Formation mechanism of iron tubercles during corrosion of water supply pipes

V.A. Chukhin[®]* and A.P. Andrianov[®]

Moscow State University of Civil Engineering (National Research University), Yaroslavskoe shosse 26, 129337 Moscow, Russian Federation *E-mail: <u>sigma85@yandex.ru</u>

Abstract

The literature data and own results of the study of corrosion mechanism and tubercle structures formation in steel and cast iron pipes are analyzed. Several possible ways for the nucleation and growth of tubercles are considered: local accumulation of corrosion products and the formation of a hemispherical membrane when the solubility limit of iron oxides is exceeded, the effect of redox processes on corrosion products under oxygen deficiency, and the participation of a template formed by hydrogen bubbles in the formation of tubular structures that subsequently form tubercles. It is shown that all mechanisms of tuberculation growth can take place in pipelines of water supply systems depending on the conditions (including hydrodynamic). At the initial stage the tuberculation corrosion proceeds with oxygen depolarization, and then, as denser layers of corrosion deposits are formed, the process begins to proceed with hydrogen depolarization. Long-term observation of the corrosion process of steel pipe in hot water showed the influence of the release of hydrogen gas on the growth of elongated tubercles and the validity of the third version of growth mechanism by analogy with ferrotubes. It is emphasized that hydrodynamic conditions along with the composition of water and the intensity of the initial stage affect the type of the formed tubercles (with or without liquid) and their integrity. Formation of large loose tubercles filled with liquid contributes to autocatalytic corrosion process inside the pitting with the appearance of through fistulas.

Received: May 13, 2022. Published: June 10, 2022

doi: 10.17675/2305-6894-2022-11-2-24

Keywords: pitting corrosion, corrosion tubercle formation, carbon steel, water supply systems.

1. Introduction

Corrosion of steel and cast iron pipes in water supply systems proceeds, as a rule, with the formation of a scale (or sediment) in the form of individual or alternating tubercles. Tubercles, in turn, are most often the tops of pits – at best, they are small and wide, causing slow degradation of the pipeline, at worst, they are deep and narrow, causing through holes (fistulas) in the pipe wall [1]. Examples of tubercles that were formed in different cold and hot water supply systems are shown in Figure 1.





b)



Figure 1. Examples of corrosion deposits formed on the inner surface of pipes: a - steel main water conduit DN900; b - fire sprinkler water supply [2]; c - galvanized pipe DN100, hot water supply system; d - galvanized steel pipe in a dry pipe system DN100 [3].

The presence of tubercles on pipe surface causes an increase in hydraulic resistance, worsens the quality of drinking water, and the presence of pits under the tubercles leads to abnormally rapid corrosion of even galvanized pipes and the appearance of fistulas [4, 5].

The structure and composition of tubercles have been studied quite well [6-12]; as for the mechanism of tubercle formation and growth, final conclusions have not yet been made. In the absence of precise information about the mechanism of tubercle growth, it is impossible to choose a strategy of counteraction.

The purpose of this article is to understand the nature of the formation of tubercle deposits at an early and later stages, to identify the factors that affect this process and its rate.

2. Structure and composition of tubercles

Herro [8], studying iron corrosion products formed in cooling water systems, defined tubercles as structurally complex corrosion cells in which accumulations of metal oxides, deposits and corrosion products cover local areas of metal loss. He pointed out that tubercles grow as a result of both internal (anodic, under the tubercle) and external (cathodic, outside the tubercle) reactions, *i.e.*, anodic dissolution of metal leads to accumulation of iron (II) and iron (III) ions, while cathodic reactions outside the tubercle cause pH increase and deposition

of corrosion products and other elements contained in water, whose solubility decreases with increasing pH.

The tubercles, according to various literature data, consist of four or five structural elements. Many authors have described the internal morphology and presented schemes of tubercles. Herro [8] concludes that tubercles have the following structural features: an outer shell, an inner dense layer providing structural integrity of the sediment, a core - a cavity filled with liquid, and a corroding base. Sarin *et al.* [9, 11, 12] indicate the presence of a surface layer, shell and porous core over the corroding metal. A significant difference between the models of Herro [8] is the absence of a liquid-filled cavity in the model of Sarin [12]. Gerke *et al.* [6] investigated the morphology, mineralogy and chemical composition of five tubercles from 90-year-old cast-iron pipes removed from the water supply system at one of the facilities in the USA. The general morphology of all five samples was the same: a core with a hard shell covered by surface material. Magnetite, lepidocrocite, and goethite are the three predominant iron minerals in all five tubercles, but in different proportions.

The schemes proposed by Herro [8] and Gerke [6] are similar in the following details: a shell of magnetite covered with a reddish-brown crust, and a core. The liquid-filled cavity between the core and the corroding base described by Herro [8] was not observed in the tubercles in Gerke's work [6]. Gerke *et al.* [6] indicate a core of goethite or lepidocroquite, while Herro [8] indicates a core of iron hydroxide, siderite (iron carbonate), and phosphate. In Gerke's model the knoll core enters the depression and is an exact copy of the profile of the inner part of the depression formed on the surface of the metal.

