Aerobic Microbiological Corrosion of Water Pipes. II

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In a previous paper[1], we have dealt with corrosion and proposed the hypothesis that iron bacteria play a prominent, primary part in this phenomenon of electrochemical nature. In our opinion, their mode of action should be as follows:

1. Primarily, the formation of 'differential aeration cells' by the growth of iron bacteria on limited regions of the iron surface.

2. The felt-like structure of the sheaths of iron bacteria causes a mechanical strengthening of the 'tubercle', which becomes resistant to the flow of water in the main.

3. Increasing anaerobiosis below the tubercles formed by the iron bacteria which are oxygen consuming. Hereby, the anode potential decreases and the potential difference between the anode (under the tubercle) and the cathode (outside the tubercle) and, consequently, the corrosion flow, increase.

In the present investigation an attempt has been made to obtain experimental corroboration of our assumptions.

As a first step towards the verification of the assumption that the corrosion is of bacterial origin, a bacteriological investigation of the tubercle has been carried out. As mentioned in the previous paper, it was observed that those parts of tubercle shells, found in the closest proximity to the iron surface, consisted of amorphous, recrystallized hematite (Eisenglanz) and, towards the surface, of a felt of mostly empty, largely iron-incrusted sheaths of iron bacteria. This is most beautifully seen on younger tubercles (2—3 months old). In Fig. 1 such a felt is depicted in ca. 20 fold magnification. The surface

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Fig. 1. Internal structure of a 3 months old tubercle. The single threads covered with a very thick knotted sheath are easily seen. Magnification ca. 20 x.

of the tubercle is removed. It consists of an ochre-yellow, porous, amorphous, very thin layer of strongly hydrated ferric oxide, which is easily soluble in dilute hydrochloric acid. The iron compound in the recrystallized layer and in the sheaths of the iron bacteria is sparingly soluble in dilute hydrochloric acid.

The bacterium felt shows little electric resistance, but is an effective membrane inhibiting both percolation of water and oxygen diffusion.

In our experimental pipes, iron bacteria grew especially well on bakelite packings, while a continuous flow of tap water was led through the pipes. Here, a velvet-like, rather firmly fixed layer of iron bacteria developed.

Long threads, approx. 1 μ thick and 100—500 μ long, were formed. Most of these were entire, however, many of them were divided into separated cells, 1 $\times$ 10 μ large. The older threads were surrounded by a yellow-brown sheath of hydrated ferric oxide, while the quite new ones lacked these sheaths. With increasing age the sheaths become darker brown and thicker. Incrustation seems to occur in such a way that single grains of hydrated ferric oxide appear on the sheath and, in the course of time, a larger and larger number of grains develops until, finally, the whole surface is covered by a brown, knotted layer (Fig. 2).
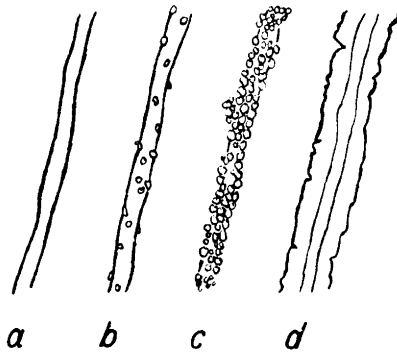
Fig. 2. Scheme of the formation of the sheath. a — uncovered, young threads. b, c — the threads covered with single grains of hydrated hematite. d — completely developed sheath.

Generally, the threads appear to be unbranched, but some are actually ramified. Morphologically, they seem to belong to the *Crenothrix* group, but some types forming ramifications recalled definitely the *Clonothrix* or *Leptothrix* types.

At the present time, however, the classification of iron bacteria is rather doubtful, and it appears probable that the multifarious types should in reality be condensed into a few, since the morphology, the most important grouping basis, may vary considerably according to the exterior conditions (*cf.*, for example, Beger [2], Bergey [3], Pringsheim, [4]).

