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Corrosion of Steel in Laminar Flowing Water

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When studying corrosion from tap water in galvanized and non-galvanized iron pipes, the author attempted to investigate the formation of the rust layer upon an iron surface overflown by water. For this purpose a test cell as shown in Fig. 1 was built.

THE TEST CELL

The test cell consisted of a circular iron disk with a machined surface and a glass disk secured at a distance of 2 mm from the iron surface by means of a 2 mm thick circular rubber ring. Above the glass there was another rubber ring, and on the top of that a metal ring, connected to the iron disk by means of screws and nuts. The long cylindrical heads of the screws formed four legs supporting the cell.

The iron disk had an outside diameter of 140 mm and the openings in the metal ring and the rubber rings were 90 mm in diameter.

The space between the iron disk and the glass was filled with water, flowing in a steady stream from a hole in the disk, placed 39 mm from the centre, to another in the diametrically opposite position. To avoid the entrapping of air bubbles the iron disk was supported in an inclined position so that the outlet was located at a higher position than the inlet.

The water was taken from the tap to a reservoir with an overflow giving it a head of approximately 350 mm above the cell (Fig. 2). From the reservoir the water was led through a rubber hose to a stainless steel tube screwed into the bottom of the disk.

An air vent was arranged just before the inlet to the cell. The hole in the iron disk which formed the outlet for the water flow had a smaller cross section than any other part of the circuit, and consequently it controlled the discharge of water. Most of the tests were made with disks having a 2 mm

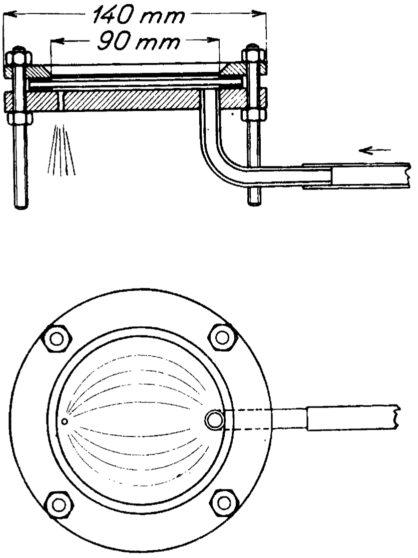

Fig. 1. The test cell.

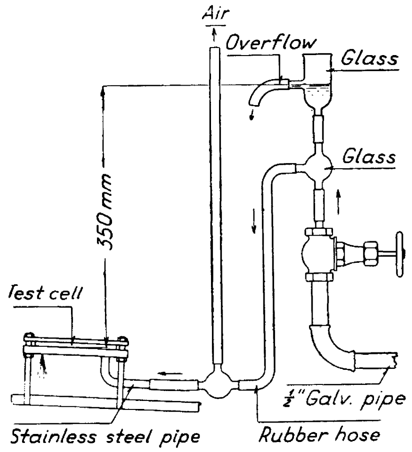

Fig. 2. The connection of the tap to the test cell.

slightly countersunk outlet hole, corresponding to a discharge of 5 ml per second or 18 litres per hour. The flow pattern in the cell was purely laminar except for an area around the inlet. Here a three-dimensional flow with local eddies prevailed.

PREPARATION OF A TEST CELL

The test cells were prepared in the following manner. The iron disk was burned out of a plate, and holes for the inlet, outlet and screws were drilled. As the last operation, the front surface of the disk was machined by turning without using oil or any other coolants on the tool. The final cut was made with a feed of 0.025 mm, equal to one thousandth of an inch, per revolution. The tool was well sharpened, and the surface of the finished disk appeared bright and uniform with a fine spiral groove from the last cut. Only in special cases the surface was afterwards polished with emery cloth. Without being touched by hand, the surface was then washed in absolute alcohol with a stiff non-metallic brush in order to remove all chips. The rubber ring and the glass cover were placed on the disk, on top of that the second rubber ring and the metal ring, all parts being kept together by the four screws. The inlet pipe of stainless steel was screwed into its place. When the test was to begin the cell was connected to the water reservoir by means of a rubber hose. The water flow to the reservoir was started in advance in order to remove air from the pipings.

