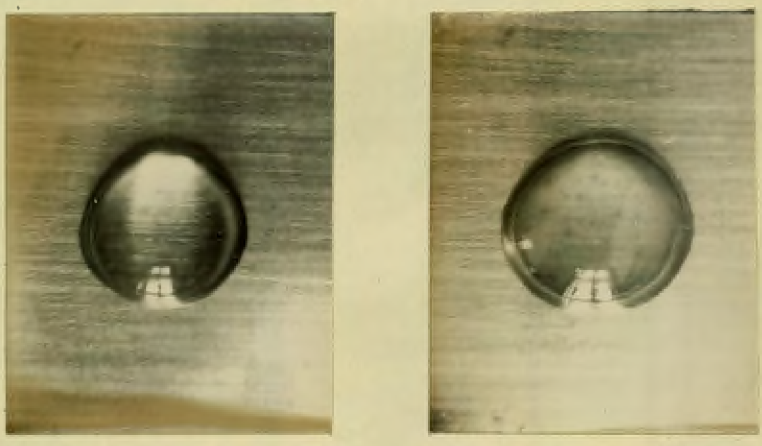
The hydrogen atoms either associate to form hydrogen molecules or dissolve in the metal. The ferrous ions are present in solution as ferrous hydroxide, which is oxidised by diffusing oxygen and precipitated initially as a green intermediate hydroxide, which is finally converted to brown ferric hydroxide when sufficient oxygen is available. When the deposit becomes thick enough to limit the supply of oxygen, anhydrous magnetite is produced in contact with the metal. Membrane formation takes place once again at the edge, after which it travels up over the drop as migrating ferrous ions penetrate to the surface and are precipitated, until the whole is enclosed.

Ammonium Nitrate Condensate.

Condensation corrosion tests for ammonium nitrate gave low values for corrosion (page 101), whereas one drop test indicated that rapid corrosion might be expected by drop-cell attack. A second drop test was carried out which confirmed the first result. The low condensation corrosion results were due to the small number of points of attack, and not because of a

DROP TEST
with
AMMONIUM NITRATE CONDENSATE

Plate 35.



a. Start of Test. b. After 1 hour.

c. After 3 hours. d. After 7 hours.

e. After 24 hours.

low rate of attack in the drop-cell. The progress of the corrosive attack in the electrolytic cell was as follows.

A brown ring became visible within the drop of condensate after it had been resting on the steel for about half an hour. The ring was quite definite after an hour (Plate 35b), and was situated just inside the edge of contact between the metal and the solution. A faint greenish gel could be seen within the circle of brown corrosion deposit. The ring of corrosion product grew in bulk, and more green product was also formed on the inside (Plate 35c). Eventually (Plate 35d), the green product became yellow-orange and finally changed to brown. (Plate 35e). At the end of twenty-four hours exposure, the corrosion product had increased considerably in bulk, and the drop spread slightly, which only increased the area that was unattacked.

The mechanism of attack is similar to those of other drop-cells and follows the pattern described on pages 119 to 121 for ammonium thiocyanate.

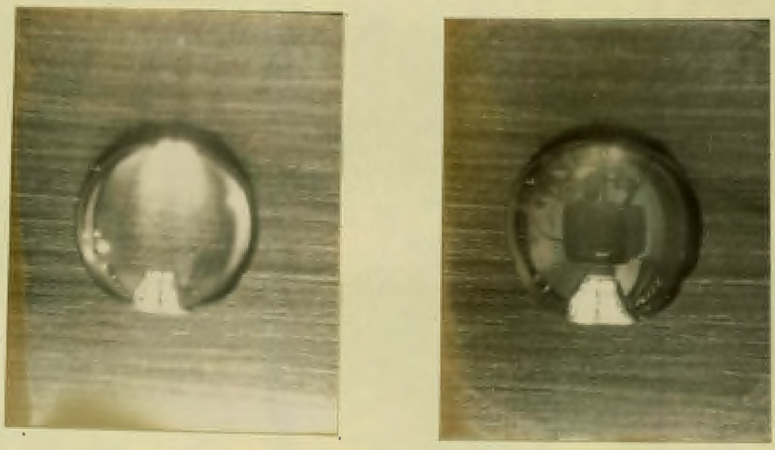
Ammonium Chloride Solution.