It was our aim to elucidate whether iron bacteria are the primary cause of tubercle formation and, correspondingly, of corrosion. We have, therefore, investigated whether germ filtration of tap water suppresses these phenomena, and whether inoculation of sterile main water with iron bacteria causes tubercle formation. The experiments were performed in the following way.
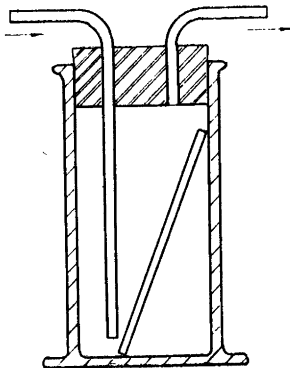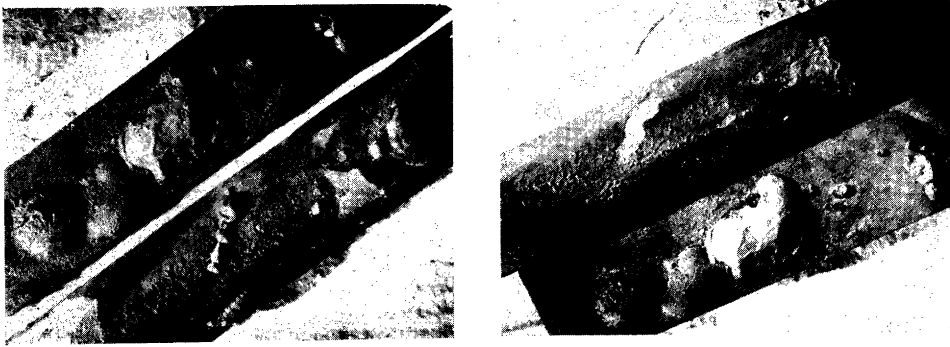

Fig. 3. Glass cylinder with a piece of iron sheet for experiments with sterile and unsterile water. → indicate the flow of water.

Figs. 4 and 5.   Iron sheet pieces with well developed tubercles.   After removal of the tubercle, the corrosion cavities become visible (on the upper iron piece of Fig. 5).

Main water was directly filtered through a Seitz filter into a level flask. From here, it was led into two parallel series of sterile glass cylinders (200 ml), each containing a square piece of iron sheet, $20 \times 100 \times 0.5$ mm (Fig. 3).

Into the first cylinder of one of the (inoculated) series was mounted a piece of folded filter paper containing a culture of iron bacteria — this caused a very vigorous inoculation. Unfortunately, we have not yet succeeded in producing a completely pure culture of bacteria, but there is no reason to assume that this should affect the results presented here.

After a lapse of 4—6 days, the metal sheet plates in the uninoculated series were covered with a thin, firm, protective layer ('chalky rust').

In the inoculated series, however, small, velvet-like colonies on the iron surface appeared after a few days. They grew rather rapidly into common tubercles with light-yellow, rather smooth and porous surfaces and, after 2—3 months, they were up to approximately 2 cm in diameter and 5 mm high.

In other experiments, non-sterile tap water was led through glass cylinders with iron sheet plates without special previous inoculation. Also in these cases, the growth of the bacteria appeared, even after a presumably very slight inoculation. In the last mentioned experiments, however, single tubercles were observed which were spread over the surface of the iron sheet, while after strong inoculation almost the whole surface was overgrown. Fig. 4 shows the appearance of the tubercles and, in Fig. 5, corrosion is seen after the tubercles were removed from the iron sheet pieces. Fig. 1 is also taken from this experiment.

