The mechanism and identification of corrosion of steel pipes in hot water supply systems

Valentin Chukhin¹, Alexey Andrianov¹ and Dmitriy Spitsov²

¹ Moscow State University of Civil Engineering, Yaroslavskoe shosse 26, Moscow, 129337, Russia
² Moscow Institute of Architecture (state academy), Rozhdestvenka street 11, Moscow, 107031, Russia

E-mail: AndrianovAP@mgsu.ru

Abstract. The problem of corrosion of steel pipes in hot water supply systems is very relevant in Russia. In a number of cases, the accelerated corrosion of pipelines and fittings installed in hot water supply networks is observed. The purpose of this study is to investigate the mechanism of corrosion of steel zinc-coated and non-galvanized pipes in hot water supply systems, to analyze the causes of corrosion and to develop methods for identifying active corrosion processes occurring in water supply systems. According to literature review the microstructure and composition of the zinc coating and the methods of its application are studied. A SEM/EDS study of the structure and elemental composition of inner zinc coating on new and used steel galvanized pipes is conducted. This study shows the nonuniform distribution of zinc layer which can lead to a rapid corrosion of both the zinc layer and the metal substrate and the development of pitting corrosion. A structure and composition of corrosion sediments formed on the inner surface of pipes was studied. The different causes and factors of steel corrosion in hot water are considered and discussed. A method of corrosion identification of galvanized pipes and heat exchange equipment based on the determination of corrosion products, in particular zinc and copper, was proposed.

1. Introduction

The high rate of corrosion of steel pipes leads to the fact that design and construction organizations use plastic, copper or stainless steel pipes for residential plumbing systems. However, based on fire protection and economic considerations, a technical solution are widely used where the main pipelines are made of galvanized steel pipes and the risers and connections to the fixtures are made of polypropylene or metal-plastic pipes. Nevertheless, the problem of corrosion remains relevant, and the number of consumer complaints concerning water quality does not significantly decrease. This is especially true for hot water supply systems.

A lot of cases of hot and cold water pipes corrosion can be found in the literature [1-9]. Thus, in [2], the results of a survey of heating and hot water supply systems at various buildings in Moscow are presented. According to the authors, one of the reasons for accelerated corrosion of pipelines is electrical currents flowing through them, connected with the disruptions of electrical systems operation in these buildings. Corrosion is observed despite compliance with the basic requirements for the water composition. The measurements carried out showed that alternating current from 0.1 to 18.2
A is flowing through the pipelines [2]. Such phenomena occur when metal pipelines are used to ground electrical appliances or when a neutral conductor is connected to the equipment body galvanically connected to the pipeline.

In addition to the quality of source water and leakage current a number of reasons for high corrosion rate of galvanized pipes in hot water systems can be adduced: the high temperatures of transported water (over 60 °C), installation different pipes in the same water supply system (eg. copper and steel pipes), welding of galvanized pipes without meeting the standard requirements, the presence of microbiological corrosion [4, 5], low water flow velocities [3, 6, 10].

As a result of monitoring the operation of water supply systems assembled from pipes made of various materials, it was concluded that it is undesirable to place pipes made of steel (except for stainless steel), aluminum or zinc after copper ones (in the direction of flow of water) to avoid premature corrosion of these pipes. In case when the installation of equipment made from such metals is inevitable after the section with copper pipes, it is necessary to provide the presence of passive anodes (magnesium or aluminum) in this equipment.

When a metal copper is deposited on a zinc surface, a short-circuited element is formed in which zinc is an anode and copper is a cathode. Since copper is in contact with zinc and both these metals are surrounded by water, the galvanic cell is "turned on". Zinc in the form of the Zn$^{2+}$ passes into water and the remaining electrons pass to a more electropositive metal – to copper. Hydrogen ions go to the copper cathode, they take electrons and are converted into hydrogen atoms, and then into hydrogen molecules. Thus, in the presence of a depolarizer the process proceeds until all of the zinc is dissolved.