A 5% solution of ammonium chloride was used in a drop test. Apart from a stain of greyish colour on the surface of the metal, the only sign of corrosive action was that a surface membrane was formed. This membrane started after about an hour, and progressed in the usual manner until the whole surface was covered. After that, it grew in thickness and developed a wrinkle on the top. The mechanism of attack is similar to that encountered with ammonium nitrate solution.

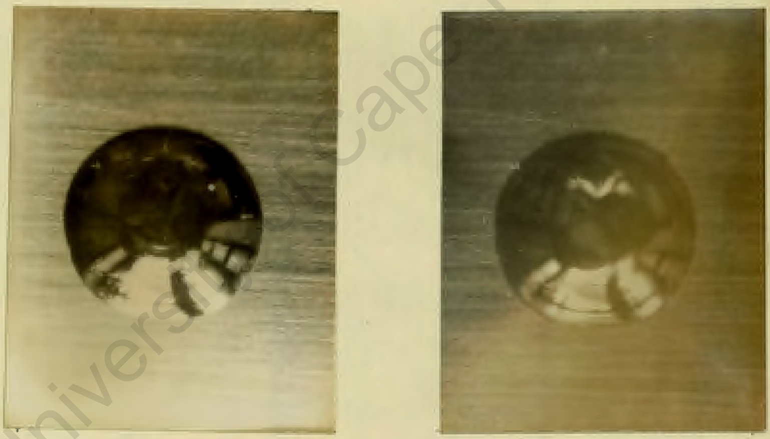
A distillate from the solution of ammonium chloride was obtained, but since it gave no indication of ammonium ion or of chloride, it is clear that corrosion by vapours from solutions of ammonium chloride should follow the

DROP TEST
with
AMMONIUM CHLORIDE SOLUTION

Plate 36.



a. Start of Test. b. After 1½ hours.



c. After 6 hours. d. After 24 hours.

water vapour curve. Hence no special condensation corrosion tests were done.

Ammonium Carbonate and Bicarbonate Solutions.

Though carbon dioxide and ammonia are both present in vapours from solutions of ammonium carbonate and bicarbonate, the ammonia is so dominant from the corrosion standpoint, that it affords complete protection when the vapours are condensed on steel surfaces. Solutions of the carbonates are also non-corrosive on account of the high pH.

CONCLUSIONS

A discussion of the results and the conclusions drawn from them with regard to corrosion by condensing vapours is considered in this section.

The corrosion of metal by condensing vapours can be divided into two classes of attack according to the way in which condensation takes place on the metal surface. It does not appear that the state of the metal surface has much effect on the type of condensation that takes place when the vapour conditions are such that the rate of condensation is very small. This only applies if the metal surface is free from contaminants that may change the nature of the condensation. Under normal conditions then, condensation is dropwise; small droplets condense as a mistiness on the cold surface of the metal, and if any change is brought about, it must be due to a special constituent of the vapours.

Dropwise Condensation Corrosion.

Pure water vapour and ammonium thiocyanate vapour condensed on the surface of the test specimens in the form of little drops, and the corrosion occurred in the form of small pits which were covered by a layer of corrosion product. This is the first type of attack which always was associated with dropwise condensation. Dropwise condensation results in the formation of drop-cells, in which the drop of liquid forms a separate electrolytic cell which is produced on account of differential aeration conditions. The outer edge of the metal under the drop becomes cathodic, since oxygen freely diffuses to this section. The main function of the oxygen is that of a depolariser of the cathodic reaction. The metal surface included in this outer ring has relatively little oxygen and becomes the anode area of the cell. The dissolved ammonium salt generally assists at the anodic area by increasing the hydrogen ion concentration when hydrolysis occurs. Thus the solution of metal is promoted by a transfer of electrons from the hydrogen ions. The salt also accelerates attack by increasing the conductivity of the solution. Once the dissolved metal reaches the cathodic solution which is alkaline, it is precipitated as hydroxide or hydrated oxide. This precipitate eventually provides a covering to the anodic area, and since it is formed some little distance away from the metal surface, it may not retard the attack, but might even promote it by excluding diffusing oxygen more effectively from the anode of the drop-cell. On the other hand, it reduces the mobility of the ions.