Hence, it was possible to show that sterile water does not cause tubercle formation and, moreover, that the iron bacteria are the cause of tubercle formation and, correspondingly, of corrosion.
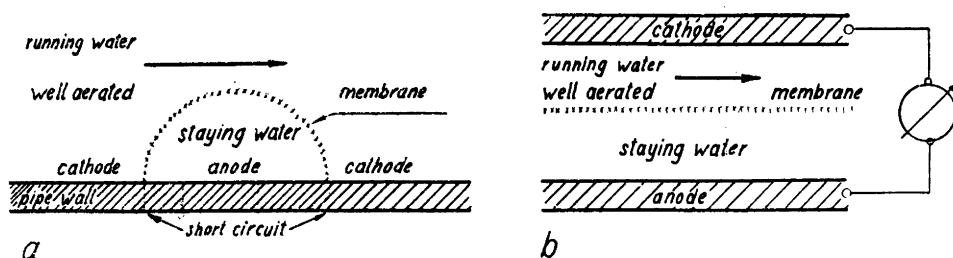
Fig. 6. Schematic comparison of the conditions during pitting with tubercle formation and by artificial differential aeration cell.

In order to further prove the significance of iron bacteria in iron corrosion, a series of experiments were performed in which it was attempted to produce the effect of the tubercles by means of artificially constructed 'differential aeration cells'.

Fig. 6 a shows schematically the conditions prevailing in a water pipe. Under the membrane ('the tubercle') built up by the iron bacteria we have stagnant, practically oxygen-free water, and the underlying part of the iron surface acts as the anode. The iron surface outside the tubercle is continuously in contact with water saturated with air and, therefore, forms the cathode relative to the covered part. The two terminals are short-circuited through the pipe wall.

In order to imitate these conditions, two iron plate terminals were placed parallel to each other and separated by a membrane of hardened filter paper. In this way, the cell formed two compartments, one of which containing stagnant water, while continuous flow of water passed the other compartment of the cell. The two iron plates, short-circuited through a micro-amperemeter, thus formed anode and cathode, respectively. The principle of this arrangement is seen in Fig. 6 b.

Fig. 7 shows the construction of the cell. It consists of four bakelite plates (denoted by 1, 2, 3, 4), 50 × 50 × 10 mm. A hole, 30 mm in diameter, was drilled into thé two central plates (2, 3), whereby an internal cylindrical cavity (A · B) was formed.

At the ends of this cavity, two iron plates (a, b) were placed, their position being fixed by the external bakelite plates. The filter paper membrane (c) was placed between the two internal bakelite plates, thus dividing the cell into two compartments (A and B), each 10 mm deep and 30 mm in diameter. The arrangement was held together by iron clamps (not shown in Fig. 7).

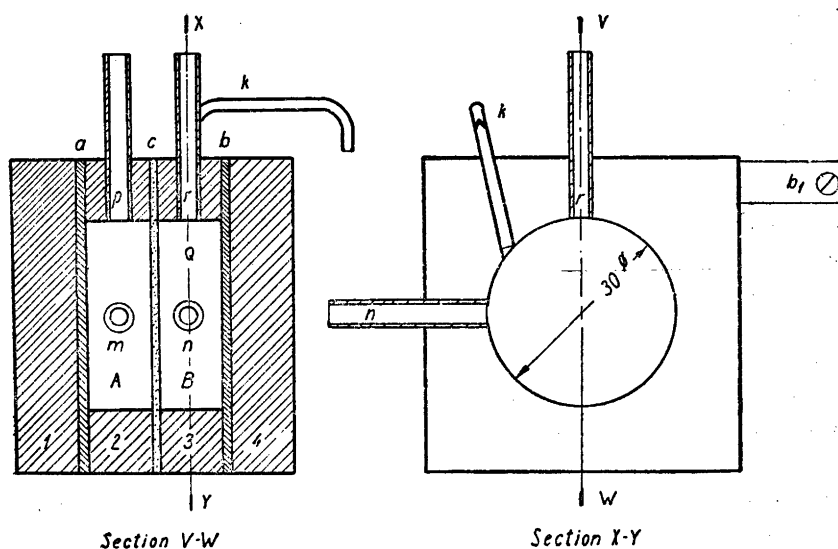Section V-W   Section X-Y

Fig. 7. Differential aeration cell. 1,4 — external bakelite plates. 2,3 — internal bakelite plates; the holes drilled form the real cell compartment A—B. a, b — iron plate electrodes, b₁ — terminals for the electric connection of the iron electrode with the measuring apparatus. c — membrane made of filter paper. m, n — water inlet pipes. p, r — water outlet pipes. k — agar salt bridge for the potentiometric measurements.