The authors of this article, when studying tubercles in pipes that have been in operation for a long time, came to the conclusion that the lower part of the core adjacent to the metal can be considered as its base (bottom), since the composition and morphology of the base and core differ significantly [13, 14]. The core contains a mixture of amorphous and crystalline iron oxides, while the bottom layer consists almost entirely of iron corrosion products with impurities contained in steel (carbon, manganese, and sulfur). This layer is characterized by a more homogeneous and dense crystalline structure. The absence of elements characteristic of the surface layer indicates that this layer is formed in the absence of contact with water flowing through the pipe. In our model, the base is an exact copy of the depression on the metal surface. In addition, we did not detect cavities in all tubercles that could be filled with water.

In a number of works, the authors give values of tubercle sizes and their growth rate. For example, in [7], when studying corrosion, it was found that the maximum size of the tubercle after 3 years was 6×10 cm. It was also noted that the growth of the tubercles included the possibility of their merging, as indicated by several major areas formed during the observation period. In comparison, tubercles from a 90-year-old cast-iron pipeline were approximately 4-6 cm in diameter and 2-3 cm high [6]. It is noted that the depth of pitting and the height of the tubercle above the metal surface, as a rule, are not connected with each other.

It should be noted that under certain conditions, a layer of corrosion deposits can work as a protective layer, preserving the metal from further rapid destruction and transferring the corrosion process to a sluggish one [15].

3. Tubercle formation

Menzies [16] described the formation of abiotic tubercles at breaks or discontinuities in an oxide film exposed to an oxygen-saturated environment as follows: "Anodic dissolution takes place and as metal ions concentrate in the solution the solubility product of the solid hydroxide is exceeded locally and hydroxide precipitates out as a hemispherical membrane which surrounds and covers the original discontinuity. This result in effective screening of the anodic area from available oxygen and the metal at the discontinuity remains anodic".

The very first stage of tubercle formation is the destruction of the passive layer and the initiation of pitting. This an important stage that is well described in [1, 17-19], but, as we believe, it is not critical for the further fate of the pipeline. Numerous inspections of water supply systems pipelines have shown that eventually their entire surface (for external and internal systems) or part of the surface (for internal systems) is covered with lumpy deposits. And here at the forefront is the question of what will happen to these micropitting further, how quickly they will develop and what factors will affect the speed of this process.

Here it should be mentioned that the possibility of nucleation and further existence and development of pitting is described by a certain characteristic potential of the passive metal, *i.e.*, pitting potential (E_p) [17, 18]. E_p is the lowest voltage or potential at which pittings form or grow on the metal surface. The main manifestation of the pitting condition is a shift of the electrochemical potential towards more positive than some critical value, considered as a pitting potential. The value of the pitting potential (E_p) is also affected by the concentration of chlorides, carbonates and bicarbonates in the water [20].

There are three main stages in pitting corrosion: destruction of the passive layer, metastable pitting and stationary pitting [1]. The nucleation stage of pitting occurs within a very short period of time (microseconds). Parameters that contribute to the primary occurrence of pitting include [19]: local damage to the protective oxide film; aggressive water parameters that can contribute to the destruction of the film (low pH, high chloride concentration and low dissolved oxygen concentration); improper zinc coating application or its damage; presence of nonmetallic inclusions in the metal.

Aggressive media that promote active pitting are well known, such as seawater or desalinated water, as well as water with high chloride content [1]. It is easy to predict rapid metal corrosion for such media, but it is much more difficult to predict for "ordinary" water composition, because a number of other factors come into play [21]. Pitting corrosion in stainless steel is influenced both by the absolute concentration of chlorides and hydrocarbonates and by the ratio of sulfate and chloride concentrations, where the sulfate act as corrosion inhibitor [21].

The occurrence of pitting is also affected by temperature, which becomes especially important when studying corrosion in hot water supply systems. The concept of critical pitting temperature (CPT) was introduced by Brigham and Toze1 – it is the temperature below which metastable pittings cannot exist under given conditions [22]. When the critical temperature is exceeded, the passive oxide layer is destroyed and stable pittings begin to form. For example, for stainless steel 904L CPT is 48–49°C, and it depends little on the chloride content [22] and even on the pH of the medium [23]. In [24] it is shown that the CPT technique is also suitable for assessing the corrosion of carbon steels.

4. The mechanism of tubercle growth

In the paper [11] Sarin with coauthors consider two possible variants of corrosion process development. In doing so, they note that the initial stage of corrosion scale formation involves only the initiation of a precipitate on a clean metal pipe surface, and the formed precipitation lacks any structural features, such as a porous core and a dense layer. During this phase, the oxidizing agents present in the water can reach the metal-water interface and cause corrosion. Corrosion of the pipe metal is a major source of iron for scale formation and growth. Dissolved oxygen and H^+ ions are possible oxidizing agents for iron corrosion. In the presence of dissolved oxygen (corrosion with oxygen depolarization), the resulting iron (II) ions are oxidized and hydrolyzed to form various iron (hydr)oxide phases such as lepidocrocite, goethite, Fe(OH)₃, ferrihydrite, magnetite and maghemite.