When there is ammonia present in the vapour, it naturally tends to be protective to the metal surface by maintaining the oxide film over the surface. The acid constituent is in opposition by trying to dissolve the oxide and bring the metal into solution. Where the ammonia in the vapours is in excess of the acid constituent, it dominates the corrosive action. It may be however, that the acid effects the breakdown of the oxide film in certain places by localised concentrations. At these points, electrolytic attack takes place with the surface, which is protected by the ammonia, as the cathode, and the broken spot as the anode. Attack at these points will probably be more intense than in actual drop-cells, because of the much larger cathode areas compared with the anode spots and the resultant higher current density at the anode. The penetration is liable to be much greater, though the loss in weight may be less. This type of attack was associated with the corrosion by ammonium nitrate.

Although dropwise condensation produced numerous droplets over the whole metal surface, the corrosion generally did not take place in the form of a large number of drop-cells. Usually the drop-cells were larger and more widely spaced. It seems apparent therefore, that each droplet did not initiate a point of attack, but that only a proportion of them were capable of forming differential aeration cells. This phenomenon has been attributed to the non-uniformity of the surface of the steel, and that certain spots are more reactive or less passive than other places. It may be that the oxide film is not as t thick or as strong at those areas, and consequently breaks down more easily. Another suggestion to account for the phenomenon, is based on the theory that crystal grains do not exhibit the same properties in every direction. While some crystal faces are passive others are comparatively more active. Depending on which face is presented to the corrosive condensate, the drop will either attack the metal or not. As additional evidence for this theory, it is noted that drop-cells were more numerous and closely packed when the metal grain structure was finer (Plate 10). Under these conditions, more active centres would be presented for attack than when the grains were larger in size.

Film-type Condensation Corrosion.

The type of condensation of vapours on a cold surface seems to be closely dependent on the nature of the vapours themselves, and consequently on the soluble substance or substances in the solution from which the vapours originate. Vapours that arose from solutions of salts of ammonia whose acid constituent was no normally very volatile or a gas at room temperatures, condensed on the steel surface in a dropwise manner and corroded by drop-cell attack. Those ammonium salt solutions that gave rise to vapours with an acid constituent that is gaseous at normal temperatures and pressures e.g. sulphur dioxide and hydrogen sulphide, always result in film-type condensation on a cold metal surface. Where the acid constituent is fairly volatile e.g. nitric acid, a mixed type of condensation appears, in which part deposits by film-type condensation and part by dropwise. Ammonia itself has a weak tendency to promote film-type condensation when it is in appreciable amounts in the vapours. The above general observations only apply where the gases are readily soluble in water.

In the cases of film-type condensation, the attack is direct and uniform over the surface of the steel if at all. The drop tests that were carried out on these condensates, showed that the solution spread over the surface, which accounts for the film formation in the condensate. It is probable, that in some cases, the fact that film-type condensation takes place, is a factor in preventing corrosion of the steel by condensing vapours. The uniform film over the metal surface precludes the formation of electrolytic cells by differential aeration, and provided that ammonium hydroxide is in sufficient amounts to neutralise the acid and maintain the surface oxide film, no corrosion will occur. If the acid is not neutralised or if the acid constituent has the power to break down the oxide film, attack will take place.

For this reason no corrosion was found in the case of the sulphides, since there was sufficient ammonia evolved to overcome the acidity of hydrogen sulphide. The sulphite attack was a different matter. For here some corrosion took place even when there was a considerable amount of ammonia in excess; and the only satisfactory way to reduce corrosion to zero or negligible amounts was to lower the vapour pressure to such an extent, that there were only traces of sulphur dioxide in the condensate. Sulphur dioxide has the power to break down the thin oxide film even when completely neutralised and in the presence of excess of ammonium hydroxide. The greater the concentration of sulphur dioxide, the more vigorous the attack.