Through the bores of the internal bakelite plates, water could pass into and out of the two compartments of the cell through cemented glass tubes (m, n, p, r).

During the experiment proper, water was led through one compartment (A) only, while the other one (B) contained stagnant water. During the corrosion process, the oxygen will rapidly be consumed and the iron plate, therefore, become anodic relative to the other plate which is in continual contact with oxygen containing water. Oxygen diffuses only slowly through the hardened paper and, in the compartment with stagnant water, we shall therefore rather soon find (after some hours) that highly anaerobic conditions prevail near the iron surface, becoming more and more aerobic in the direction of the membrane.

The iron plates were short-circuited except for the time when the measurements were performed. These included corrosion current as a function of time, potential between the iron plates, their individual potentials measured by means of a calomel electrode (saturated KCl), the internal resistance of the cell to d.c. and a.c., and the electric capacity of the cell.

The water flow was 100 ml/min. Each experiment lasted for 15—30 days.

In the first experiments, ordinary main water flowed through the cell. When the cell was opened after the lapse of 3 weeks, vigorous growth of iron bacteria was found to occur on the non-aerated part of the filter paper membrane. The bacteria formed a 1—2 mm thick felt. The non-aerated electrode (anode) was quite bright and homogeneously affected. The weight loss of this electrode approximately agreed with the loss calculated from the measurements of the corrosion current, the weight loss being about 10 % higher than the Coulomb equivalent of the current. The cathode was covered with a compact, thin, yellow layer of 'chalky rust' which stuck firmly. The cathode seemed to be especially well protected under this layer.

The described development of iron bacteria was observed in all cases where untreated main water was led through the cell. This apparatus can, therefore, also be applied to the demonstration of iron bacteria in water.

For the sake of comparison, a series of experiments was carried out under sterile conditions, the water being germ-filtered through Seitz filters and led through two parallel cells of the type shown in Fig. 7. One of the cells was strongly inoculated by introducing the iron bacteria grown in the above mentioned experiments into the anodic part of the cell, the other one remained sterile. The results of these measurements are shown in the diagrams (average of 5 series), and it appears that the bacteria have a rather small, but pronounced effect on the decrease in potential of the non-aerated electrode, which causes a greater potential difference between the electrodes and an increase in the corrosion current (Fig. 8, I).

It could, however, be observed that strong inoculation with iron bacteria very rapidly brought forth a decrease in the electric potential of the non-aerated electrode to the ensuing, rather constant value observed later.

The potential of the aerated electrode decreased much slower owing to the high EMF of the cell at the start of the experiment and, thus, of the vigorous corrosion current (Fig. 8, II).

In the uninoculated cell, however, a rather simultaneous decrease in electric potentials of both electrodes could be observed. The potential difference thus fluctuates around zero and, therefore, in the first hours of the experiment, the corrosion flow shows low positive and negative values * (Fig. 8, II).

This difference in the initial course of corrosion indicates that iron bacteria may be the primary cause of corrosion in new pipes. In regions where the

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* This must be considered the explanation of the undefined directi on of current in the beginning of the experiment with 'differential aeration cells' as discussed by Evans [5] who, however, does not explain the phenomenon.