As the thickness of the scale increases, it becomes increasingly difficult for the oxidant to diffuse to the metal-water interface. At this stage, various structural features of corrosive deposits begin to form. The deposits formed on the surface are not homogeneous, and therefore oxidants penetrate into some areas at the metal-water interface. This causes the formation of concentration oxidation cells that contribute to a localized attack on bulk iron. Under these conditions, metallic iron is dissolved at the anode sites beneath the thicker deposits, while electrons are discharged at the adjacent oxidant-rich cathode sites. Localized corrosion results in larger deposits above the anode and the formation of tubercles. The thickness of the shell-like dense layer corresponds to the depth of oxidizer penetration into deposits. Within the sediment, a slower rate of Fe (II) oxidation is predicted, and the formation of goethite, magnetite and green-rust phases is possible. A shell-like dense layer, which is a mixture of goethite and magnetite, is expected to form under these conditions, thereby creating a complete tubercle structure. As the tubercles grow, they cover more and more surface areas and may eventually merge with other tubercles, covering the entire pipe surface (Figure 1).

If oxidizing agents such as dissolved oxygen or chlorine are present in the water and contact with the surface of the corrosion sludge and the water inside the core of the tubercle is acidic, there is a second possible way for the cathodic corrosion half-cell to develop. The H^+ ions in the water in contact with the metal surface can accept electrons and form H_2 (gas) within the deposit near the water-metal interface (corrosion with hydrogen depolarization). The fraction of the corrosion reaction that follows this pathway will depend on the presence of H^+ ions within the tubercle and the potential of the resulting hydrogen gas escaping [11].

Since the main structure-forming element of tubercles is a dense layer, apparently, its formation is associated with transformation process of primary corrosion products [25]. The transformation of goethite and lepidocrocite into magnetite occurs when the oxygen content in water decreases to values less than 1 mg/l. Another condition for tubercle growth is the violation of the continuity of the primary oxide film on the metal surface due to chemical or mechanical effects; as a result, a deoxygenated water containing salts enters the metal surface, which leads to the development of corrosion with hydrogen depolarization.

Conclusions, made in [11] about two different mechanisms of deposit formation and tubercles nucleation can be illustrated by photos of a fragment of carbon steel pipe made of St.3 (analogues – 1.0114, Fe37-xx, S235) (Figure 2). Microphotographs were obtained by the authors using SEM Quanta 250FEI in the course of corrosion research of steel water supply pipes in the laboratory of Water supply and wastewater disposal department. The pipe sample was kept in a tank with cold tap water for 90 days. The water in the tank was periodically refreshed. A solid layer of sediment was formed on the inner pipe surface as a result of corrosion. There were several round holes in the form of craters (Figure 2a), going deep under the layer of sediment. Figure 2b shows the surface of this sample after removal of the sludge.



Figure 2. Examples of corrosion sludge layer formation during corrosion with predominantly oxygen depolarization: a - surface of corrosion sediment; b - metal surface after removal of loose sediment layer.

The micrograph shows that there was uniform corrosion on most of the surface, and at one point there is a deepening in the form of pitting. The corrosion of the sample occurred with an increase in total weight, which is characteristic of experiments carried out under static conditions. The sediment on the sample surface is loose and permeable to oxygen, so under the layer of sediment the formation of tubercles is possible due to local oversaturation of corrosion products over the section of pipe surface. The average corrosion rate determined by metal loss was $0.118 \text{ g/m}^2 \cdot \text{h}$. However, the same fragment has deep surface damage, indicating that the corrosion process proceeded at a high rate in the pitting, which is more typical for corrosion with hydrogen depolarization. In [26], devoted to the study of pitting corrosion, it was shown that in cold water the formation of a dense layer starts above the anode with gradual overlapping of its entire surface. At the same time, the anode zone of metal destruction is constantly moving, as evidenced by the many overlapping hemispherical depressions on the steel surface. The displacement of anodic and cathodic areas, *i.e.* their repassivation, ends when the dense layer is finally fixed on the metal surface due to electrostatic forces. In the experiment conducted, the formation of tubercles began after 56 days.

Similar conclusions can be found in [11], which emphasizes that the formation of tubercles is associated mainly with local corrosion and occurs above the anode zones. The most likely reason for the appearance of individual deep holes on the metal surface under the precipitate, in our opinion, can be heterogeneity in the metal composition, which is also noted in a number of works. In [27] the role of inclusions in the initiation of corrosion pitting on the surface of high-strength pipeline steel in NaCl solution was investigated. It was found that inclusions with a typical composition of Al–Mg–Ca–S–O, which, as a rule, have a spherical shape, cause the formation of circular pittings. In [28], sulfide inclusions were found to be the most corrosive. This was also confirmed in [29], where 3 characteristic types of inclusions containing both oxides (Al, Ca)O and sulfides (Mn, Ca)S were considered.

The presence of metals with electrochemical potential more negative than iron in the structure of the surface layer leads to the appearance of local electrochemical cells in which the cathode is iron, and the anode is inclusions that enter the metal during the manufacture of pipes. In the studied samples such inclusions usually were manganese (E=-1.185 V) and aluminum (E=-1.7 V). The presence of an anode in the center of the corrosion cell leads to a decrease in pH and triggers the mechanism of pitting. Figure 3 shows microphotographs of indicator samples of pipes made of St.3, exposed to short-term contact with tap water.