Effect of Air on Corrosion.

It is obvious that air must be an essential factor in the corrosion by differential aeration, for it provides the oxygen necessary for the formation of the cathodic area in the drop-cell. Its effect has been demonstrated in tests using nitrogen as the vapour carrier. When drop-cells normally developed in air, the use of nitrogen prevented such attack and complete protection was experienced in corrosion tests.

It cannot be stated with any finality that air does or does not play a part in the attack when corrosion occurs under film condensation conditions. It depends upon the standpoint from which the question is approached. There was no alteration in the total corrosion, when nitrogen was used in place of air for the sulphite corrosion tests. There was, however, a change in the appearance of the corroded test specimen and in the products of corrosion. It was deduced that the actual direct attack was not influenced by oxygen, but that there was a subsequent reaction between the corrosion products and the condensate, which did not take place in the absence of air. It may be that under certain circumstances the attack itself may be affected by side reactions of the corrosion products.

Effect of the Ammonium Ion.

An examination of the mean value corrosion curves shows a very wide variation in corrosion rates and types of curve for the substances considered. The water vapour curve is nearly a straight line; ammonium nitrate vapours corrode in

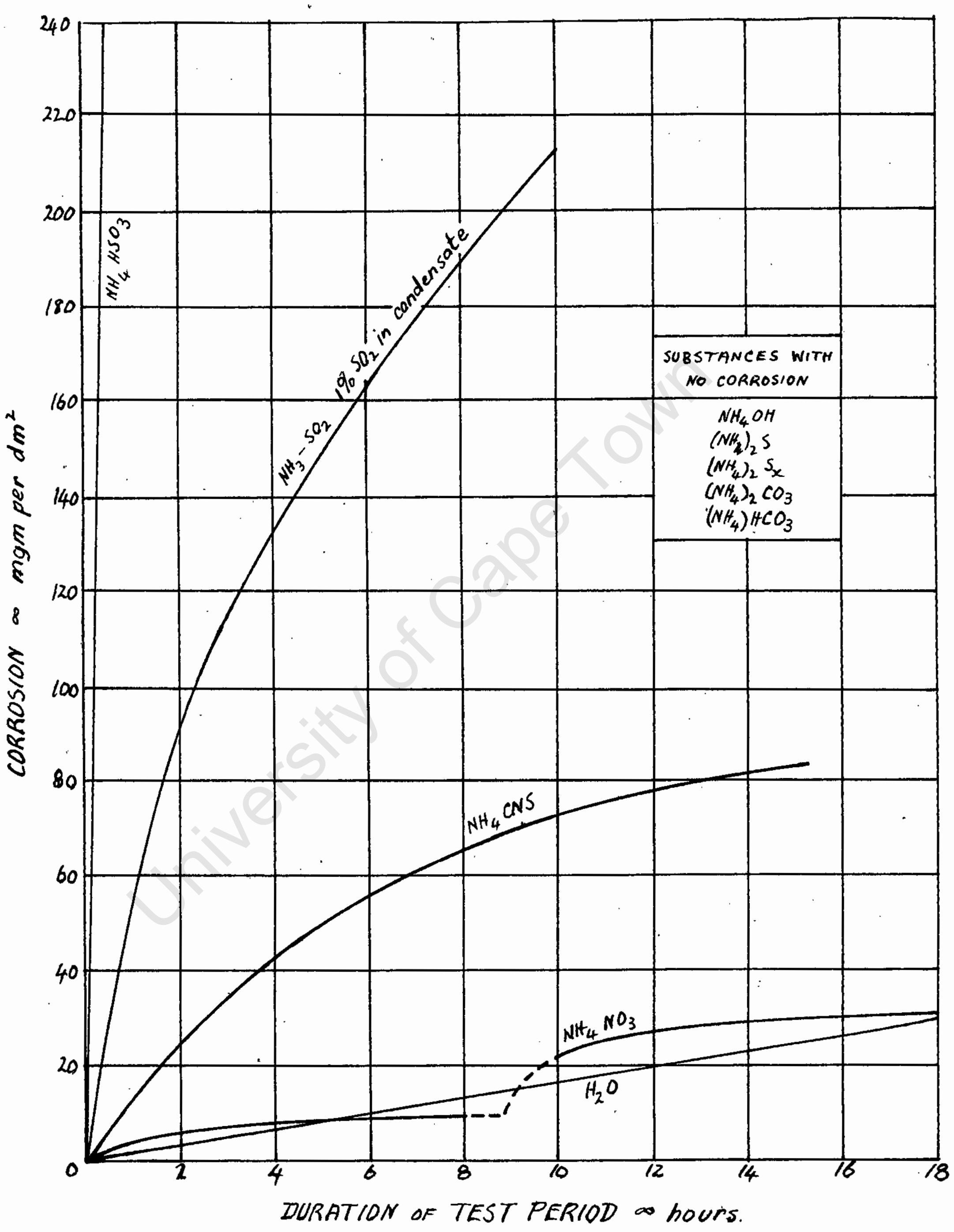


Figure 16. MEAN VALUE CORROSION CURVES

steps; the ammonium thiocyanate curve shows an asymptotically decreasing rate of attack; and the ammonia - sulphur dioxide attack varies from zero to extremely high rates. The type of attack also takes two forms, so that it can be concluded that the ammonium ion is not the controlling factor from the corrosion standpoint.

