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CONTACT WITH CHLORINATED WATER: SELECTION OF THE APPROPRIATE STEEL

KONTAKT S KLORIRANO VODO: IZBOR USTREZNEGA JEKLA

Leon Gosar[1,2], Darko Drev[1,3]

[1]Institute for Water of the Republic of Slovenia, Hajdrihova 28, 1000 Ljubljana, Slovenia
[2]University of Ljubljana, Faculty of Civil and Geodetic Engineering, Chair of Fluid Mechanics with Laboratory, Hajdrihova 28, 1000 Ljubljana, Slovenia
[3]University of Ljubljana, Faculty of Civil and Geodetic Engineering, Institute of Sanitary Engineering, Hajdrihova 28, 1000 Ljubljana, Slovenia
leon.gosar@izvrs.si

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In water-supply systems and public swimming pools, the presence of highly chlorinated water can result in very aggressive corrosion. When choosing the appropriate type of steel, the extremely corrosive conditions that can occur are often forgotten. Under these conditions, corrosion-protection layers (zinc layer, polymer colour) can be quickly removed, and stainless-steel corrosion may occur as well. The high risk of the corrosion of galvanized steel pipes can also be caused by the improper implementation of disinfection. With aggressive disinfectants, the zinc layer is quickly dissolved, which leads to corrosion of the steel pipe. Therefore, we must select a particular type of stainless steel, thereby ensuring a much higher corrosion resistance than normal stainless steel. It is very important that the selection of materials is determined at the design stage of the project. In the contact of steel elements with swimming-pool water, in most cases extremely aggressive oscillations do not occur under normal operating conditions, because the content of chlorine and other elements that affect corrosion are mostly low and stable. However, even in these cases, from time to time, aggressive shocks may occur as a result of the cleaning treatment. Therefore, with the selection of the appropriate stainless steel the corrosion risk can be prevented. The contribution of the paper is mainly focused on experiences relating to the appropriate materials selection in the field of sanitary engineering.

Keywords: stainless steel, corrosion, sanitary engineering

Pri vodovodnih sistemih in javnih kopališčih se lahko pojavi močno klorirana voda, ki je korozijsko zelo agresivna. Ko izbiramo ustrezno vrsto jekla, pogosto pozabimo na ekstremne korozijske razmere, ki se lahko pojavijo. V njih se lahko zelo hitro odstranijo protikorozijski zaščitni sloji (cinkov sloj, polimerna barva), lahko pa se pojavi tudi korozija nerjavnega jekla. Veliko nevarnost za korozijo pocinkanih jeklenih cevi lahko npr. povzročimo z neustreznim izvajanjem dezinfekcije. Z agresivnimi dezinfekcijskimi sredstvi hitro raztopino zaščitni sloj cinka in povzročimo korozijo jeklene cevi. Zato je zelo pomembno, da se že v fazi projektiranja odločimo, katere materiale bomo izbrali ter na kakšen način se bo izvajala dezinfekcija. Pri izbiri jeklenih elementov, ki so v kontaktu z bazensko vodo, v večini primerov nimamo tako ekstremnih sprememb agresivnih razmer. Vsebnost klora in drugih sestavin, ki vplivajo na korozijo, je v kopalni vodi večinoma vedno nizka in stabilna. Kljub temu pa se lahko tudi v teh primerih pojavijo občasno agresivni šoki, ki lahko nastanejo v fazi čiščenja. Zato je treba z ustrezno izbiro nerjavnega jekla preprečiti nevarnost korozije. V prispevku je poudarek predvsem na izkušnjah pri izbiri ustreznega materiala s področja sanitarnega inženirstva.