At low water velocity, as well as in static conditions, corrosion appears to proceed uniformly on most of the sample surface (Figures 3a and 3b). However, after gentle removal of sediment it is possible to see a large number of depressions randomly scattered on the surface (Figure 3c); as a rule, there are round and having diameter up to 50 microns. In the depression center in some cases lighter spots are observed, which at the further study by means of SEM and energy dispersive spectroscopy, were identified as manganese or aluminum inclusions (Figure 3c and 3d). Thus, it can be assumed that the depressions on the metal surface shown in Figure 2 were also formed as a result of local corrosion in the presence of metal inclusions more negative than iron. In this case, the high corrosion rate leads to rapid formation of tubercles, as shown in Figure 1b and 1d.

Figure 4 shows microphotographs that demonstrate the nucleation of tubercles on a polished cast iron surface [25]. At pH = 5.9, the deposits initially consisted of a set of nodules oriented in the direction of water flow (Figure 4a). The shape of the tubercle in the form of a crater may indicate that corrosion proceeds with hydrogen depolarization and with the formation of hydrogen bubbles forming their structure.











Element	С	Ν	Ο	Mg	Al	Si	Р	S
Wt,%	12.13	0.8	15.42	0.1	23.97	0.14	0.05	0.06
At < %	26.49	1.49	25.28	0.11	23.30	0.13	0.04	0.05
Element	Cl	К	Ca	Mn	Fe	Cu	Zn	
Wt,%	0.07	0.08	4.62	0.48	41.75	0.19	0.16	
At < %	0.05	0.05	3.02	0.23	19.61	0.08	0.07	



Figure 3. Microphotographs of corrosion indicators (a, b) with surface inclusions of aluminum (3c) in the experiment with hot water and manganese (3d) in the experiment with cold water.



Figure 4. Sequence of scanning electron micrographs showing the effects of deoxygenation upon the structure of scale formed on cast iron at 50°C and pH = 6. a, b – after oxygenation at 18.00 ppm O₂ showing γ -FeOOH overlying Fe₃O₄; d, e – after deoxygenation to <0.03 ppm O₂ showing substantial removal of γ -FeOOH [25].

The experiments described in [25] demonstrated that the cathodic reduction of γ -FeOOH to Fe₃O₄ takes place when the corrosive deposits are in contact with deoxygenated water. The reaction can occur: (1) when the O₂ concentration is reduced to <~1.0 ppm and γ -FeOOH is significantly removed from the sediment and (2) in oxygenated water, when γ -FeOOH continuously forms on the outer surface of the sediment and is then cathodically reduced to Fe₃O₄ which eventually becomes the predominant phase of the precipitate.

From the analysis of the mechanism of transformation of iron forms depending on the oxygen content in water, noted in [25], it can be concluded that tubercles can grow while maintaining a constant thickness of a dense layer, due to dissolution from the inside with a lack of oxygen, and growth with external with its excess.

Loto [30] made an important observation about the nature of pitting growth, as it seems to us. He notes that the corrosion process inside the pitting is self-sustaining due to the constant migration of chloride ions to maintain electrical neutrality and hydrolysis of corrosion products inside the pitting. The chloride ions cause acidification and hence prevent repassivation. This mechanism is autocatalytic because increased acidity accelerates the rate of metal dissolution in the pittings [30].

Another approach to describing the mechanism of tubercle formation and growth is given in [6]. Gerke et al. [6], based on the analysis of Stone's and Goldstein's research results [31], made the assumption that tubercles grow on the cathode of the electrochemical cell. The authors suggested that "if, with further investigations, it can be proven that tubercle formation does occur at the cathodic site of the electrochemical cell, it will significantly add to our understanding of tubercle formation and growth". In their work, Stone and Goldstein [31] studied the effect of patterns on the formation of tubular structures formed electrochemically in iron sulfate and ammonium sulfate solutions. The authors describe the self-organized process of tubular structures growth as a result of the template action of gas bubbles (Figure 5). Bubbles formed at the cathode of the electrochemical cell move the film formed at the gas-solution interface; bubble detachment leaves a ring of material that elongates the tube, and the process continues. The bubbles form and collapse at intervals of one to several seconds and the "ferrotubes" grow to millimeters in tens or hundreds of minutes. The patterning of the bubbles and the redox gradient results in a regular tubular shape. In addition, it was found that the iron oxides/hydroxides in the tube wall are arranged in an oxidation sequence (Figure 6).

The tube radius decreases with decreasing current (Figure 5b), so at very low currents, when the gas bubble hang time increases to hundreds of seconds, the tubes are closed because the sediment film is so dense and thick that it can withstand the bubble pressure.



Figure 5. Tube morphologies. A – columnar precipitation around injected jets of aqua ammonia; B – tube diameter varying as current is transiently decreased (narrow region) then increased and held at a higher level (wider upper half of tube); D – bent tubes grown over small magnets. (Scale bars, 5 mm.) [31].



Figure 6. Mechanisms involved in tubular precipitation templated by bubbles [31].