It does reduce corrosion in those cases of uniform attack where it reacts with the acid radicle, but in drop-cells it promotes corrosion by acting as a cathodic stimulator. On the whole, therefore, it is the acid anion that controls the corrosion, since it determines the nature of the attack - whether by drop-cells or by direct attack, according to the condensation, and the magnitude of the total loss in weight by corrosive action.

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APPENDIX I

Variation in Surface Temperature of Test Pieces. (Water Vapour Corrosion)

Nomenclature

A - area of heat transfer surface, sq.ft.
C - specific heat at constant pressure, B.t.u./(lb)(°F).
D - diameter, ft.
h - individual coefficient of heat transfer, B.t.u./(hr)(sq.ft)(°F).
k - thermal conductivity, B.t.u./(hr)(sq.ft)(°F/ft)
l - thickness, ft.
N - length of heat transfer surface, ft.
Q - quantity of heat, B.t.u.
t - temperature, °F.
U - overall coefficient of heat transfer, B.t.u./(hr)(sq.ft)(°F).

Low Cooling Water Temperature.

Temp. of cooling water - Inlet .... 17.62°C
Outlet ... 18.09°C
Mean .... 17.85°C (64.2°F)
Rate of flow of cooling water ..... 255 g.c./min.
Temperature rise ....0.47°C
Total heat removed in water .... 120 cal/min.

$$= \frac{120 \times 60}{252}$$

$$= 28.6 \text{ B.t.u./hour.}$$

$Q = U.A.T.$ T - temperature difference.

$$U = \frac{Q}{A.T}$$

$$= \frac{28.6 \times 144}{2.36 \times 4 \times (176 - 64.2)}$$

$$= \underline{3.91 \text{ B.t.u./(hr)(sq.ft)(°F)}}$$

$$\frac{1}{U.A} = \frac{1}{h_g A_g} + \frac{1}{h_v A_g} + \frac{l_m}{k_m A_m} + \frac{l_p}{k_p A_p} + \frac{1}{h_w A_w} \qquad (76)$$

The wall of the test piece is so thin that the differences in the areas are negligible.

