Pipelines corrosion during water supply process

Nikolay Atanov, Pavel Gorshkalev, Michail Chernosvitov, Angelina Smirnova
Samara State Technical University, Academy of Civil Engineering and Architecture, Molodogvardeyskaya St., 194, Samara, Russia, 443001
kafvv@mail.ru

Abstract. Buildings and structures reliability is a key question in human life and activities. Corrosion processes affect reliability of all water supply and distribution systems in buildings and structures. This research provides results of the tests for corrosion rate and for the time of steel water-pipes inhibition of corrosion in Samara. A gravimetric method was used to determine corrosion rate. The test subjects were surface (the Volga river) and underground (water treatment facilities of 113 km, Kuibyshev district) water supply sources. These tests proved that river water was highly aggressive in respect to other materials. Here the corrosion rate reached 0.1665 g/(m²/h) during in the 5th month of exposure, and the specimens were damaged by pitting corrosion (within 1 month) and by cankers (within 5 months). The value of the corrosion rate in underground source water was within the range of 0.01-0.06 g/(m²/h), and the specimens were not subjected to any significant corrosion damage. The time of experience was not enough for complete inhibition of corrosion. The authors studied a sample with 50-year operational lifetime and proved that all corrosion processes affecting this sample had stopped, this sample material integrity had been pre-served which meant that steel pipes complete inhibition of corrosion was possible. The experiments also showed that the inner surface of the pipe was later filled with corrosion deposits. The thickness of corrosion deposits in the tray zone reached up to 7 mm.

Keywords: corrosion, corrosion damage assessment, corrosion processes, gravimetric method, electrochemical corrosion.

1. Introduction
In the last century water supply systems laid on the territory of Samara were built mainly of steel and cast-iron pipes. There is minor but constant water leakage from these pipes. It brings considerable economic and environmental damage to the country. In the cities with worn out communication lines most leakage is a result of these communication lines failure.

The length of water supply networks in Samara is approximately 25 thousand km. The networks are made up of 37.1% steel pipes, 56.5% cast-iron pipes, 5.3% polyethylene pipes and 1.1% – reinforced concrete pipes [1]. Steel pipes are responsible for 56.96% of all failures in the pipeline system of the city. Steel pipes failure mainly occurs because of water pipes corrosion cracks resulting from the process of electrochemical corrosion.

Electrochemical corrosion occurs as a result of the metal structure electrochemical heterogeneity. When water is supplied through steel pipes there are anodic and cathodic areas on the metal surface. On the surface of the anode the metal atom develops into Fe²⁺ ion. This process brings into operation
an electric circuit of electrons moving in the metal from the anode to the cathode at which the process of depolarization occurs [2].

The process of the steel pipe inhibition of corrosion with oxygen depolarization (that is the process when metal surface becomes inactive) with the formation of protective thin skins preventing corrosion, consists of three main stages [3]:

1. Oxygen transfer from the mass of flowing water into the laminar layer of cathode zones of the pipe internal surface.
2. Oxygen ionization: depolarization of electrons of the anodic process according to reaction.

\[ O_2 + 4e + H_2O = 4OH^- \]  \hspace{1cm} (1)

These two stages occur at the moment when metal contacts with water. The process further depends on the concentration of calcium bicarbonate Ca(HCO\(_3\))\(_2\) in water. Process 3.1 evolves in alkaline water when the stability index J>0 \([4; 5; 6; 7; 8]\).

3.1. The process of protective skin formation takes place right on the cathode according to the following chemical reaction:

\[ HCO_3^- + OH^- = CO_3^- + H_2O \]  \hspace{1cm} (2)
\[ Ca^{2+} + CO_3^- = CaCO_3 \]  \hspace{1cm} (3)

The newly formed sediment CaCO\(_3\) is characterized by a high degree of adhesion and creates a dense skin which makes the rate of corrosion processes slower and impedes the flow of oxygen to the metal surface. Calcium bicarbonate Ca(HCO\(_3\))\(_2\) is a natural corrosion inhibitor for steel water-supply pipelines.

At Stage 3.1 the minimum number of hydroxyl anion OH\(^-\) diffuses to the anode zones for the formation of ferrous hydroxide Fe(OH)\(_2\).

For water with low alkalinity concentration and the stability index J<0 \([4; 5; 6; 7; 8]\) the process of protective skin formation takes place during Stage 3.2.