If, in spite of all precautions, air bubbles collected on the inside of the glass, they could be washed away by a blow dealt to the cell by hand. It was very important, during the preparations, to keep the iron surface absolutely free from any grease. Even a slight touch with a finger would easily be traceable later.

THE DEVELOPMENT OF RUST DURING A NORMAL TEST

28 tests were made under what may be described as normal conditions:

1. The test disk was cut out of a piece of rolled steel containing 0.10—0.40 % C.
2. The outlet hole had a diameter of 2 mm, giving a flow of 5 ml per second or 18 litres per hour.
3. The water was Copenhagen tap water. Its composition varied daily, and some examples are given in Table 1. (The variations were due to the water being a mixture drawn from several groups of wells, to which the city mains are connected through a number of feed pipes. Several water reservoirs are also connected to the mains. Therefore, the composition of water delivered to the consumers will depend upon the flow condition in the city mains.)

The water temperature was 12—16° C.

The following description gives the general trend of the development of rust. The individual test disks showed variations in the rapidity of rust formation and in the ratio of areas of rust and bright iron. It was not possible to relate these variations to differences in the carbon contents of the steel or to any known characteristics of the water.

In the beginning of a test the appearance of the iron surface changed very quickly; later on the changes were developing more slowly. Therefore, the description is referred to a series of stages considered with increasing time intervals. Each stage applies to the appearance of an "average" test disk.

1. stage. 3-5 minutes after the start of the water flow. Faint green lines become visible on the upper half of the test piece (the half next to the discharge opening). The lines evidently follow the stream lines and their spacing varies between a fraction of a millimetre and several millimetres.

2. stage. 30 minutes after start. The lines have become very clear and some finer lines have combined into broader ones. Their colour is green-blue, and their starting points are located at a distance of 15— 30 mm from the inlet hole.

3. stage. 3—4 hours after start. The lines show a faint sepia colour at their sources. Short green—blue lines are to be seen near the inlet hole; they are direc-

Table 1. Analyses of Copenhagen water (examples).

		$^{9}/_{7}$ 1949	$^{22}/_{9}$ 1949	$^{23}/_{11}$ 1949	$^{31}/_{1}$ 1950	$^{20}/_{3}$ 1950	$^{24}/_{5}$ 1950
Hardness (German)	total	18.2	19.6	18.6	16.6	18.6	17.8
	permanent	2.2	3.1	2.6	.6	2.4	2.7
	temporary	16.0	16.5	16.0	16.0	16.2	15.1
pH		7.7	7.75	7.8	7.65	7.75	7.6
Total solids	p.p.m.	520	584	588	524	520	480
Calcium (Ca^{++})	»	97	97	97	94	97	91
Magnesia (Mg^{++})	»	20	26	22	15	22	22
Iron (Fe^{++})	»	.06	.02	.02	.04	.03	.04
Manganese (Mn^{++})	»	0	0	0	0	0	.022
Sodium (Na^{+})	»	55	67	69	69	61	44
Bicarbonate (HCO_3^{-})	»	348	360	348	348	354	329
Chlorid (Cl^{-})	»	78	92	85	71	76	56
Sulphate (SO_4^{--})	»	49	66	74	58	66	62
Nitrate (NO_3^{-})	»	traces	traces	0	0	0	0
Phosphate (PO_4^{---})	»	0	0	0	0	0	0
Iodine (I^{-})	»	.02	$<$ .01	.04	.02	.01	.02
Sulphuretted hydrogen (H_2S)	»	0	0	0	0	0	0
Silica (SiO_2)	»	16	18	18	18	16	16
Free carbondioxide (CO_2)	»	8	9	9	13	11	11
Dissolved oxygen (O_2)	»	9	8.1	8.7	9	9	8.7
Alkaline bicarbonates ($NaHCO_3$)	»	0	0	0	0	0	0

ted towards the inlet and are traces of the eddies set up by the incoming water. Their configuration is similar to a bouquet of flowers in a vase (Fig. 3).