The model of ferrotube growth shown in Figure 6 assumes five main sequential stages, starting at the base of the tube and moving up [31].

- 1. Water and H⁺ ions are reduced at the cathode surface, producing hydroxide ions and hydrogen gas, and ammonium ions are deprotonated to produce ammonia gas.
- 2. The mixed gases move up through the tube as individual bubbles and acts as a pump, pushing the alkaline solution out of the open top.
- 3. When the bubbles remain at the tube opening, the alkaline solution and ammonia react with the bulk, acidic, ferrous solution. The green rust precipitates around the rim and over the surface of the bubble as a thin film.
- 4. The bubble detaches, leaving a ring of deposited material around the rim.
- 5. The green rust quickly turns into magnetite inside the tube and oxidizes to lepidocrocite on the outside.

The authors compare the obtained ferrotubes with the corrosion tubercles described by McEnaney and Smith [25]. The hollow corrosion tubercles shown in Figure 4 formed on ferrous metals show a three-layer structure: oxidized iron in form of lepidocrocite on the outside, reduced iron such as green rust inside and magnetite sandwiched between them [25].



a)

b)



c)







h) i) Figure 7. The formation of ferrotube-like tubercle during corrosion of a galvanized pipe in a hot water supply system (a-c, f, g); structural elements of tubercles (d, e, h, i).

The tubercles shown in Figure 7 can serve as an illustration of possible occurrence of ferrotube-like structures in steel pipes. The tubercles shown in Figure 7, were found by the authors of this article when studying the corrosion of steel galvanized pipes in a hot water supply system. The diameter of the pipe was 15 mm, and the time spent in the HWS system was 224 days. The water temperature was 50°C, flow velocity was 6 cm/s. In the course of the experiment, the composition of sediment formed on the pipe walls during operation was studied and the degree of zinc coating damage was determined.

The tubercle shown in Figure 7a has a diameter of 1.5 to 2.0 mm and a height of 4 mm. The growth rate of the tubercle is 5.3 mm/year. However, in contrast to the ferrotube schematically shown in Figure 6, the core of the tubercle consists of loose amorphous sediment.

Figure 7c and 7d show two tubercles formed under similar conditions in the experiment described above. In Figure 7d after removing the top of the tubercle, one can see a thin dense layer and a loose core. For the tube samples shown in Figure 7, the structure and composition of the sediment was analyzed on a Quanta 250 FEI electron microscope. Lepidocrocite predominates in the upper part of the tubercle and Fe₃O₄ – in the bottom. A microphotograph of a depression on the metal surface under a large tubercle is shown in Figure 7e. Micrographs of a number of similar tubercles from the same experiment are shown in Figure 7f, g – in their shape they are most similar to the ferrotubes shown in Figure 5.

Important note: under the ferrotube, which grows according to the model described in [31], in theory, there can be no pitting, since the metal dissolves at the anode. There are always depressions in the metal under the tubercles, and the very structure of the tubercle, in particular, the presence of the bottom layer, confirms that the destruction of the metal occurs under the tubercle. However, this model can be fully adapted to the case of ordinary corrosion: the source of hydrogen gas is pitting corrosion with hydrogen depolarization, which occurs at the second stage, when the pitting begins to overlap with a dense layer and the access of oxygen to it is hindered. The resulting hydrogen bubbles partially destroy the dense layer, carry out part of the liquid with iron compounds, and form walls of precipitated iron oxides at the points of their exit from the tubercle. In Figure 7h and 7i one can see the supposed place of gas release at the top of the tubercle. At the same time, in contrast to the classical ferrotube (Figure 5), there can be several gas outlet points on one tubercle. Obviously, further observations and verification of this theory under water supply system conditions are needed.

As a possible variation of the described mechanism of tubercle formation, we can mention the growth of a single macrobubble covered with a film of iron (hydro)oxides. Such tubercles can be seen in Figure 1b and 1d, they look like frozen bubbles, with a thin shell and almost empty inside. It can be assumed that the released hydrogen accumulated in a macrobubble with a film of corrosion products gradually formed on its surface; and this film gradually hardened over time. Such a growth mechanism is favored by the absence of water flow (plus oxygen deficiency conditions as a consequence) typical for fire suppression systems. Also, the resulting gases can lift part of the upper layer of sediments without the breakthrough of gases to the outside – like a "bubble inflation". We sometimes found similar completely hollow tubercles in pipelines when examining hot water supply systems.

In conclusion, another possible corrosion mechanism in pipelines should be mentioned is microbiological corrosion caused by iron bacteria [32]. Thus, in [2] it was found that the reason of abnormally rapid pipe corrosion was bacteria secreting acids as metabolic products, aggressive to carbon steels of pipelines of water supply systems. We also sporadically found traces of iron bacteria inside the tubercles. However, biologically induced corrosion is not considered within the scope of this article.

5. Discussion of results

Work [11] formulates the conditions under which metal corrosion can develop. The corrosion cell or area where corrosion occurs has four main components: (1) the anode, the place where metal oxidation and dissolution occurs; (2) the electrolyte solution in which the oxidized metal ion dissolves and which provides the ion transfer between the anode and cathode to maintain electrical neutrality; (3) the cathode, the place of the reduction reaction; and (4) the path for electronic conduction between the anode and cathode. If any of these components are missing, corrosion is not possible. The anode and cathode may be located in close physical proximity to each other or may be located at distant locations, provided conditions (2) and (4) are met.