Fig. 8. I. Time-potential curve of the aerated electrode (cathode) and the unaerated electrode (anode) for sterile and inoculated differential aeration cell.
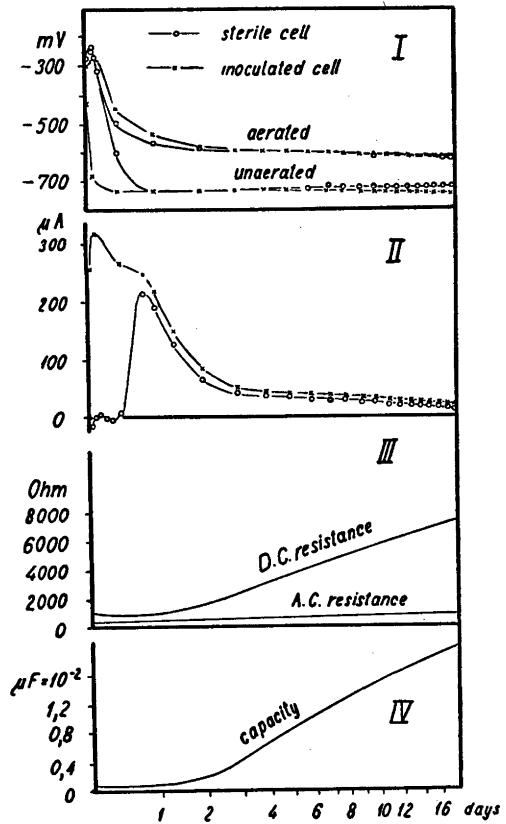
II. Time corrosion current curve.
III. Time d. c. resistance curve.
   »   a. c.   »   »
IV.   »   capacity curve.

   The curves III and IV are practically identical for inoculated and uninoculated cells.

bacteria are deposited, the potential of the iron decreases rapidly, whereby primary micro-'differential aeration cells' are formed. Corrosion and formation of 'tubercles' by precipitation of hydrated ferric oxide start momentarily and, simultaneously, also the bacteria colonies grow.

   Experiments with sterile water, moreover, showed that, in the course of a week, the potential of the anode was — 720 — 740 mV, measured against a calomel electrode (saturated KCl). This potential deviates, practically spoken, only very little from the potential of the iron in completely O_2-free medium under otherwise similar conditions. *

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   * After some days the potential of the iron in O_2-free main water was rather constant — 775 mV against a calomel electrode (— 553 mV against normal H_2-electrode). The concentration of ferro-ions was 0.85 millimol/1. These values are in good agreement with the normal potential of the iron, — 441 mV against a normal H_2-electrode.

From these results it becomes clear that the iron bacteria cannot further decrease the potential of the anode. After 'tubercles' have been formed, the iron bacteria practically do not play any part in the progressing corrosion. In our experiments, the iron bacteria caused an average increase in corrosion by ca. 10 % (Fig. 8, I and II).

Thus, there is no possibility of inhibiting corrosion by killing the iron bacteria. However, such a measure — for example, frequent addition of chlorine to the main water — will presumably suppress the formation of new corrosion fields [8, 9].

One way in which inhibition of corrosion might be obtained is to cover the tubercles with a thick protective layer. Hereby, the current density on the anode is largely decreased and the corrosion effectively inhibited.

The normal equilibrium water (with respect to the system $CaCO_3 - CO_2 - H_2O$, Bauer, Kröhnke, Masing [6] and others), forming protective 'chalky rust' layers in iron pipes, will not form such layers on the tubercle surface because of the hydrolysis of ferric and ferrous ions which gives an acid reaction. The equilibrium (pH) of the water is changed and the water dissolves chalk rather than forming protective layers. Only after alkalizing the water (for example, by addition of lime water or filtration through freshly burnt magnofilters) do the conditions on the surface of the tubercles favour the formation of tight layers of 'chalky rust'.

Preliminary experiments indicated that newly filled magnofilters completely inhibit the formation and growth of 'young tubercles' (Mansa [7]).

We found that fresh magnofilters increase the pH by 0.5 — 0.8, while a filter with old filling (ca. 6 — 12 months old) only caused an increase in pH of 0.1. This filter proved to be ineffective in preventing corrosion.

The effect of freshly burnt magnofilters seems to be based not only on the adjustment of the equilibrium state of the water, but also on the alkalization. This involves a super-saturation with chalk which, in the course of time, causes (1) precipitation of a protective layer on the 'tubercle' in a zone where the degree of acidity is suited for the readjustment of the equilibrium of the water, and (2) precipitation of a porous layer of $CaCO_3$ on the wall of the pipe outside the 'tubercles' which may choke up the pipe. Therefore, the alkalization of the water must be performed very cautiously, in the right places, and over the right period of time.