4. stage. One day after start. All lines have become sepia-coloured. It can be observed through a magnifying glass that they are of a certain height, while the green and blue lines only consist in a stain of the iron surface.

5. stage. One week after start. All lines have become more dark and have grown in width and height, now forming a system of hedges. In some cases one or two tubercles (sepia in colour) have grown up at the edge of the inlet hole (Fig. 4).

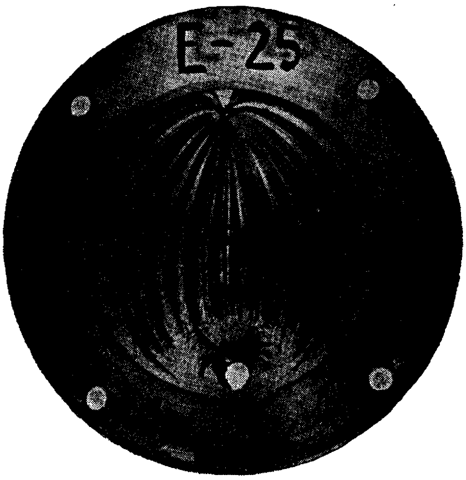

Fig. 3. Disk of SM-steel, 3 hours after the start.

Fig. 4. Disk of the SM-steel, 7 days after the start.

6. stage. One or two months after start. The lines have grown in width and height and in some places show a kind of dark brown fractures with fresh growth, light sepia in colour, in the middle of the fracture.

When a disk was to be preserved for later reference, it was carefully dipped in a bath of absolute alcohol, dried in the air for some minutes and then dipped in a bath of nitro—cellulose lacquer (if the dipping was not done carefully, loose rust would be washed away). When the lacquer had dried, the plate could be touched without impairing the rust.

If the abrasion of the disk itself was to be studied, the corrosion products were removed by dipping the disk in diluted and inhibited hydrochloric acid. The disk showed corroded grooves and caves where rust had collected, and lanes of untouched iron between the grooves.

THE MICROSCOPICAL DEVELOPMENT

Most observations in microscope are made with a 25 time magnification; 100 times are used for a few checks.

The green and blue colours to be seen shortly after the start of a test are, as mentioned, only a stain of the iron surface. All details in the surface, such as turning grooves, small burrs *etc.*, are equally visible after the staining.

The sepia colouring can in the microscope be seen to originate in small pins of the said colour, standing on ends in contact with the metal surface. Their diameter ranges from less than 0.01 mm to 0.02 mm, their height is about 0.03—0.05 mm. Observing the same spot at time intervals their number is steadily increasing. It is characteristic that they seem to prefer to settle to the lee side of any obstacle. Any collection of pins is therefore followed downstream by a tail of less concentrated pins, the tail growing with time in concentration and length. At any spot where pins have once begun to settle, they will after one or two days have covered the iron surface completely, hiding all marks and grooves once to be seen around the spot.

At this stage, the mass of pins take the shape of diminutive coral reefs, growing in height and width for some weeks. Then the growth seems to decrease in speed, and some day deep fractures may appear in the reefs; they disclose a dark brown colour behind the lighter exterior. A day or two later, light brown regions are growing in the fractures, thereby increasing the height of the reef until the growth again is retarded.

Through the microscope pins can be seen also on the bright iron stripes between the coral reefs, their number is increasing very slowly and the stripes appear macroscopically to be bright for weeks or even months.

THE DEVELOPMENT OF RUST DURING TESTS DIFFERING FROM THE NORMAL CONDITIONS

Each of the conditions described in the following section has been tested only a few times; the results must therefore be taken as rather preliminary.