Examples of abnormally high corrosion rates of galvanized pipes can also be found in literature [7-9]. So, in hot water installations in Gdańsk Wrzeszcz (Poland), the zinc coating was completely destroyed within 3-4 years [7]. A high level of oxygen and aggressive carbon dioxide in the water as well as chloride and sulfate ions in the total amount of more than 50 mg/L were named as a reason of accelerated corrosion. The water temperature and especially the temperature drops are also of great importance, since they cause cracks and destruction of created layers of corrosion products that have protective properties. According to the authors of this paper [7], one of the effective ways to reduce the rate of corrosion is to maintain a constant water temperature below 55 °C at pH 7.4-7.8.

It should be noted that in the literature devoted to corrosion of galvanized pipes and evaluation of the influence of various factors, the least attention is paid to quality of zinc coating, which is primarily exposed to unfavorable factors.

It is known that metal pipes used for water distribution systems corrode because of their thermodynamic instability. To avoid corrosion, steel pipes are covered with a protective layer of zinc with a coating thickness of 20 to 85 μm, depending on the requirements of regulatory documentation [4].

In Russia, the production of steel pipes is normalized by generally accepted standards related to water and gas pipes (GOST 3262-75*) and electrically welded straight pipes (GOST 10704). On these pipes the zinc coating is applied. Requirements for water-gas-conducting galvanized pipes in accordance with GOST 3262-75* are formulated as follows: the coating of water-supply galvanized pipes should be continuous and the thickness of the zinc layer should be at least 30 microns. The coating for galvanized steel pipes is applied according to various technologies, the choice of which depends on pipe diameter, the quality requirements and the strength of the zinc layer. Steel galvanized pipes are produced by the following methods [11, 12].

Electrogalvanization. The method is based on dissolving zinc electrodes in an electrolyte solution under the influence of an electric current. In the process of electrolysis, zinc is deposited on the surface of the tube. Advantages: even coating; the thickness of the layer reaches 30 μm. Disadvantages: weak adhesion; the porosity of the coating determines a small service life (up to 5 years).

Hot dipping. This method allows you to get the most reliable coating, on an industrial scale, it is used quite often. For coating the cleaned steel preform is immersed for a certain time in molten zinc or zinc alloy, and a reaction take place to form a metallurgically bonded coating. Disadvantages: a build-
up can be formed on the pipe surface, so a repeated machining will be required. There is a limitation on the grade of steel to which this method can be applied – the carbon content is not more than 0.24%.

Advantages: experience has shown that hot-dip galvanized steel can serve up to 50 years without visible corrosion damage and the resumption of zinc coating.

**Thermodiffusion zinc coating.** A galvanized steel pipe is produced by applying zinc vapor to the surface of the billet, the whole process is carried out in sealed containers, which ensures high environmental safety of the process. Advantages: considerable hardness of the coating; no flowing, the ability to handle details of complex configuration (thread); the service life of the pipes exceeds 15 years.

The zinc coating protects the steel from corrosion, at one hand, by creating a barrier that separates the steel from the corrosive environment, and at another hand, the zinc coating is an anode to the iron, providing electrochemical protection. When choosing an anticorrosive protection, the focus is on the rate of destruction of the coating and the need for its renewal. This indicator for zinc is 0.5–6 μm/year, depending on the operating conditions.

The microstructure of the coating differs significantly depending on the method of its application. In figure 1 shows the microstructure of a zinc coating obtained by hot-dip galvanizing [12]. According to the literature, the optimal structure of the zinc coating includes four layers: gamma (G), delta (δ), zeta (ζ) and this (η), having different thicknesses and performing different functions [4]. To be effective, the outer η-layer should be at least 45% of the thickness of the entire coating [4].

![Figure 1. Photomicrograph of batch hot-dip galvanized coating](image)

The hardness in Vickers units indicates for each layer in figure 1. It can be seen that all three intermetallic layers are harder than the base steel, whereas the outer layer "Eta" has a low hardness and high plasticity. This combination of zinc coating properties provides its high resistance to wear. Iron, as follows from figure 1, in greater or lesser quantity is always present in the zinc alloy. It enters the alloy mainly during the galvanizing process due to the interaction between the molten zinc and the product iron surface. As the iron content in the alloy increases, the thickness of the coating increases significantly, and its plasticity and appearance deteriorates. In this case, a large number of inclusions are present in the upper layer of the zinc coating (η-phase).