It can easily be shown that water which passed through a fresh magnofilter and is supersaturated with chalk is above the equilibrium curve of the Tillman and Heublein [6] diagram (p. 224). If ca. 50 cm long glass tubes are inserted in both sides of the magnofilter, a thick chalky precipitate is observed on the walls of the tube inserted behind the filter, while the tube leading to the filter is unchanged.

After precipitation of the excess chalk, protective layers on or inside the tubercles can no longer be formed. The pretreatment of the water should, therefore, be performed in the proximity of those parts of the pipe which must be saved, for example by instalment of a magnofilter in the attacked houses for a shorter period of time (some months).

Finally, it should be mentioned that, in parallel experiments with inoculated and uninoculated cells, the internal resistance of the cell to a.c. and d.c.,
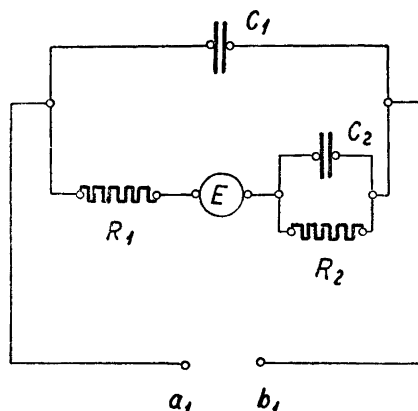
*Fig. 9. Electrical scheme for the different-
ial aeration cell (explanation in the text).
a_1, b_1 — the terminals of the iron electrodes.*

and the electrical capacity, did not show any deviation (Fig. 8, III and IV). However, the results are typical. The initial d.c. resistance* of ca. 800 ohms increased after the lapse of 24 hours and after 8 days it was 7—8 times as high.

At the same time the a.c. resistance ** increased only by ca. 50 %. The capacity of the cell increased in the beginning proportional to the d.c. resistance.

These observations may be interpreted as follows. Let us consider the scheme of Fig. 9. In the beginning, we have only the resistance (R 1) of the water layer between the electrodes. The two iron electrodes, separated by the water layer, form a condensor (C_1). (E) is the electromotive force of the cell. These values change only insignificantly in the course of the experiment.

By the formation of the chalky rust layer more or less covering the cathode surface, two new components (R_2 and C_2) appear which cause the vigorous increase in total resistance and capacity of the cell.

If the chalky rust covered cathode is replaced by a new iron sheet, the initial C_1 and R_1 values are reestablished.

It might be possible by means of this 'differential aeration cell' to measure quantitatively the capacity of the water of forming protective layers. In this case, all dimensions and all experimental conditions must be standardized.

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* The d. c. resistance was calculated from the changes in current caused by an increase in the external resistance of the circuit by 500 ohms. The inner resistance of the micro-amperemeter was 20 ohms.

** The a. c. resistance was measured by means of a Wheatstone bridge. A tube generator with a frequency of 1000 cycles served as a current source. The capacity of the cell was balanced by a variable condensor inserted parallel to the variable decade resistance of the Wheatstone bridge.

SUMMARY

An attempt was made to prove experimentally our previous hypothesis regarding the activity of iron bacteria during corrosion of water pipes. This hypothesis comprised three arguments.

The first and second arguments, the primary formation of the 'differential aeration cell' by iron bacteria and the mechanical reinforcement of the 'tubercle' could be completely corroborated in parallel experiments, using germ filtered water with and without inoculation with iron bacteria and, moreover, by microscopic observations.

The iron bacteria play a decisive part in these phenomena. However, iron bacteria play only a minor part in the establishment of anaerobic conditions under the tubercle during the main period of the corrosion (third argument).

In other words, after the tubercle has formed, corrosion (pitting) proceeds practically independent of the metabolic activity of iron bacteria.

It has been attempted to inhibit further corrosion by changing the equilibrium of the water in such a way that a compact protective layer of 'chalky rust' is formed on the surface of the 'tubercle'.

LITERATURE

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