On a disk of the same material as the normal ones but *polished* with fine emery-cloth, the number of lines was smaller and their spacing larger, depending upon the smoothness of the surface. Lines once started developed in the same way as previously described, but it seemed to be more difficult to get a line started here than upon an unpolished surface of the same material.

Cast iron, machined but not polished, did not show any lines for the first half hour. The first traces appeared in the eddy region around the inlet. When the lines became visible also in the laminar flow region, they were very closely spaced and darker in colour than upon steel. One day after the start the whole disk was dark brown with darkgreen stripes. Bright iron was only visible in a ring-shaped area around the inlet hole, where iron was seen in short streaks arranged in a featherlike design.

At *smaller velocities* (discharge hole 0.5 mm) the test disk of ordinary steel quickly became almost completely covered by lines. The green-blue colour changed within 2—3 hours to sepia, but in addition to the fixed rust on the disk fine brown rust flakes collected under the glass and in the discharge hole. The cells had to be cleaned several times every day to prevent complete obstruction of the discharge and to allow inspection of the disk.

At *larger velocities* (discharge hole 4 mm) the formation of lines was less distinctive but the difference in colours between the beginning and the end of the lines was after some time more pronounced than for the 2 mm discharge. After two days the colours of the stripes were golden-yellow near the inlet and dark-brown, almost black, near the discharge.

Chips not removed from the iron disk invariably caused the formation of distinct lines beginning in each chip. The lines were visible 3—5 minutes after the start of the water flow. The question arose whether the lines were in reality caused by small chips in all cases, also after the most careful cleaning with alcohol and a non-metallic brush. A microscopic study of the lines revealed no chips on thoroughly cleaned disks, not even at the sources of the lines. Furthermore, after some experience. a method was found by which deficiencies in removing chips could be detected during the cleaning procedure: About half a minute after the surface had been flushed with alcohol, any chips not removed could be seen as small projections from the half-wet surface.

Experiments showed that not only metallic chips but also small pieces of rubber or pats of glue got a tail of rust. It was concluded that any obstruction to the true laminar flow will cause a line of rust downstream.

Disks with a galvanized zone were made by shaping a flat groove 19 mm wide diametrically across the iron disk, hot galvanizing the total of the disk and then turning away so much of the surface that the zinc coating disappeared except in the groove. The depth of the groove was chosen so that iron and zinc constituted a smooth surface after the turning. A ring of zinc was also left outside the test surface, to avoid rusting under the rubber ring. Incidentally this ring of zinc also protected a part of the iron surface inside the rubber ring.

The iron did not show any rust for a week but one day after the start the zinc had dark lines, following the stream lines and being more intense at the edges near the iron than at the inner part of the belt. After a week a tubercle had formed on the iron at the inlet hole (Fig. 5). The picture shows protected bright iron surfaces in the following three places:

1) Between the zinc belt and the outlet.
2) Along the circumference.
3) In a narrow zone upstream of the zinc belt.

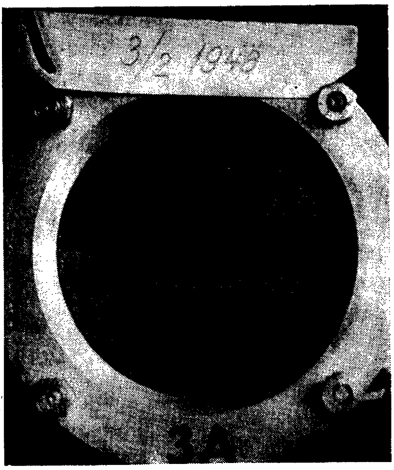

Fig. 5. Disk of SM-steel with a galvanized zone, 9 days after the start.