It is known that silicon, manganese and phosphorus significantly increase the rate of interaction between steel and molten zinc, as a result of which the growth of the alloy layer in the coating is enhanced. With a high content of silicon and phosphorus, the coating consists mainly of iron zinc compounds, which are columnar δ- and ζ-crystals. The ζ phase is particularly well developed. The layer of pure zinc (η-phase) in such coatings is very thin, and sometimes completely absent. The surface of the coating becomes light gray.

The minimum thickness of the zinc coating according to EN 10240 is 55 μm on the inside of the galvanized steel pipe (25 μm more than the Russian standard) and 28 μm for welds. Measurements of galvanized coating thickness along a 10 cm long section of tube show that the standard is most of the
time not respected. Moreover, the average thickness of this sample (41.5 ± 8.6 μm) is less than that required by the European standard [4].

Figure 2. Optical micrographs of hot-dip galvanized steel defects (etched with 4 vol.% Nital), such as too thin η-layer (a), missing η-layer (b) and irregularities as ζ-layer reaching the surface (c). [4]

Figure 2 shows moreover that, even when the minimum thickness of 55 μm is respected, the microstructure of the galvanized coating can be inadequate, with an outer protective pure zinc eta (η) layer too thin to ensure effective protection of the steel substrate against corrosion. When the coating is very thin (less than 20 μm) (figure 2b), its structure is composed of nearly 50% delta (δ) layer and 50% zeta (ζ) layer, and the outer protective pure zinc eta (η) layer is missing. In some cases, irregularities of the galvanized coating lead to a too thin pure zinc eta (η) layer, with a zeta (ζ) layer reaching the surface of the coating with a lack of delta (δ) layer in some places, impeding protection of the steel substrate against corrosion (figure 2c) [4]. Wherein, coatings where the zeta phase is absent or too thick and represented by a columnar structure do not protect the steel from general corrosion.

When studying the pipeline corrosion, it is important not only to establish the causes, but also to predict the corrosion rate and the pipe life before leaks appearance or pipe destruction. To evaluate the lifetime value of pipelines, a computational methods based on taking into account pitting corrosion, fatigue stresses, surface corrosion proceeding with oxygen depolarization are proposed.

2. Materials and methods
To clarify the reasons for accelerated corrosion in plumbing system of a residential 17-story building in Moscow, samples of a pipe having a zinc coating with traces of corrosion were submitted for metallographic studies. A pipe with a diameter of 40 mm was removed from hot water supply network after 2 years of operation. Moscow tap water can be characterized as slightly corrosive (Langelier index ranges from 0 to –0.9). For comparison, a new galvanized pipe with a diameter of 15 mm was also examined. Metallography was carried out using optical and electron microscopes (Quanta 250 FEI) and EDX measurement of zinc coating structural components (GENESIS APEX 2 EDS System with APOLLO X SDD EDAX). The preparation of polished sections for structural analysis was performed using grinding paper with grain size 50-63 μm and 7-10 μm. Samples were etched using hydrochloric acid, 0.1 N and 0.4N solutions.
3. Results and discussion
Microphotographs showing the variation in the zinc coating thickness of the pipe fragment are shown in figure 3. The Table 1 shows the results of the energy-dispersive analysis of this coating. Based on the analysis of water supply system condition, experts who found fistulas in hot water pipes concluded that the cause of accelerated corrosion is current leakage. Measurement of zinc layer thickness shows that at a nominal thickness of 30 μm, most of the layer has values of about 50 μm, but in some areas this thickness is reduced to 18 μm, which can lead to local disruption of the zinc coating during operation.

Figure 3. Photomicrographs of the zinc coating (cross-section) on the internal side of a steel pipe with a diameter of 40 mm
Table 1. The results of EDX analysis of zinc coating

| Element | Figure 3a Weight percent Wt, % | Figure 3a Atomic percent At, % | Figure 3c Weight percent Wt, % | Figure 3c Atomic percent At, % |
|---------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| C       | 15.07                         | 38.99                         | 11.81                         | 35.37                         |
| O       | 11.48                         | 22.29                         | 7.93                          | 17.83                         |
| Al      | 1.92                          | 2.22                          | 0.37                          | 0.49                          |
| S       | 0.35                          | 0.34                          | 0.29                          | 0.33                          |
| Cl      | 0.55                          | 0.48                          | 0.61                          | 0.62                          |
| Fe      | 25.93                         | 14.43                         | 19.93                         | 12.84                         |
| Zn      | 44.70                         | 21.25                         | 59.06                         | 32.51                         |

When examining the inner surface of the pipe fragment using a stereoscopic microscope, the smallest traces of corrosion sites were found on the general field of undisturbed coating (from the water side). This corrosion traces have a size of about 0.1 mm (figure 4). An analysis of zinc coating structure on the inner pipe surface verifies that uneven distribution and discontinuity of the zinc coating can cause the appearance of through fistulas during electrochemical corrosion.