(a)
$$\frac{1}{U} = \frac{1}{h} - \frac{1}{h} - \frac{1}{k} - \frac{1}{k} - \frac{1}{h}$$

$$h_w = 1.65 \frac{k}{D} \left(\frac{N C_p}{k N}\right)^{1/3} \qquad (77)$$

$$= \frac{1.65 \times 12 \times 0.35}{0.75} \left(\frac{34.4 \times 1}{0.35 \times 1/3}\right)^{1/3}$$

$$= 9.25 \times (295)^{1/3}$$

$$= \underline{61.5}$$

For steel $\frac{l_m}{k_m} = \frac{1/16 \times 1/12}{26.0} = \frac{1}{5000}$ $k_m = 26.0$ (78)

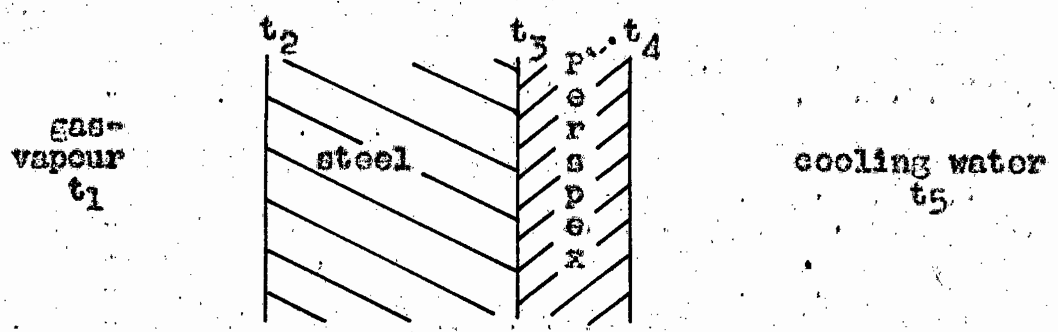
For Perspex $\frac{l_p}{k_p} = \frac{\frac{1}{1000} \times 1/12}{0.12} = \frac{1}{1440}$ $k_{(celluloid)} = 0.12$ (78)

The coefficients of heat transfer for the gas and condensing vapour are combined:

$$\frac{1}{h_{gv}} = \frac{1}{h_g} + \frac{1}{h_v}$$

From equation (a),

$$\frac{1}{h_{gv}} = \frac{1}{3.91} - \left(\frac{1}{5000} + \frac{1}{1440} + \frac{1}{61.5}\right)$$
$$= 0.255 - (0.0002 + 0.0007 + 0.0163)$$
$$= 0.238$$
$$h_{gv} = \underline{4.2}$$



$$h\,(t_1 - t_2) = U.(t_1 - t_5)$$
$$t_1 - t_2 = \frac{3.91 \times 111.8}{4.2}$$
$$= 104^\circ F$$
$$\underline{t_2 = 72^\circ F}$$

<u>High Cooling Water Temperature.</u>

Temp. of cooling water - Inlet .... 20.83°C
Outlet ... 21.31°C
Mean ..... 21.07°C (69.9°F)
Rate of flow of cooling water ..... 260 c.c./min.
Temperature rise .... 0.48°C
Total heat removed in water .... 126 cal/min.

$$= \frac{126 \times 60}{252}$$
$$= 30.0 \text{ B.t.u./hour.}$$

A similar calculation was made to that above.

$$Q = U.A.T$$
$$U = \frac{30.0 \times 144}{2.36 \times 4 \times 106.1}$$
$$= \underline{4.31}$$

$$\frac{1}{h_{gv}} = \frac{1}{4.31} - \left(\frac{1}{5000} + \frac{1}{1440} + \frac{1}{61.5}\right)$$
$$= 0.215$$
$$h_{gv} = 4.65$$

$$t_1 - t_2 = \frac{4.31 \times 106.1}{4.65}$$
$$= 98.5^\circ F$$
$$\underline{t_2 = 76.5^\circ F}$$

There is hence a difference of 4.5°F (2.5°C) in the mean surface temperature of the specimen when the inlet temperature of the cooling water rises by 5.8°F (3.2°C).

APPENDIX II

The Rejection of Data. (Chauvenet's Criterion)

Number of readings, n	Reject all values having residuals greater than:-
	(Probable deviation of a single reading) times i.e. r x
10	2.9
20	3.3
30	3.5
50	3.8
100	4.2
500	4.9

APPENDIX III

Values for k for Probable Deviation. $r = ks$

Number of readings, n	Value for k
2	1.00
3	0.816
4	0.766
5	0.740
6	0.728
7	0.718
10	0.703
20	0.699
∞	0.674