Aerobic Microbiological Corrosion of Water Pipes. I

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As is well known, internal corrosion of water pipes is liable to occur in some areas. As often described in literature, such corrosions manifest themselves in the following way:

First, traces of rust are found to appear on the external surface of the pipes, and, subsequently, leakage occurs through an initially small hole in the pipe wall which, however, gradually increases in size.

On the internal side of the pipe wall, numerous crust- or tubercle-shaped dark-brown or ochre-coloured salient spots, of considerable size, can be detected. These prominences are porous and can easily be cut through with a knife. It then appears as if they consist of a dark-coloured to black core in the centre, which is surrounded by different, generally somewhat clearer, layers with a soft rust-coloured layer on the outermost side. The 'tubercle' chiefly consists of hydrated ferric hydroxides; pH 5—6. In the pipe wall, below the tubercle, a crater-shaped hollow is seen in the steel, deepest in the middle, where the pitting of the pipe initially occurs. Generally, concentric rings of less and less corroded parts of the crater appear toward its edge. In galvanized pipes the zinc has generally disappeared below the tubercle.

Corrosion is most frequently found at many places in the same pipe and, generally, several or many neighbouring pipes show corrosion. Those parts inside a galvanized pipe which are not occupied by tubercles are, just as uncorroded pipes, covered with a smooth or granular, yellow or ochre-coloured layer, a socalled protective layer, which protects the metal against corrosion. According to Haase[1], this layer consists chiefly of calcareous ferric hydroxides of variable composition, with an admixture of small quantities of Mg and Si.

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A microscopic investigation showed that the tubercles, in addition to large quantities of amorphous ferric hydroxides, contained iron bacteria surrounded by sheaths; and, moreover, sometimes typical filaments of iron hydroxides from *Gallionella ferruginea*. The sheaths-forming bacteria were lying in coiled 'balls', strongly incrusted by iron oxides and hydroxides. When this was dissolved with hydrochloric acid, the bacterium filaments or, more correctly, the empty sheaths, became clearly visible.

When inoculated in sterile tap water with a nail as iron source, a rather strong growth of the thread-forming bacteria can be obtained, which seems to be a *Leptothrix sp*. Thus, there may be a possibility that iron bacteria in one way or another play a part in the corrosion phenomena described above. These bacteria, which cannot corrode metallic iron, are, however, certainly not the direct cause of the corrosion; but, as was first shown by Winogradsky [2], primarily oxidize Fe^{+2} into Fe^{+3} (by means of oxygen dissolved in water), whereby they gain the energy necessary for the assimilation of carbon dioxide and the building up of the organic substances of the cells. This is a process analogous to that in which the green plants use the energy of the sunlight. Thus, iron bacteria are autotrophic organisms; but as they are still scantly explored, it is unknown whether others than *Gallionella* are obligate autotrophic.

In summary, the formation of energy can be expressed by the following equation:

$$2\ Fe^{+2} + (x + 2)\ H_2O + 1/2\ O_2 \rightarrow Fe_2O_3 \cdot xH_2O + 4\ H^+ + Q\ \text{cal}$$
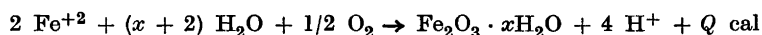
Ferrous ions are taken up in the bacterial cells where they are oxidized to ferric ions which are discharged and gradually hydrolyzed. Subsequently, they coagulate in the surrounding water and are precipitated as hydrated ferric hydroxide.

According to Beger [3], sheaths, without bacteria or with dead bacteria, are able to precipitate ferric hydroxide for a long time, only more slowly than the living bacteria.