Ključne besede: nerjavno jeklo, korozija, sanitarno inženirstvo

1 INTRODUCTION

In this paper we focus on facilities, which in addition to structural strength, also require sanitary adequacy. The latter requirement is particularly important for the selection of the stainless steel used in water-supply systems, public baths, food-processing facilities, kitchens, etc.[1] In these facilities, aggressive corrosive conditions in some parts of the water-supply systems may appear. [2] In the case of swimming pools, due to the presence of chlorinated water, the requirements for additional corrosion resistance need to be met.[3] Planners and designers often do not pay enough attention to the operating conditions in such facilities.

A particular case is the construction of a waterslide structure, where it is crucial for corrosion-resistant stainless steel to be selected to prevent endangering the stability of the structure. In addition, the surfaces must be completely smooth and free of corrosion effects, which is a sanitary requirement. This problem can be solved with the appropriate surface protection, [4] which may be questionable in the junctions,[5] if galvanic cells occur. Conversely, in the case of some steel surfaces (e.g., in food-processing facilities), contact with the surface where zinc is gradually being dissolved is prohibited. [6] Galvanized steel surfaces are resistant to corrosion by first dissolving the less-noble metals, e.g., zinc, thereby protecting the steel against corrosion. This method of corrosion protection is also used in galvanized-steel water-system pipes. However, in this case, corrosion protection is not only important for maintaining the stability of the installation, but also to ensure healthy drinking water.

The following types of steel corrosion can occur: [2]

- Uniform corrosion: the metal loss is uniform on the surface.
- Crevice corrosion: due to the specificity of the electrochemical process in crevices where the

changes in pH occur in the medium, the corrosion is progressing rapidly.
- Pitting corrosion: produced locally in the form of notches.
- Intergranular corrosion: localized attack along the grain boundaries, or immediately adjacent to the grain boundaries, while the bulk of the grains remains largely unaffected.
- Stress-corrosion cracking: unexpected sudden failure of normally metals subjected to in a environment.
- Hydrogen brittleness: arises from the destructive action of absorbed atomic hydrogen or hydrogen protons in the crystal lattice.
- Erosion corrosion: degradation of the material surface due to mechanical action, often by impinging liquid, abrasion by a slurry, particles suspended in fast-flowing liquid or gas, bubbles or droplets, s etc.

On steel surfaces, rust may occur as a result of chemical reactions in the steel. The characteristic brown colour appears in the presence of Fe^{+2} and Fe^{+3} iron compounds. Iron enters the Fe^{+2} and Fe^{+3} forms due to chemical reactions. However, these reactions occur more rapidly if the steel is not sufficiently "noble", e.g., it does not contain a sufficient amount of elements that are less susceptible to corrosion (nickel, chromium, cobalt, manganese, etc.).

The rate of the corrosion processes is affected by the steel composition, temperature, atmosphere, and the substances in contact with the steel construction (sheet metal). The purpose of corrosion-protection coatings is to reduce these processes to a minimum. If a connection with the moisture and the oxygen from the air is prevented, corrosion will progress very slowly. In this case, the necessary liquid electrolyte and the atmosphere that would enable an adequate decay rate of iron are absent. Since in the transformation of elemental iron in its compounds electrons are being emitted, this forms a galvanic cell. For the galvanic-cell formation to occur, both the electron donor and the recipient must be present. There exist several chemical reactions, where elemental iron passes over into its compounds. These compounds are of a brownish colour and can be seen on the outside as rust. [2]

$$Fe \rightarrow Fe^{2+} + 2e^{-}O_2 + 2\ H_2O + 4e \rightarrow 4\ OH$$

$$Fe + H_2O + ½\ O_2 \rightarrow Fe(OH)_2$$

$$Fe \cdot H_2O + 1/2\ H_2O + 1/2\ O_2 \rightarrow Fe(OH)_3$$
$$\text{e.g. } ½\ (Fe_2O_3 \cdot 3\ H_2O)\ ...$$