3.2. Convective or diffusional anions OH\(^-\) transfer develops from cathode areas to the anode zones, where sediment formation takes place according to reaction:

\[ Fe^{2+} + 2OH^- = Fe(OH)_2 \]  \hspace{1cm} (4)

Fe(OH)\(_2\) sediment which is formed at the anode zone, is characterized by porosity sufficient for diffusion of anions OH\(^-\) to cations Fe\(^{2+}\). The presence of oxygen in water leads to compaction of sediments due to oxidation of hydrosaline Fe(OH)\(_2\) to hydroxide Fe(OH)\(_3\). Probable change of the potential depth of the anode to the cathode (depth electrochemical heterogeneity) leads to compaction of sediments up to the formation of an anaerobic zone at the metal surface. In the anaerobic zone sulphur reducing bacteria (SRB) enable transformation of sulfate according to reaction

\[ SO_4^{2-} + CO_2 + H_2O \xrightarrow{CBE} H_2S + HCO_3^- \]  \hspace{1cm} (5)

The formed anion HCO\(_3\) increases the pH value of the water environment, and hydrogen sulphide H\(_2\)S oxidizes metal pipes to iron sulphideFeS which has a characteristic black color. The anaerobic process is terminated with the exhaustion of sulfates under a dense layer of sediments, and the corrosion process stops.

2. Methods
To better understand the process of protective skins formation on steel piping systems of drinking water supply, let us conduct a series of experiments using a gravimetric method for the determination of corrosion rate by mass loss.
To obtain comparable results we undertook field studies to determine the corrosion rate of steel samples. The samples were made as rectangular plates from a single sheet of carbon steel of St3 Grade, the so-called "coupons". Each coupon was assigned a unique number. Their dimensions were measured with a Vernier scale accurate within 0.1 mm. Before testing, the working plane of the coupons was processed in accordance with generally accepted corrosion testing requirements (grinding, polishing and degreasing) [9]. After testing, the coupons were weighed on an electronic weighting unit VIBRAHT accurate within 0.001 g.

As there are no regulations on the exposure time to determine the corrosion rate by the gravimetric method, at three coupons were established on the structures at one and the same time for a period of 1 and 5 months.

After the deadline, the coupons were removed from the tanks, cleaned of corrosion products [10], their corrosion damage was carefully described and the coupons were reweighted. The obtained results were processed in the following way: weight losses of coupons were measured, corrosion rates were calculated, and the obtained data was analysed.

The corrosion rate of the specimens was calculated by the formula

$$\rho = \frac{\Delta P \cdot T}{F}, \text{ g/(m}^2\cdot\text{h}),$$

(6)

where $\Delta P$ is the loss of the sample mass, g, calculated by the formula

$$\Delta P = P_1 - P_2, \text{ g},$$

(7)

where $P_1$ is the initial mass of the coupon, g; $P_2$ is weight of the coupon after removal of corrosion products, g; $F$ is the surface area of the coupon, $m^2$; $T$ is the test duration, $h$.

Average permeability is calculated according to the mass loss,

$$\Pi = 8.76 \cdot \rho / \gamma, \text{ mm/year},$$

(8)

where $P$ is permeability, mm/year; 8.76 is a conversion coefficient; $\rho$ is the corrosion rate, g/(m$^2$/h); $\gamma$ is metal density, g/cm$^3$.

For carbon steel St3, when $\gamma = 7.85$ g/cm$^3$, permeability is determined by the equation

$$\Pi = 1.12 \cdot \rho, \text{ mm/year}.$$  

(9)

3. Results

To obtain comparable results, two sources of water supply in Samara were taken as objects of this study: surface and underground objects. The first and the main source of water supply is the Volga river. The coupons were installed at waste-disposal plants of hot-water supply in a tank with webbed drum filters. Carbonate hardness of water in the river Volga is 1.5–2.5 mEq/L. The stability index is $J < 0$.

The second source of water supply is underground water. The coupons were installed in a vortex mixer of waste-disposal plants in 113 km of Kibyshevskiy district.

The results of experimental determination of water corrosion rate from the surface water source (the river Volga, hot-water supply) are given in Table 1.

At the end of the experiment the following changes on the surface of the coupons were observed:

• the surface of the coupons turned red (different shades);
• there are mostly anode zones on the coupons surface covered with dense and lumpy deposits;
• there are sufficiently thick corrosion crusts in some zones;
• these formations can be removed from the surface of the coupons with a wire brush [3];
• the most unfavorable value of the corrosion rate goes up to $\rho_{\text{max}} = 0.1665$ g/(m$^2$/h).