In the literature, indications are found of the assumption that iron bacteria may play a part in corrosion. Most frequently, however, the injurious effect of iron bacteria in water pipes became obvious by the fact that their abundant growth made the water muddy (so-called 'red-water') and caused blockage of the narrow pipes (*e. g.* Schorler [4]). Brown [5] described such formations and showed a cross section of an old tubercle. It appears as if its central part consists of a dark core, which is largely iron sulphide, which is surrounded by some layers of a yellowish-red »iron-meal», containing numerous *Gallionella-*

filaments incrusted with ferric hydroxide, chalk, and manganese. The external layer is a mantle of iron hydroxide and chalk with a coating of living *Gallionella*.

Schorler[4] also found that the tubercles initially consist of a loose *Gallionella*-felt, which later disappears and is recrystallized in the form of hexagonal hematite-(Eisenglanz)-like crystals. These crystals grow together into shapeless aggregates, in which no iron bacteria can be distinguished. Ellis[6] mentions that iron bacteria, in water pipes, cause 'slimy streamers, tubercular incrustations', the formation of which is furthered by carbon dioxide, and 'iron incrustation on non-ferrugineous surfaces'. The other physiological and bacteriological theories of this author, which have been strongly critisized by Winogradsky[2], will not be further discussed here.

Hermann[7] observed very large incrustations of iron bacteria *(Gallionella)* in asphalt-coated pipes. In uncoated pipes or in pipes where the asphalt was damaged, deep corrosions (pitting) with superimposed tubercles were found. Inside the tubercle recrystallization to hematite (Eisenglanz) was seen to occur. Thresh, Beale and Suckling[8] state that 'they (iron bacteria) may play some part, probably a subordinate one, in the formation of tubercular incrustations in iron mains. This leads to interference with the flow of the water, and destruction of the pipes'.

Minder[9] reports that by immersing polished iron strips into wells, the growth of iron bacteria is initiated and that corrosion takes place under the crust. Similar phenomena were found to occur in the filter kettle of a closed iron-removing plant. On the wall above the sand were found lens-shaped, rust-coloured deposits, several cm in diameter and up to 1 cm thick. Under these deposits hollows in the iron wall appeared. After drying, the 'lenses' were light, almost like a dry sponge and consisted of a felt of iron bacteria.

Beger[3] assumes that *Gallionella ferruginea* is alone responsible for incrustation in pipes and is contributory to corrosion.

Other authors, however, have found that *Leptothrix ochracea* and *Crenothrix polyspora* also very frequently grow in water pipes.

Haase[1], who thoroughly dealt with these problems, stated that water causing corrosion (pitting) always contained a great deal of organic substances and iron bacteria.

Von Wolzogen Kühr[10] has shown in a very convincing way, that external corrosion of iron pipes buried in the soil may be due to sulfate-reducing bacteria. These are anaerobic and use oxygen from sulphates for oxidation of organic substances and, to a minor degree, also for oxidation of hydrogen for production of energy — at the same time forming hydrogen sulphide.

Starkey [11], furthermore, directs attention to the fact, that the presence of oxygen concentration cells in the soil should be considered. Thus, for instance, a pipe buried in a moist anaerobic area will prove to be anodic in relation to another piece of the same pipe in a well-aerated moist area, where the hydrogen produced is oxidized to water by the oxygen of the air. Iron is dissolved on the anode and is transformed into ferrous hydroxide, and, if sulfate reducing bacteria are present, also into iron sulphide.

We are, of course, here concerned with quite other conditions than those prevailing in water pipes with a more or less continuous current of airsaturated water, and the above mentioned papers on sulphate reducing bacteria have been mentioned only in order to show that corrosion may be due to biological causes.

Bunker [12] (and, also Butlin, Adams and Thomas [13]) assumes that the sulphate-reducing bacteria may be active under the anaerobic conditions under the tubercles, and he has isolated *Vibrio desulfuricans* from such places. It can hardly be doubted that the conditions for growth are favourable here, since there are organic substances from water and destroyed bacterial cells *, a small supply of sulphate-containing water, and rather anaerobic conditions.