Purbaix [7] constructed the following potential/pH diagram (**Figure 1**). Based on this diagram, one can rapidly assess the corrosion resistance of various metals in water at 25 °C. He defined the possible equilibrium between the metal and H_2O. A simplified Pourbaix diagram indicates regions of "Immunity", "Corrosion" and "Passivation" and is a guide to the stability of a particular metal in a specific environment. Immunity means that the metal is not attacked, while shows that a

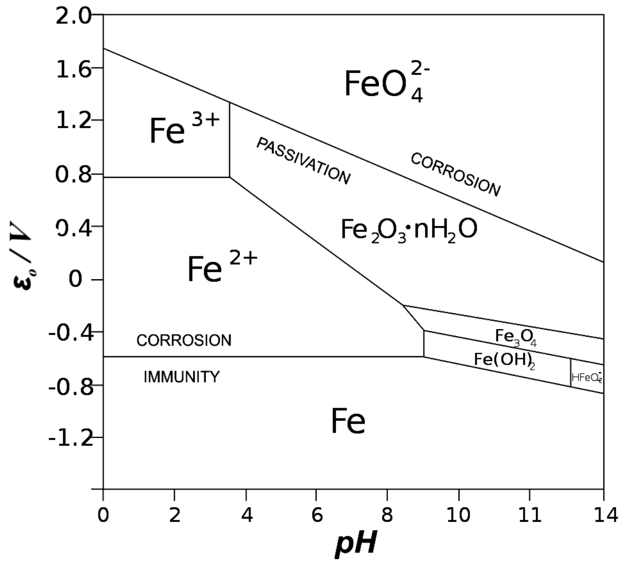

Figure 1: Purbaix diagram of iron [7]
Slika 1: Purbaix-ov diagram za železo [7]

general attack will occur. Passivation occurs when the metal forms a stable coating of an oxide or other salt on its surface.

In presence of chlorine ions, a high probability of the formation of porous or pitting corrosion exists. This result is the formation of small pits on the surface of the metal. Pitting corrosion is often difficult to differentiate from other, similar corrosive processes that may occur, such as crevice corrosion or the dissolution of zinc (both involve disparate mechanisms of corrosion). The critical pitting potential depends on the concentration of Cl-ions, the inhibitor potential of various anions in the solution, their concentration (OH^-, SO_4^{2-}, NO^{3-}, CrO_4^{2-}), as well as the temperature of the solution. In the case of swimming-pool water, we have a significant content of Cl^- and SO_4^{2-} ions and a relatively high water temperature. While this is conducive for the formation of pitting (porous) corrosion, a relevant microstructure of metals and their alloys need to be present as well.

In the case of drinking-water systems in the food industry, stainless steel should be selected. The same holds for waterslide structures and other facilities in and around swimming poles. However, it is important to note that even with the use of stainless steel, corrosion can still occur if:
- the stainless steel is not of adequate quality for the given conditions of use,
- the stainless steel forms a galvanic cell,
- there is contact with highly corrosive chemicals,
- the stainless-steel surface was not properly treated etc.

2 EXPERIMENTS AND RESULTS

We reviewed several examples of corrosion phenomena in steel and stainless steel in the field of sanitary engineering (water-supply network, baths, spas, kitchens, etc). These were in most cases expert opinions and related research inquiries into the causes of corrosion in real-world structures. Due to the sensitive nature of these studies, we are not able to present specific details about the individual structures that were the focus of these investigations. Nevertheless, we are able to present all the relevant data and facts to support our findings and conclusions.

2.1 Corrosion in an internal water-supply network

When planning a complex, internal water-supply network, it is first necessary to determine the properties of the available water and what the purpose of the local water-distribution network will be. The designer must decide which materials to use in order to facilitate disinfection. If a specific type of disinfection is not prescribed in advance (e.g., by law), the materials have to be selected to allow the effective execution of a broad range of disinfection procedures. When using galvanized steel pipes and components made of stainless steel, copper and brass, the designer should take into account the possibility of galvanic cell formation and the removal of protective zinc coatings. Zinc layers can easily be dissolved by repeated disinfectant shocks. When using plastic pipes, the possibility of heat shocks must be considered. Heat shocks are often used to disinfect an internal water-supply system when the presence of Legionella bacteria is suspected. If heat shocks are implemented, the water pipes need to withstand temperatures up to 90 °C. In addition to water pipes, thermal stability is also expected for the seal components and other parts of the installed structure.