Figure 4. Optical photo of an internal surface of a steel zinc-coated pipe DN 40 mm with traces of corrosion

Figure 5. Photomicrographs of the zinc coating on the new steel pipe DN 15: a) without etching the surface, b) when etching 0.4N HCl
After the disturbance of the zinc coating, the corrosion process in hot water is accelerated several times. We studied the rate of corrosion of plate specimens cut from a steel zinc-coated pipe in cold and hot tap water. Depending on the experimental conditions, the average mass corrosion rate, measured from the sample weight change, was 0.148 g/m$^2$h for cold water conditions and the average deep corrosion rate calculated from the Faraday law is 0.165 mm/year. The studies carried out on the same samples in hot water at a temperature of 50 °C showed that the mass corrosion rate was 0.492-0.834 g/m$^2$h, and the depth rate was 0.545-0.93 mm/year. Thus, it can be concluded that the appearance of fistulas in case of damaged zinc coating surface and pipe wall thickness of 3 mm can occur in 2-3 years. This is comparable to the data given above.

Figure 5 presents photomicrographs of the zinc coating of a new tube with a diameter of 15 mm. The SEM images demonstrate the coating unevenness – the same as in the case of pipes that were in operation. It can be noted that the pure zinc content in the zinc layer is higher than in the used pipes, which indicates that zinc is "washed out" during corrosion not only from the surface layer but also from deeper layers (Table 2).

### Table 2. The results of a comparative analysis of the zinc coating of a new pipe and a pipe that was in operation

| Element | New pipe DN 15 | Old pipe DN 40 |
|---------|----------------|----------------|
|        | Weight Wt, %   | Atomic At, %   | Weight Wt, %   | Atomic At, %   |
| C      | --             | --             | 24.38          | 55.51          |
| O      | 4.25           | 14.79          | 10.01          | 16.79          |
| Al     | --             | --             | 0.61           | 0.61           |
| Cl     | 1.36           | 2.14           | --             | --             |
| Fe     | 19.09          | 19.02          | 19.92          | 9.58           |
| Zn     | 75.29          | 64.06          | 45.08          | 18.52          |

### 4. Conclusion

It can be concluded that, in spite of collected information on the corrosion of galvanized pipes, it is impossible to state definitely, which of the many factors leads to the fistulas appearance. Of course, the version that the leakage currents with a great values are the most clear in comparison with the rest versions. Calculation shows that a current of 23 μA over the course of a year leads to the appearance of pitting having a surface of 0.1 cm$^2$ in the pipe wall with a thickness of 3 mm [7]. However, these data refer to electrochemical corrosion, and the currents noted in [2] should lead to faster corrosion rate than observed. Therefore, experts, assessing the causes of corrosion of steel galvanized pipes, in the absence of sufficient information, come to the conclusion that corrosion is a consequence of a combination of different factors. In our opinion, precise determination of the causes of accelerated corrosion can be carried out on analysis of corrosion products and sediments removed from the pitting zone.

A special case is the corrosive destruction by electrolysis, in which the appearance of caverns occurs without the formation of corrosion products in them. Corrosion during electrolysis has a significant difference from conventional electrochemical corrosion, consisting in the fact that the source of the electric current creating the corrosion circuit is external, i.e. there is a leakage current. In the case of electrochemical corrosion, cavities are not only filled with corrosion products, but also form outgrowths (hillocks or tubercles) above the surface of the metal.

The earlier the identification of the beginning of corrosion is made, the faster technical measures can be taken to prevent economic damage and water quality deterioration. Based on the results of the structure and composition investigations of the corrosion sediment formed on the inner pipe surface, the authors develop an identification method based on the determination of corrosion products, in particular zinc and copper, in the sediment composition. The method allows to detect corrosion of galvanized pipes and heat exchange equipment from the beginning of water supply system operation.
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