According to [2], Metal is referred to "reduced-resistant" elements according to a scale of metal corrosion activity.

Table 1. The results of experimental determination of water corrosion rate from the surface water source
The plates cleaned from corrosion products made it possible to evaluate the change of their surface (see Fig. 1 and 2).

The samples of river water show numerous pitting (see Fig. 1) and corrosion cankers (see Fig. 2). After corrosion products removal, we saw dark gray and black areas, which were a waste product of SRB. It means we can observe the results of Stage 3.2 on the test coupons. It is assumed that an anaerobic zone is a protective layer that prevents intensive corrosion processes. The rest of the thickness of the corrosion crust is an accumulation of iron oxides and the result of Fe(OH)$_2$ and Fe(OH)$_3$ from other zones. There is a process of encrustation.

The results of experimental determination of the rate of corrosion of the under-ground water supply source (water treatment plant on 113 km of the Kuibyshevskiy district) are given in Table. 2.

The samples of river water show numerous pitting (see Fig. 1) and corrosion cankers (see Fig. 2). After corrosion products removal, we saw dark gray and black areas, which were a waste product of SRB. It means we can observe the results of Stage 3.2 on the test coupons. It is assumed that an anaerobic zone is a protective layer that prevents intensive corrosion processes. The rest of the thickness of the corrosion crust is an accumulation of iron oxides and the result of Fe(OH)$_2$ and Fe(OH)$_3$ from other zones. There is a process of encrustation.
Figure 2. The nature of St3 corrosion damage in the water of the river Volga after 3528-hour exposure.

The results of experimental determination of the rate of corrosion of the underground water supply source (water treatment plant on 113 km of the Kuibyshevskiy district) are given in Table 2.

Table 2. The results of experimental determination of the rate of corrosion of the underground water supply source.

| Sample № | Duration of exposure, T | The beginning of the tests | The ending of the tests | Rate of corrosion ρ, g/(m²·h) | Permeability P, mm/year |
|----------|------------------------|---------------------------|------------------------|-------------------------------|-----------------------|
| 694      | 35 days, 840 h         | 26.02.16 10:00            | 1.03.16 10:00          | 0.01448                       | 0.01622               |
| 765      | 35                     | 840                       |                        | 0.01216                       | 0.01360               |
| 995      |                        |                           |                        | 0.01053                       | 0.01180               |
| 694      |                        |                           |                        | 0.0381                        | 0.0427                |
| 765      | 147 days, 3528 h       | 29.06.16 10:00            | 23.11.16 10:00         | 0.0405                        | 0.0454                |
| 995      |                        |                           |                        | 0.0544                        | 0.0609                |

We can observe the following changes on the surface of the coupons:
- there are neither dense no lumpy deposits on the surface of the coupons;
- the surface of the coupons is covered with a thin layer of iron oxides which can be removed easily;
- the values of corrosion rate does not exceed the critical values and are in intervals of ρ_{av} = 0.01–0.06 g/(m²·h), which are two to three times lower than values of corrosion rate of the surface source.

After 3528-hour exposure coupons had no evident or significant corrosion damage (see Fig. 3).

The absence of pitting or corrosion canker destruction is the natural result of cathodic protection. Underground water is characterized by carbonate hardness of 5-8 mEq/l and the stability index J>0. Heavy carbonate hardness contributes to the formation of natural carbonate skin on the coupons surface. This skin protects metal from corrosion at Stage 3.1.
4. Discussion

These studies show that 3528-hour exposure is not enough for metal coupons full inhibition of corrosion.

Let us consider the process of corrosion formation in St3 Grade steel taking a segment of a pipe from a water well equipped with a water pump, the exposure time of which was ~50 years (1996-2016) as a rest sample. The well is located on the water supply network and is supplies with water from the river Volga.

We cut up a pipe segment into 2 parts lengthwise (a vault head and a culvert) and gave a visual assessment of the inner surface.

There are thick corrosion red and brown crusts (see Fig. 5). The measurements are as follows: the maximum sediment thickness on the pipe vault head reaches 4 mm, on the culvert – 7 mm (see Fig. 6).
Figure 5. A sample of deposits from the inner surface of the drinking water pipeline with NSF-1, after a 50-year operation period: a) vault head; b) culvert.

There is an intensive deposits formation (outgrowth) seen on the inner surface of the segment. Both parts of the segment (a vault head and a culvert) were cleaned from deposits [10] formed during the operation life-time.

Figure 6. The thickness of deposits in the context of: a) on the vault head; b) culvert.