In the analyzed cases of the internal water-supply network, we found that multiple chlorine shocks and large concentrations of disinfectants (**Table 1**) resulted in the dissolution of zinc coatings on steel pipes. Corrosion also occurred inside stainless-steel water tanks (**Figure 2**).

Figure 2: Corrosion inside a cold water reservoir
Slika 2: Korozija v notranjosti rezervoarja hladne vode

Table 1: Disinfectants recommended by the National Institute of Public Health of Slovenia for water supply systems.
Preglednica 1: Dezinfekcijska stredstva za vodovodne sisteme, ki jih priporoča IVZ

Disinfectant	Quantity / mg/l	Recommended resources for neutralization
Chlorine in gaseous form Cl_2	50 (Cl form)	Sulphur dioxide (SO_2) Sodium thiosulphate ($Na_2S_2O_3$)
Sodium hypochlorite NaClO	50 (Cl form)	Sulphur dioxide (SO_2) Sodium thiosulphate ($Na_2S_2O_3$)
Calcium hypochlorite $Ca(ClO)_2$	50 (Cl form)	Sulphur dioxide (SO_2) Sodium thiosulphate ($Na_2S_2O_3$)

Table 2: Conversion table for stainless steel AISI 304 tags to the European standard [8]
Preglednica 2: Tabela za pretvorbo oznake nerjavnega jekla AISI 304 v evropski standard [8]

Standard (Europe)	AISI	Chemical composition / %			
		C max	Cr	Ni	Mn max
X5 CrNi 18-10	304	0,07	17-19,5	8-10,5	2

In one of the internal water-supply network cases, the designer prescribed stainless steel AISI 304 (**Table 2**). In the lists of stainless steels for use in chlorinated water conditions, Deutsches Institut für Bautechnik recommends stainless steel with the same chemical composition as AISI 304, no. 1.4301.[8]

Extensive corrosion on all the surfaces of the reservoir has shown (**Figure 2**) that it could not result from conventional chlorine shocks alone, but instead required the presence of much higher concentrations of chlorine. This reservoir was constructed of stainless steel X5 CrNi 18-10 as recommended by the Deutsches Institut für Bautechnik for structures in contact with pool water that may be highly chlorinated. In the case of the water supply, disinfection with the recommended agents was employed to destroy the bacteria of the Legionella group (**Table 1**). Since this was not successful, the disinfection was repeated several times, each time with an increased concentration of disinfectants. When it was determined that the disinfectants were not appropriate, oxidizing agents effective for the removal of biological deposits and the destruction of Legionella bacteria were introduced into the system. This resulted in a corroded internal water-supply system and poor quality of the drinking water. However, by adding an oxidizing disinfectant based on hydrogen peroxide and small amounts of colloidal silver particles, one can indeed achieve microbiological water disinfection. However, this water will also likely be organoleptically and chemically unsuitable [9] due to the resulting water-pipe corrosion.

2.2 Stainless-steel corrosion in a public swimming pool

Swimming-pool water is always chlorinated to prevent the development of adverse microorganisms. Such water is very aggressive to metals and can easily cause corrosion. Swimming-pool water also typically contains sulphates in addition to chlorine ions. In the presence of organic matter, chlorine forms chlorinated hydrocarbons, i.e., trihalomethanes, which are classified as carcinogenic substances.[10] This process can be prevented by the use of a large amount of Cl_2. The addition of a large quantity of Cl_2 is associated with a shortened contact time that prevents the formation of trihalomethanes. Residual chlorine can then be removed from the water by the addition of SO_2. This practice explains why SO_4^{-2} ions were detected in the water. However, it is important to note, that the concentration of the SO_4^{-2} in comparison with the chlorine is less important for corrosion.