A review of the literature thus has shown, that frequently tubercle formations, connected with pitting, occur similar to those cases discussed in the present paper. Iron bacteria were always found — most frequently *Gallionella ferruginea*, but also *Leptothrix ochracea* and others — as constituents of these tubercle formations. All authors agree about the necessity of a cautious statement of the part played by iron bacteria in connection with these phenomena (Knudsen [15], Reddick and Linderman [20], Thomas [21], Brown [22], O'Connel [23], Pillai, Rajagopalan and Subrahmanyan [24]).

The manuals available, dealing with metal corrosion, also pass lightly over this question; thus Kröhnke, Maas and Beck [16] (p. 88) write, that the growth of bacteria is found on the internal walls of water pipes, and at the bottom and on the sides of water reservoirs, partly as 'schlemige Streifen', and partly as 'Verkrustungen' or tubercles. By the activity of the iron bacteria, a danger of obstruction and corrosion arises. In the handbook on corrosion by Bauer, Kröhnke and Masing [17], no notice is taken of microorganisms in connection with corrosion; only the investigations of von Wolzogen Kühr on sulphate-reducing bacteria are mentioned.

Evans [18] states that iron bacteria, no doubt, often are connected with a rapid perforation of the material; their activity ceases at pH 8.2—8.6.

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* According to Butlin and Adams [14] sulphate-reducing bacteria can live under strictly autotrophic conditions.

Hadley [19] writes that the role of iron bacteria in corrosion is still obscure. Their most important contribution to corrosion probably results from the creation of a barrier capable of maintaining oxygen concentration gradients between metal and solution. 'Additional data are admittedly required to clarify the relationship which exists between the iron bacteria, the sulphate-reducing bacteria, and tuberculation.'

The authors believe that iron bacteria are of considerable, primary significance in the development of corrosion and the formation of tubercles. We now shall make an attempt to explain how this interpretation is in agreement with the facts.

MECHANISM OF CORROSION

It is generally assumed, that corrosion in water pipes (only internal corrosion of iron water pipes conducting well-aerated tap-water of normal hardness is discussed here) depends essentially on the existence of short circuited local cells, an assumption whose general validity can hardly be doubted. Differences of opinion only arise in the discussion of details of the mechanism. For a survey of these problems reference is made to the book by Evans [18], from which theories, which are in best agreement with experimental data have been taken. (Only the theory of bacteria playing an essential part seems to be new.)

It is of some importance to know the relative size and distribution of anodic and cathodic areas (anodic: places where the electric current passes from the metal to the liquid, cathodic: places where the current goes in the opposite direction). If cathodic and anodic areas are quite evenly distributed over the whole internal surface of the iron pipe, corrosion everywhere on the surface is possible with an even diminution of the thickness of the wall. This type of corrosion is due to heterogenic structure of the iron surface with evenly distributed non-iron impurities, and is not very dangerous on account of the very low rate of destruction. The mechanism of this type of corrosion is shown in Fig. 1. In the present case, however, it is known by experience, that supply pipes tend to rust locally ('pitting'). This means, of course, that the anodic areas, the places where metallic iron is dissolved according to the equation:

$$Fe \rightarrow Fe^{+2} + 2e \qquad (1)$$

are relatively small.

It can therefore be assumed either that some factors making the metal less noble (more negative) occur in isolated spots, and that the cathodic (nobler, less negative), areas are more extended (which, of course, means, that the current density is great at the anodic spots and small on the cathodic
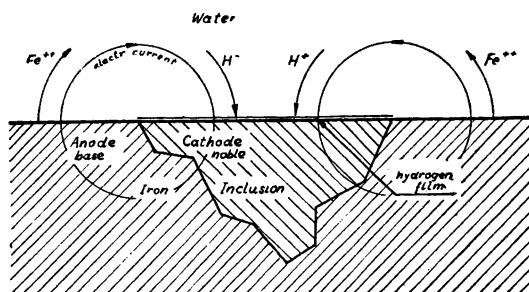
Fig. 1. Scheme of the corrosion in non-aerated water due to the activity of local electro-chemical cell.

areas); or that impurities making the metal nobler (more positive) occur over extended areas and that the more negative places occur in isolated spots.