Of the four components listed, the electrolyte solution has variable properties that depend on many external factors. As the precipitate layer builds up, the electrolyte that penetrates into the lower layers is freed from oxygen and alkaline anions and becomes more acidic. The appearance of a local oxygen gradient causes the formation of a dense layer at the metal-sediment interface. The location of the dense layer along the contour coincides with the location of the anode. As the tubercle grows, the corrosion process within it becomes increasingly independent of the oxygen content outside the tubercle. A solution without oxygen and saturated with chlorides and sulfates enters the depression formed by the fully dissolved inclusion. The iron released at the anode is hydrolyzed to form hydrogen ions (it is assumed that the pH decreases to values less than 3), which, in turn, participate in the reaction at the cathode and form hydrogen gas.

The presence of a loose core in the tubercles (Figure 7d) indicates that the formation of the tubercles differs from the pattern shown in Figure 6. Apparently, there are many microgalvanic cells on the metal surface (Figure 7e), including all four components. Microgalvanic cells generate microbubbles of hydrogen, which unite in the upper part and in the boundaries of the dense layer form a tubercle as shown in Figure 7a, 7c and 7f. The decrease in diameter of the tubercles in the upper part is associated, in our opinion, with difficulties in the inflow of external solution to the corrosion site and, consequently, an increase in electrical resistance. Thus, the limiting stage of the corrosion process is the inflow of the solution to the metal surface. In this case, if there is a lot of electrolyte inside the tubercle, the process ends with the appearance of through pitting. Otherwise, the corrosion process slows down or stops completely.

If the water temperature or water velocity had changed dramatically in this experiment, the tubercles could have collapsed and the corrosion process with hydrogen depolarization would have stopped. In our experiment, the velocity of water flow was quite low – much lower than the typical velocities in indoor water supply systems. Such hydrodynamic conditions contributed to the formation of elongated tubercles and the preservation of their integrity. It is quite possible that for those systems where hydrodynamic parameters change frequently and significantly, the pipeline service life appears to be longer.

As the electrical resistance increases, the corrosion current decreases, the corrosion process slows down, which leads to the overlap of the tubercle. If some water remains in contact with the metal, corrosion does not stop, and the released hydrogen eventually finds an outlet where the strength of the dense layer is minimal. The flow of the solution flows out and the scale layer builds up on the surface of the previously formed tuberlce. Thus, the next dense layer (shell) and core are formed, and the old tubercle ends up inside the new one.

The observations cited at the beginning of the article indicate two structural features of tubercles – in the presence of internal liquid and without liquid. Most likely, there are two different mechanisms for corrosion processes development. The first mechanism is characterized by slow growth, leading to the formation of dense tubercles that slow corrosion, and the second, in contrast, leads to accelerated pitting corrosion and the formation of large, loose tubercles filled with liquid inside.

Understanding how tubercles form and grow makes it possible to identify any ways to influence their growth and prevent the negative effects associated with pipeline failure and water quality degradation. The tubercles shown in Figure 7 were formed under conditions of maintaining a constant flow rate and temperature of hot water for a long time, so the growth of tubercles proceeded uniformly, and if the experiment was continued, it would lead to the appearance of through pitting. Our accumulated experience of examination of various pipelines shows that prolonged operation with constant parameters to a greater extent contributes to accelerated corrosion. Figure 1a shows a steel main water pipeline with uniformly distributed tubercles around the perimeter, which has been in operation for 43 years. The most suitable explanations for prolonged operation could be seasonal variations in water quality, fluctuations in daily water consumption, and, most likely, changes in temperature during the summer and winter months.

6. Conclusions

Studies of the morphology of tubercle corrosion deposits show that they have the following structural elements: a dense shell, which provides structural integrity of the deposit, the surface layer, the core and the base.

Three possible mechanisms of nucleation and growth of tubercles have been considered: local accumulation of corrosion products and formation of a hemispherical membrane when the solubility limit of iron oxides is exceeded, the impact of redox processes on corrosion products under oxygen deficiency, the participation of a template formed by hydrogen bubbles in the formation of tubular structures that subsequently form tubercles. Based on a literature review, our own laboratory researches and the study of samples from existing water supply systems, the most plausible mechanism can be described as follows.

The initiation of pitting and the possibility of intense pitting corrosion are influenced by such parameters as pitting potential (E_p), chemical composition of water and temperature. An important role in the initiation of individual pittings is played by heterogeneities – inclusions in the metal, and propensity to pitting corrosion depends on chemical composition of inclusions.

The first stage of pitting corrosion proceeds according to the following scheme: first, the process goes with oxygen depolarization, anode zones are formed over the entire surface of the metal, which can move and overlap each other; then more dense areas of corrosion deposits are gradually released, and there under conditions of oxygen deficiency the corrosion process proceeds with hydrogen depolarization and release of gaseous hydrogen, and the tubercle begins to grow.