Metals with a negative potential are easier to dissolve (corrode) than metals with a positive potential. It is clear that iron dissolves when in contact with chlorine. Chlorine is present in bathing water, as well as in various disinfectants and cleaning agents. The normal potential for iron is –0.44 V, while for chlorine it is +1.36 V, an absolute potential difference of 1.80 (**Table 3**).

One of the inspected cases was that of a waterslide. In its project documents, stainless-steel AISI 316 to AISI 316Ti was the prescribed material for the construction. AISI 316 stainless steel contains a chromium (Cr), nickel (Ni) and molybdenum (Mo) alloy of metals (**Tables 4 and 5** [13]). In addition, it contains small quantities of phosphorus (P), sulphur (S), as well as some other elements.

We note that in the table of stainless steels recommended for swimming-pool construction by the Deutsches Institut für Bautechnik, AISI 316 and AISI 316Ti are not listed. [8] This was overlooked by the designer, thus the resulting corrosion is not a coincidence and corrosion appeared on the stainless-steel nuts (**Figure 3**), which can endanger the the stability of structure. Due to the occurrence of corrosion, protective coatings were applied to the inappropriately chosen stainless steel. However, this did not ensure adequate protection; as shown in **Figure 4** the protective layer peeled off the protected surface and consequently the investor enforced the warranty for the waterslide structure.

Table 3: Metals typically used in construction [11,12]
Preglednica 3: Najbolj poznane konstrukcijske kovine [11,12]

Metal	Voltage /V	Metal	Voltage /V	Metal, nonmetal	Voltage /V
potassium	– 2.9	cadmium	– 0.40	silver	+ 0.80
sodium	– 2.7	cobalt	– 0.29	mercury	+ 0.86
manganese	– 2.34	nickel	– 0.25	gold	+ 1.68
aluminum	– 1.28	tin	– 0.14	platinum	+ 1.18
manganese	– 1.05	lead	– 0.12	sulphur	– 0.51
zinc	–0.76	antimony	+ 0.20	hydrogen	0.00
chromium	– 0.56	arsenic	+ 0.30	oxygen	+ 0.39
iron	– 0.44	copper	+ 0.34	chlorine	+ 1.36

Table 4: Features of the stainless steel prescribed by the designer
Preglednica 4: Lastnosti nerjavnega jekla, ki ga je predpisal projektant

W.Nr.	DIN	AISI	JUS
1.4436	X5CrNiMo 17 13 3	316	Č.45706
1.4571	X6CrNiMoTi 17 12 2	316Ti	Č.4574

Table 5: Conversion table for stainless steel AISI 316/316Ti tags to the European standard
Preglednica 5: Tebela za pretvorbo oznak nerjavnega jekla AISI 316/316Ti v evropske standardne oznake

Standards (Europe)	**Chemical composition / %**				
	P max	S max	Si max	Mo	Other elements
X5 CrNiMo 17-12-2	0,045	0,015	1	2-2,5	N 0,11 max
X6 CrNiMoTi 17-12-2	0,045	0,015	1	2-2,5	Ti=5 x C_{min}; 0,7 max

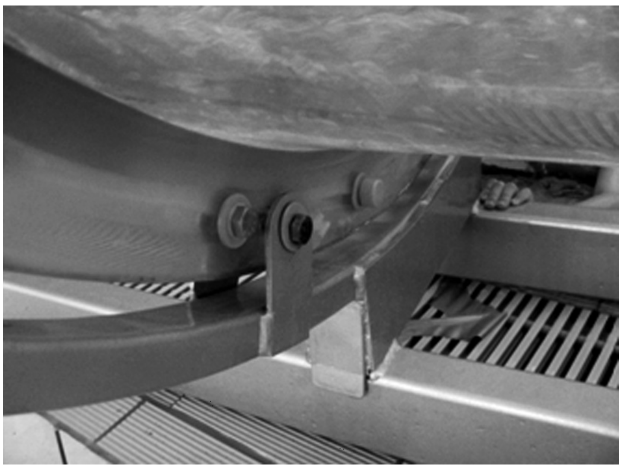

Figure 3: Corroded stainless steel nuts on the waterslide structure
Slika 3: Prikaz korozije na matici izdelani iz nerjavnega jekla na konstrukciji tobogana