The causes of the differences in electrochemical behaviour may be of various kinds; *e. g.* the well known passivating action of oxidizing agents, *i. a.* oxygen itself may very well play an important role. One might, for instance, imagine that almost the whole inner surface of the tube is passivated (made nobler) by oxygen, but that some spots, for one reason or another, remain active.

However, it is not necessary, at present, to dwell on these different possibilities and theoretical aspects. What is needed is 1) a mechanism which will initiate corrosion at certain spots and 2) a mechanism to make the conditions stationary and favourable to corrosion at the same spot for an extended period of time.

1. The start of the corrosion requires, of course, not only the occurrence of reaction (1) in one place, but also a reaction whereby electrons are used up. In view of the conductivity of the metal this reaction may take place anywhere on the surface and over extended areas. One possibility is the reduction of water:
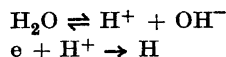
$$2e + 2H_2O \rightarrow H_2 + 2OH^- \tag{2a}$$

another the reduction of oxygen

$$2e + 1/2\ O_2 + H_2O \rightarrow 2OH^- \tag{2b}$$
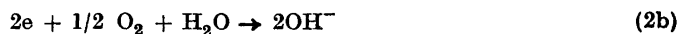
According to Evans both may occur, but it is obvious that (2b) is by far the most probable.

It is highly probable that they take place through intermediary stages, some of which are identical to both reactions. As such steps one might imagine:

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$e + H^+ \rightarrow H$$

and it must be assumed that the hydrogen atoms are adsorbed on the cathodic areas. From these areas they are removed either by association (formation of H_2) or by reaction with oxygen (formation of H_2O). This latter reaction probably also proceeds through intermediates (HO_2, H_2O_2) but, for the present purpose, it is not necessary to enter into details on this point.

Another point, however, seems rather important. The water contains not only oxygen, but also dissolved carbon dioxide, which must react with the hydroxyl ions according to the well-known scheme. Consequently, we get instead of (2b)
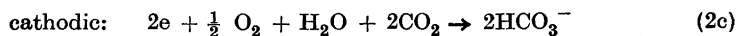
$$2e + 1/2\ O_2 + H_2O + 2CO_2 \rightarrow 2HCO_3^- \ldots \ldots \qquad (2c)$$

Obviously, the corrosion thus displaces the equilibrium

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$
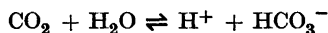
towards the right. This has the consequence that, if the water originally was saturated or nearly saturated with calcium carbonate, which very often is the case, the corrosion process will cause a supersaturation resulting in a tendency of the water to form scale.

Conclusions: At the start, anodic spots in cooperation with more extended cathodic areas will cause the occurrence of closed electric currents coupled with chemical reactions:

$$\text{anodic:} \quad Fe \rightarrow Fe^{+2} + 2e \qquad\qquad (1)$$

$$\text{cathodic:} \quad 2e + \tfrac{1}{2}\ O_2 + H_2O + 2CO_2 \rightarrow 2HCO_3^- \qquad (2c)$$

2) For the reaction to proceed it is necessary to protect the anodic (active) spot against the influence of passivating agents, e. g. oxygen. Now, especially if water in the pipe is stationary, this can easily be achieved. Quite apart from the electrochemical process described above the ferrous ions are easily oxidized to ferric ions or, in not too acid solution, to hydrated ferric oxide, the stoichiometrical equation being:

$$2Fe^{+2} + \tfrac{1}{2}\ O_2 + (x + 2)H_2O \rightarrow Fe_2O_3 \cdot xH_2O + 4H^+$$
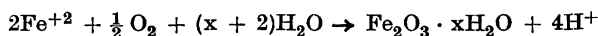
As the ferrous ions and the oxygen come from either side, a film of colloidal hydrated ferric oxide may be formed around the anodic spot. Inside this film
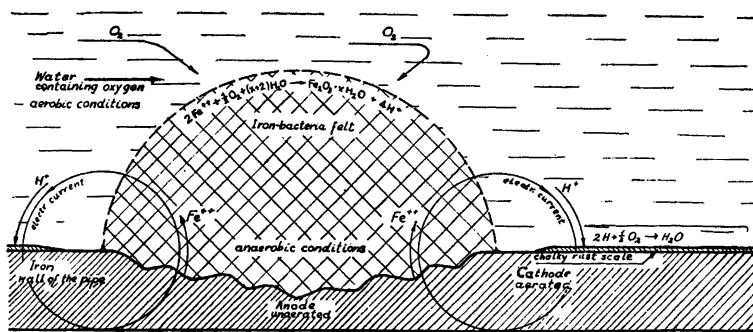
Fig. 2. Scheme of the corrosion in well-aerated, running water after the formation of a »tubercle» (from an iron bacteria »felt») on the internal surface of a water pipe.

the oxygen concentration will remain low on account of the continual flow of ferrous ions released from the active spot, which consumes the oxygen diffusing in from the outside. At the same time, the hydrogen ion concentration remains rather high and, in case such a film can be formed and remain undisturbed, the conditions will be highly favourable for the process to continue. Concerning the cathodic process whose occurrence, of course, is just as necessary as the anodic one, there seems to be no great probability of its inhibition. The surface of the cathodic areas must be expected to be rather easily accessible for dissolved oxygen which, thus, without difficulty can exert its depolarizing influence (removal of hydrogen atoms).

Remembering the low density of the cathodic current, one would expect that only a hard, tight scale with excessively low electric conductivity and high resistance against diffusion might have some effect.

It thus seems possible that a purely inorganic mechanism may be operative, but, if the conditions prevailing around the anodic (active) spots are considered, it soon becomes clear that they are ideal for the growth of certain bacteria and that, on the other hand, a colony of these bacteria will be ideal for maintaining the conditions of corrosion at that spot.

THE THEORY OF THE AEROBIC BACTERIOLOGICAL CORROSION

The types of corrosion described in the introduction to this paper are, no doubt, caused by electrochemical processes. The iron surface is divided into two systems, within and without the tubercles. The water of the supply pipes in question contained about 8 mg/liter of oxygen. The non-tubercle areas are violently washed by this water and consequently aerated. Under the tuber-

cles, however, there is a very slow percolation of the water and consequently weak aeration. Thereby, a short-circuited electric cell is created (fig. 2), in which the aerated parts have a higher potential (more positive) and thereby take over the function of the cathode, while the iron surface under the tubercles has a lower (baser) potential and acts as an anode. Iron goes into solution at the anode ($Fe \rightarrow Fe^{+2} + 2e$), and at the cathode hydrogen is evolved in atomic or molecular form ($H^+ + e \rightarrow H$), and is oxidized by the oxygen contained in the water. At the cathode there is a continuos consumption of hydrogen-ions, and the consequent surplus of hydroxide-ions causes a ,wall alkalinity' which, however, is limited by the current of water flowing through the pipe. The ferrous-ions going into solution at the anode are immediately hydrolized

$$Fe^{+2} + HOH \rightleftharpoons Fe(OH)^+ + H^+$$
$$Fe(OH)^+ + HOH \rightleftharpoons Fe(OH)_2 + H^+$$
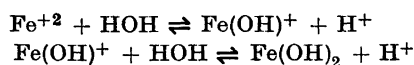
which depends upon the pH in the solution. Ferric-ions, formed by oxidation of ferrous-ions, are also hydrolyzed and to a much higher degree than ferrous-ions (the hydrating of the ions is not considered here). By the hydrolysis, hydroxyl-ions are consumed and the surplus of hydrogen-ions causes an acid reaction, which, as mentioned before, has been ascertained in the tubercles. This acid reaction in itself accelerates corrosion, as: (i) it causes greater electrical conductivity and (ii) renders difficult the formation of carbonate-containing, protective scale of »chalky rust» on the surface of the tubercle so that no increase of the electrical resistance takes place. The resistance of the cathodically formed protective scale has no very great effect because of the large surface of the cathode and the consequently low density of current in comparison with the small corroding anodic surface under the tubercles.