The mechanism of tubercles growth is still not completely clear, and apparently, depending on the conditions (including hydrodynamic), all the considered mechanisms can take place. One of the most promising versions is growth by analogy with ferrotubes, where the resulting hydrogen gas carries iron compounds and deposits them in the form of layers and outgrowths on top of the tubercle thus formed. Along with this, the second probable model also takes place – this is the rise of the formed shell by corrosion products, which increase in volume, and the simultaneous gradual expansion of the tubercle over the area, as well as continuous recrystallization in the core and shell of the tubercle. Periodic breakthrough of the shell forms new tubercles on top of the old ones.

The composition of water and the intensity of the initial stage affects the type of tubercles formed – in the presence of internal liquid or without (almost without) liquid. In the first case, corrosion is slow and a dense tubercle sediment is formed, which slows down corrosion. In the second case, pitting corrosion is accelerated and large loose bumps are formed, filled with liquid inside. The flow of solution to the metal surface is the limiting factor in the corrosion process. The presence of sufficient liquid inside the tubercle and the possible ingress of new portions of liquid and dissolved ions inside the tubercle makes the corrosion process inside the pitting self-sustaining (autocatalytic) and it ends with the formation of a through pitting. Otherwise, the corrosion process slows down or stops completely.

Knowledge of tubercles formation mechanism can help in the development of methods aimed at reducing the rate of corrosion of pipelines in water supply systems.

Acknowledgements

We express our deep gratitude to the Moscow State University of Civil Engineering (National Research University) for financial support of preparing this research work for publication.

References

- 1. G.S. Frankel, Pitting corrosion of metals a review of the critical factors, *J. Electrochem. Soc.*, 1998, **145**, 2186–2198. doi: <u>10.1149/1.1838615</u>
- 2. B.H. Clarke and A.M. Aguilera, Microbiologically Influenced Corrosion in Fire Sprinkler Systems, *Automatic Sprinkler Systems Handbook*, 2007, 955–964.
- 3. P. Su and D.B. Fuller, *Corrosion and Corrosion Mitigation in Fire Protection Systems*. FM Global 1151 Boston-Providence Turnpike Norwood, MA 02062, 2nd Edition, 2014.
- 4. V.A. Chukhin and A.P. Andrianov, Causes analysis of corrosion of galvanized pipes in hot water systems, *S.O.K. (Plumbing. Heating. Air Conditioning)*, 2018, **1**, 54–58 (in Russian).
- 5. A.P. Andrianov and V.A. Chukhin, Identification of corrosion of galvanized pipes in a water supply system, *Vodosnabzhenie i sanitarnaya tekhnika (Water supply and sanitary technique)*, 2019, **9**, 39–44 (in Russian).
- T.L. Gerke, J.B. Maynard, M.R. Schock and D.L. Lytle, Physiochemical characterization of five iron tubercles from a single drinking water distribution system: Possible new insights on their formation and growth, *Corros. Sci.*, 2008, **50**, 2030–2039. doi: <u>10.1016/j.corsci.2008.05.005</u>
- 7. R.I. Ray, J.S. Lee, B.J. Little and T. Gerke, The anatomy of tubercles: A corrosion study in a fresh water estuary, *Mater. Corros.*, 2010, **61**, 993–999. doi: 10.1002/maco.201005739
- 8. H.M. Herro, *MIC myths Does pitting cause MIC*, Paper presented at the CORROSION 98, San Diego, California, March 1998.
- P. Sarin, V.L. Snoeyink, J. Bebee, W.M. Kriven and J.A. Clement, Physico-chemical characteristics of corrosion scales in old iron pipes, *Water Res.*, 2001, 35, 2961–2969. doi: 10.1016/s0043-1354(00)00591-1
- 10. J.R. Baylis, Factors other than dissolved oxygen influencing the corrosion of iron pipes, *Industr. Engineer. Chem.*, 1926, **18**, 370–380. doi: <u>10.1021/ie50196a012</u>
- P. Sarin, V.L. Snoeyink, D.A. Lytle and W.M. Kriven, Iron corrosion scales: model for scale growth, iron release, and colored water formation, *J. Environ. Eng.*, 2004, 130, 364–373. doi: <u>10.1061/(ASCE)0733-9372(2004)130:4(364)</u>
- P. Sarin, V.L. Snoeyink, J. Bebee, K.K. Jim, M.A. Beckett, W.M. Kriven and J.A. Clement, Iron release from corroded iron pipes in drinking water distribution systems: effect of dissolved oxygen, *Water Res.*, 2004, **38**, 1259–1265. doi: <u>10.1016/j.watres.2003.11.022</u>
- 13. A. Andrianov, V. Chukhin and V. Orlov, Study of morphological and chemical characteristics of corrosion scales in steel pipes, *Proceedings of the 2nd International conference of advanced materials, mechanical and structural engineering (AMMSE 2015)*, Je-Ju Island, South Korea, 18–20 September, 2015, CRC Press, 2016, 81–86.