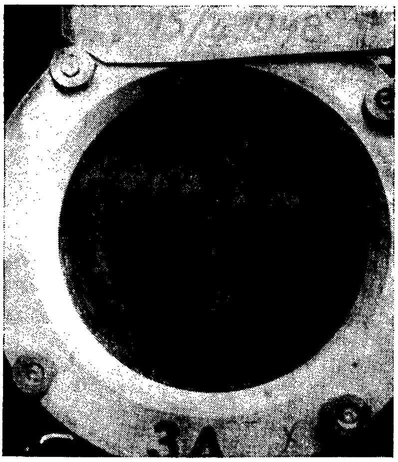

Fig. 6. Same disk as Fig. 5, almost three months after the start.

The average velocity of the water crossing the zinc belt was 28 millimetres per second, higher in the centre and lower at the edges. The protected zone had a width of 5 millimetres on an average, less in the centre (4 millimetres) and more at the edges (6 millimetres).

The dark coloured area between the inlet and the protected zone in front of the zinc belt could in the microscope be seen to be covered with small vertical pins. They were not arranged in stripes but evenly spread; in part of the area they could be seen with the naked eye.

The dark stripes on the zinc which appeared after one day grew in length and width, and after two weeks the zinc surface was dark with bright stripes only to be seen in the central part of the zinc belt. After a month, all zinc was dark, without any brightness.

At this time the tubercle caused a stripe of rust to be formed from the inlet to the outlet. It crossed the zinc belt but its adhesion to the zinc was of a much looser nature than that to the iron.

The continued flow of the water produced rust both in front of and behind the zinc belt, and after almost three months the picture Fig. 6 was taken. The great mass of rust in the upper right section was formed around an air bubble, which was not removed but continued growing by increments from air dissolved in the water.

Finger-prints and other traces of grease either protected iron or gave rise to other kinds of corrosion than those seen on a clean iron surface. In all cases, any greasy contamination of the surface could easily be detected after the start of the water flow.

Water with a small amount of Calgon (a hexameta phosphate, the strength of the solution being about 50 parts per million) gave no coloured lines or rust even after weeks of water flow. The bright surface showed some interference colours, and after some weeks dark shades could be observed, which in a microscope were seen to consist of a great number of very fine dark points. The shades followed the streamlines, but each shade was much wider than the lines appearing when no calgon was added.

ATTEMPTS AT QUANTITATIVE MEASUREMENTS

It was attempted to standardize the preparation of the disks in such a manner that possible differences in the ability of the water to form a protective layer upon the steel could be detected as differences in the proportion of bright and rust-covered iron after some fixed time. However, it was found, that some undetermined factors had as much influence upon the formation of lines as the differences in water, which could be tapped at different times of the day (Table 1). It is supposed that a very slight difference in the roughness of the surface after the machining was one such disturbing factor. It is realised that the way in which the roughness governs the initial formation of lines is of a very complex nature and that even the smallest departures from some selected type of roughness might lead to large differences in the configuration of lines. A finely polished surface is perhaps easier to reproduce, but experience has shown that the formation of lines on such a surface is even more casual than on an unpolished surface. The attempts to develop the cell into an instrument for quantitative measurements must therefore be postponed until a method is found of making a perfectly reproduceable rough iron surface.

THE ELECTRO-CHEMICAL EXPLANATION

The growth of rust on an iron surface submerged in water containing oxygen has been explained by McKay[1] and Baylis[2]. On page 377 Baylis says (see also Evans[3,p.3]).

"When a fresh iron surface is exposed to the water of any of our public water supplies, corrosion starts immediately. The dissolved oxygen within a certain zone next to the metal surface is soon used up, and precipitation of ferric hydroxide, or certain hydrous oxides of iron, usually takes place at a point a slight distance from the metal surface. When the precipitate has formed, part of it is attracted back towards the metal surface. This starts the formation of deposits of rust on the metal surface. Since ferrous hydroxide, or certain other ferrous salts, is not ordinarily precipitated within the pores of rust, but diffuses outside to where it is oxidized before being precipitated, the building up of the precipitate is from outside. In other words, iron goes into solution at the metal surface, diffuses to the dissolved oxygen zone, is precipitated probably as a hydrous oxide of iron, and the precipitate is attracted back to the surface of the metal, or precipitate already formed. In this way the precipitate builds up porous and somewhat fibrous."