The whole of this phenomenon, however, depends upon the formation of a membrane which renders difficult the percolation of water, and the diffusion of oxygen but without much resistance to the transference of ions. This membrane may also appear in connection with purely inorganic colloidal precipitations of hydrated ferric oxides where the admission of oxygen is rendered difficult by the fact that the diffusing oxygen is consumed by oxidation of ferrous-ions to ferric-ions. The colloidal hydrated ferric oxide, however, is of a granular structure and is mechanically of small resistance. Consequently, it is not always probable that in pipes with running water such membranes could be formed in a purely inorganic way without any other factors. In this connection the iron bacteria should first be considered, as filaments of iron bacteria are always found in tubercles, which is known partly from the literature partly from the authors' investigations of tubercle-forma-

tion. It should be imagined that the iron bacteria settle on the iron surface, chiefly, perhaps, on rough spots (tubercle-formations thus are often found on the welded seam). The bacteria then start multiplying and, as mentioned before, gain energy by oxidation of ferrous- into ferric-ions. Thereby the concentration of oxygen in the immediate vicinity decreases and a local micro-electrochemical cell is formed. On the areas deficient in oxygen, *i. e.* where the bacteria colonies are to be found, ferrous-ions go into solution. This favours the growth of the bacteria.

The iron bacteria will find the best conditions of life in neutral or slightly acid water containing ferrous-ions, oxygen, some free carbon dioxide, and ammonium salts or nitrates. Pipes corrosion shows all the above conditions — on the anodic surface iron is electrochemically dissolved as ferrous-ions, and by their hydrolysis the slight acid reaction appears. Simultaneously free carbon dioxide is formed from carbonates according to the reaction:

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

Thereby all conditions for the development of bacteria (even good conditions of temperature and absence of light) are present, and the bacteria contribute to the corrosion in three essential ways:

1. Primary formation of micro-differential-aeration cells due to a change in concentration of oxygen in the infected place. This cell may develop further either in a bacteriological way or, perhaps, in a purely inorganic chemical way.

2. Mechanical strengthening of tubercle owing to the 'felt structure' of iron bacteria filaments.

3. Catalytic ferrous-ion oxidation and, consequently, rapid precipitation of hydrated ferric oxide, which further strengthens the anaerobic conditions on the anodic side and, hence, increases the difference of potential between the iron surface under and outside the tubercle, whereby corrosion is increased.

It follows from the theory stated here that all microorganisms which are able to grow under these conditions, to consume oxygen, and form compact colonies, can develop or increase corrosion. As already stated iron-bacteria particularly will find favourable conditions of life in new water pipes and consequently become predominant.

An electrochemical and bacteriological investigation of the consequences of the theory is reported in a following paper.

SUMMARY

In the present paper a description is given of a type of corrosion in water pipes. The corrosion is accompanied by the formation of 'tubercles' consisting

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mainly of hydrated iron oxides and iron bacteria felt which lie over the pittings. The electrochemical nature of this corrosion is discussed and a theory advanced according to which microorganisms, especially iron bacteria, accelerate these processes.

It is proposed that

1. through their growth on limited regions of the iron surface the iron bacteria primarily form 'differential aeration cells'. These give rise to a difference of potential and consequently to a corrosion current between the site of the bacterial colony and the surrounding surface of the iron.

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

3. with increasing thickness of the tubercle the conditions inside the tubercle will be more anaerobic. This increases the difference of potential between the iron surface under and outside the tubercle, and the corrosion is thereby increased, with or without the collaboration of the bacteria.

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