- 14. A.P. Andrianov and V.A. Chukhin, Analysis of the morphology, composition and conditions for corrosion deposits formation in water pipes, *Voda i ekologiya: problemy i resheniya (Water and ecology: problems and solutions)*, 2016, **3**, 18–34.
- 15. H. Sontheimer, W. Kolle and V.L. Snoeyink, The siderite model of the formation of corrosion-resistant scales, J. AWWA, 1981, 73, 572–579. doi: <u>10.1002/j.1551-</u><u>8833.1981.tb04801.x</u>
- 16. A. Menzies, Introductory corrosion, in: J.D.A. Miller (Ed.), *Microbial Aspects of Metallurgy*, American Elsevier Publishing Co., New York, 1970, pp. 35–60.
- J.Y. Jiang, Y. Liu, H.Y. Chu, D. Wang, H. Ma and W. Sun, Pitting Corrosion Behaviour of New Corrosion-Resistant Reinforcement Bars in Chloride-Containing Concrete Pore Solution, *Materials*, 2017, 10, 903. doi: <u>10.3390/ma10080903</u>
- N. Alonso-Falleiros and S. Wolynec, Correlation between Corrosion Potential and Pitting Potential for AISI 304L Austenitic Stainless Steel in 3.5% NaCl Aqueous Solution, *Mat. Res.*, 2002, 5, 77–84. doi: <u>10.1590/S1516-14392002000100013</u>
- J. Bhandari, F. Khan, R. Abbassi, V. Garanniya and R. Ojeda, Modelling of pitting corrosion in marine and offshore steel structures a technical review, *J. of Loss Prev. Process Ind.*, 2015, 37, 39–62. doi: <u>10.1016/j.jlp.2015.06.008</u>
- M. Ergun and A. Yaşar Turan, Pitting potential and protection potential of carbon steel for chloride ion and the effectiveness of different inhibiting anions, *Corr. Sci.*, 1991, **32**, 1137–1142, doi: <u>10.1016/0010-938X(91)90098-A</u>
- A.I. Shcherbakov, I.V. Kasatkina, V.E. Kasatkin, I.G. Korosteleva, V.N. Dorofeeva and L.P. Kornienko, Influence of the stainless steel 321 (X18H10) structure on pitting corrosion in low-mineralized water. Inhibiting effect of sulfate and hydrocarbonate ions, *Int. J. Corros. Scale Inhib.*, 2021, **10**, 176–185. doi: <u>10.17675/2305-6894-2021-10-1-10</u>
- 22. N.J. Laycock, M.H. Moayed and R.C. Newman, Metastable Pitting and the Critical Pitting Temperature, *J. Electrochem. Soc.*, 1998, **145**, 2622. doi: <u>10.1149/1.1838691</u>
- 23. R. Qvarfort, Some observations regarding the influence of molybdenum on the pitting corrosion resistance of stainless steels, *Corros. Sci.*, 1998, 40, 215–223. doi: 10.1016/S0010-938X(97)00118-2
- 24. O. Yepez, N. Obeyesekere and J. Wylde, Can Critical Pitting Temperature be used on Carbon Steel? And Finding the Localized Corrosion Behavior in the Impedance Spectra of the CO₂ Corrosion Process, *in Conference*: *Corrosion 2018*, 2018, p. 11389.
- 25. B. McEnaney and D.C. Smith, The reductive dissolution of γ-FeOOH in corrosion scales formed on cast iron in near-neutral waters. *Corr. Sci.*, 1980, **20**, 873–886. doi: 10.1016/0010-938X(80)90120-1
- V.A. Chukhin and A.P. Andrianov, Wave nature of tubercular corrosion in steel and cast iron pipes of water supply systems, *Vestnik MGSU (Bulletin of MGSU)*, 2018, **13**, 385– 399. doi: <u>10.22227/1997-0935.2018.3.385-399</u>
- 27. Ya. Wang, G. Cheng, W. Wu and Y. Li. Role of inclusions in the pitting Role of inclusions in the pitting initiation of pipeline steel and the effect of electron irradiation in SEM, *Corros. Sci.*, 2018, **130**, 252–260. doi: <u>10.1016/j.corsci.2017.10.029</u>

- Wn. Shi, Sf. Yang and Js. Li, Effect of nonmetallic inclusions on localized corrosion of spring steel, *Int J Miner Metall Mater*, 2021 28, 390–397. doi: <u>10.1007/s12613-020-2018-z</u>
- 29. Z. Yang, B. Kan, J. Li, Y. Su, L. Qiao and A.A. Volinsky, Pitting Initiation and Propagation of X70 Pipeline Steel Exposed to Chloride-Containing Environments, *Materials*, 2017, **10**, 1076. doi: <u>10.3390/ma10091076</u>
- 30. R.T. Loto, Pitting corrosion evaluation and inhibition of stainless steels: A review, *J. of Materl. Environ. Sci.*, 2015. **6**, 2750–2762.
- 31. D.A. Stone and R.E. Goldstein, Tubular precipitation and redox gradients on a bubbling template, *Physics*, 2004, **101**, 11537–11541. doi: <u>10.1073/pnas.0404544101</u>
- J. Telegdi, A. Shaban and L. Trif, Review on the microbiologically influenced corrosion and the function of biofilms, *Int. J. Corros. Scale Inhib.*, 2020, 9, 1–33. doi: <u>10.17675/2305-6894-2020-9-1-1</u>

*** * ***