The process is autocatalytic (McKay p. 24) because the oxygen concentration is smaller inside the mass of the precipitate than outside, where the water flow immediately replenishes the consumed oxygen. Thereby a differential cell is set up, the covered areas being anodic and the non-covered ones being cathodic. A pit is formed under the precipitate, while the uncovered surface is protected. A concentration of precipitate is commonly called a tubercle because of its fibrous natur.

Baylis explains the retardation of the growth in this way:

"In following the progress of pitting and tuberculation it has been found that there are active and dormant periods, and that the character of the water determines largely whether a pit is active or dormant most of the time. When the precipitate overlying an area where the iron is going into solution reaches a certain thickness, which is quite variable for different conditions, the diffusion of soluble iron from the surface to where there is dissolved oxygen present slows up to where the oxygen in the water reaches the hydroxide precipitate already adhering to iron. Precipitation then begins to take place within but very near the surface of this precipitate. In other words, the soluble iron is oxidized and precipitated before it reaches the outside solution."

Baylis proceeds by explaining how the iron precipitated within the older precipitate forms a diaphragm which stops further action. After some time the diaphragm in some cases breaks, and the process continues for some time again. Inside the tubercles, some of the precipitated ferric hydroxide will be reduced to black magnetic oxide Fe_3O_4.

The explanation agrees very well with the observations made, though the reason why the precipitated ferric hydroxide is attracted back to the iron surface or the older precipitations, has not been given definitely. Baylis has seen particles of rust suddenly move at considerable speed from a point as far as 0.2 mm from an iron surface towards the surface.

The very first reason why a rust formation starts must be quite incidental. The difference between the oxygen concentration on the windward and that on the leeward side of a turning groove, small differences of structure in adjoining iron grains *etc.* give rise to the first faint potential differential and corrosion process. The oxygen consumption in connexion with this process immediately reduces the local oxygen concentration and thereby makes the spot more anodic.

If the water flow is turbulent, the oxygen deficiency is quickly replenished from all sides. Consequently, the first incident for forming a tubercle must be rather strong; when formed, it will grow in a concentrated way with only a weak tendency for the growth to follow the direction of flow.

If the water flow is laminar, the oxygen deficiency will spread downstream in a well defined line. Therefore, a differential concentration cell is formed, making the particular streamline anodic and the adjoining streamlines cathodic. The attracted precipitate of $Fe_2O_3\ (H_2O)_n$ reduces the flow velocity and thereby increases the oxygen deficiency and the potential difference.

A PROTECTIVE LAYER

It had been expected that a chalky rust layer would be formed upon the cathodic iron surfaces. No such layer could be seen, however. If, after all, there was a layer it did not give a lasting protection. It was observed that any alteration of the direction of the flow was followed by a formation of rust in areas which had previously been cathodic.

Under the conditions considered, consequently no natural absolute protection seems to occur. The continous growth of rust, and corresponding corrosion of iron, will however be hampered when the whole area is covered with an evenly thick layer of rust. The formation of such layer is counteracted by the auto-catholytic effect of rust-formation but might probably be supported by a turbulent flow of the water and by such chemical properties of the water as make the diaphragm on the surface of the rust more durable.

SUMMARY

The effect of flowing water containing oxygen upon an iron surface has often been described (Evans [3,p.317]), but no references have been found in the literature to the well defined effect of laminar flow of water. A cell with

laminar flow has been found a useful help in the study of the mechanism of rust formation on submerged iron surfaces.

LITERATURE

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2. Baylis, J. R. *Ind. Eng. Chem.* **18** (1926) 370.
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