There is an intense thinning of the pipe wall and corrosion damage on the out-side side of the pipe observed on the pipe segment which directly contacted water in the water well. The original thickness of the pipe wall is 3.5 mm. We can clearly see that the wall thickness is 3 times reduced (see Fig. 7).

The pipe protects itself from internal corrosion by the formation and accumulation of corrosion deposits which later thicken and develop corrosion crusts. As a result, all corrosion processes stop. The natural efficiency of the anode protection de-pends on the composition of the pipe material and supplied water quality, that is if the water is underground or surface. With any corrosion rate, for example, 0.1865 mm/year (see Table 1), metal of the pipe would have been completely destroyed after 50 years of exploitation. Its presence supports the theory of formation of a protective corrosion skin at Stage 3.2. However, the formation of corrosion growths leads to an increase in roughness of pipe walls, decreasing its carrying capacity and increasing pressure losses in the pipeline. Thus, much more electricity will have to be spent on water transfer.

The segment, which was in a socket of a cast-iron pipe of the water well, was protected by a cable yarn (resin-impregnated linen cloth) with asbestos-cement junction of the lock, preventing the occurrence of corrosion processes on the external side of the pipe (see Fig. 8).
Figure 7. Cleaned inner surface of the pipe segment.

Figure 8. External destruction of the pipe segment.

Corrosion damage and thinning of the wall on the external surface of the pipe up to 1 mm resulted in the formation of a water pipe corrosion crack (see Fig. 8).

Let up present a visual and mechanical evaluation of the sediments:
- dense;
- flake-like (layer-by-layer flaking);
- easily separated from the surface of the affected pipe under physical impact;
there are black layers under the crust, which may indicate processes of bio-corrosion (due to microorganisms).

The composition of deposits from the inner surface of the pipe segment supplying water in a water well with a water pump during its 50-year life-time is given in Table. 3.

**Table 3.** The composition of deposits from the inner surface of the pipe segment supplying water

| Component       | The content in the sample | mg/kg | %   |
|-----------------|---------------------------|-------|-----|
| Iron total $Fe_{total}$ | 444000                    |       | 98.8|
| Calcium $Ca^{2+}$   | 3102                      |       | 0.69|
| Magnesium $Mg^{2+}$ | 1158                      |       | 0.26|
| Aluminum $Al$      | 1110                      |       | 0.25|

The data in Table 3 show that the dominant corrosion process is that of $Fe_2O_3$ and $Fe_3O_4$ formation as the content of iron $Fe_{geo}$ is 98.8% in the sediments.

5. Conclusion
1. Full inhibition of corrosion of the inner surface of steel pipes is ensured by the formation of dense corrosion deposits.
2. The increase of the thickness of corrosion deposits leads to a decrease in pipe water-carrying capacity.
3. External corrosion of an uninsulated steel pipe in a wet environment is dominant and leads to the formation of water pipes corrosion cracks.
4. Protection of steel pipelines from external and internal corrosion is one of the most difficult tasks for the municipal water supply system. To replace steel pipe with non-corrosive plastic pipes is economically efficient.

References
[1] Strelkov A K2016 *Water delivery and sanitary engineering* No.12 p 21-25
[2] Zhuk NP 2006 *A course in the theory of corrosion and protection of metals* (M.: OOO TID "Alliance") p 472
[3] Katz N G 2010 *Fundamentals of the theory of chemical resistance and corrosion protection for oil and gas processing equipment* (M.: Mechanical engineering) p 332
[4] Atanov NA 2002 *Recycling water supply of petroleum processing plants* (Samara: Publishing house of Samgasa) p 362
[5] DeMartini F E 1938 *Journal of American Water Works Association* Vol. 30, No. 1 p 85-111
[6] Al-Ruwaih F M, Alhumoud J N and Al-Mutairi S M 2010 *American Journal of Environmental Sciences* No 6(3) p 260–267
[7] Carson H 1917 *Journal of American Water Works Association* Vol. 4, No. 2 p 252–259
[8] Kalantari R R, Yari A R, Ahmadi E, Azari A, Zade M T and Gharagazlo F 2013 *Archives of Hygiene Sciences* No 2(4) p 127–134.
[9] GOST R 9.905-2007 2007 *Unified system of protection from corrosion and ageing: methods of corrosion tests* (M: Standartinform) p 10
[10] GOST R 9.905-2007 2007 *Unified system of protection from corrosion and ageing: metals, alloys, metal coatings;methods of removing corrosion products after corrosion tests* (M: Standartinform) p 15