Figure 4: Protective coating peeling off of stainless steel structure
Slika 4: Prikaz slabe površinske zaščite nerjaveče jeklene konstrukcije v kopalnem bazenu

3 DISCUSSION

The corrosion of stainless steel can be prevented by choosing an appropriate type of steel (steel alloys with a higher content of certain metals – Cr, Ni, Mo), by chemical treatment (pickling), thermal processing (annealing) and surface treatment (grinding, polishing). To avoid the corrosion of stainless steels, it is first necessary to respect the following rules:

– no use of tools (wrenches, pliers, vices) that were previously applied for work with non-corrosion-resistant steel,
– no use of abrasive wheels that were previously used for grinding or cutting non-corrosion-resistant steel,
– the filings of non-corrosion-resistant steel must not come into contact with the surface of the stainless steel,
– no use of cutting tools (saws, files, etc.) that were previously applied for work with non-corrosion-resistant steel,
– no use of sanding cloths and brushes that were previously used for processing non-corrosion-resistant steel.

The rules that define materials used in food processing and swimming-pool structures do not detail which materials must be used. Slovenian and EU rules define which materials can be used in facilities where they may come in contact with food. It is important to note that in this case water falls under the definition of food. Similarly, the Slovenian regulations for technical measures related to the safety of swimming pools [14] do not clearly define which materials may be used in the construction and operation of these facilities. The rules only simply state (Article 25) that.[15]

(1) All swimming pools and pool platforms must meet the requirements of SIST EN 13451, parts 1–9.
(2) Waterslides must be designed and constructed in accordance with SIST EN 1069-1 and SIST EN 1069-2.

SIST EN 13451 provides general safety requirements and test methods for swimming pools, while SIST EN 1069 -1 and SIST EN 1069 -2 prescribe safety requirements and test methods for waterslides.

4 CONCLUSION

It is evident from the cases presented that in the field of sanitary engineering the use of appropriate steel types is of paramount importance. However, even when the appropriate steel type is used and standard surface protection is applied, corrosion may still occur. In the example of the internal water-supply network shown, a protective layer of zinc had been removed due to the implementation of disinfection. A need for the repeated disinfection of the water-supply network arose from the contamination of the system with Legionella bacteria. Disinfection was executed by inappropriate methods and induced a significant corrosion of the water-supply system, while the contamination problem was not solved. Legionella bacteria could not be successfully destroyed, neither by chlorine shocks nor by thermal shocks. When inducing thermal shocks, it was not possible to reach a sufficient temperature in all the parts of the system simultaneously, thus the contamination was merely transmitted from the contaminated part to the decontaminated parts of the networks. Effective disinfection was later achieved by introducing oxidative disinfectants based on H_2O_2 and Ag into the system. However, this resulted in corrosion and lowering of the chemical and organoleptic quality of water. In the case of a public swimming pool, stainless steel of insufficient quality was used and corrosion became evident after only a few months of use. When the steel was protected with a plastic coating, this started to flake. The lesson is that stainless steel should be appropriately chosen, and protective coatings should be applied before installation.

By selecting appropriate protective coatings, corrosion can be prevented for the entire lifetime of a facility. Hot galvanized steel elements can adequately protect the steel for up to ten years or more, until the protective layer of zinc is dissolved. Polymeric coatings are also effective, but it is possible for corrosion to occur at the edges of the structural elements beneath the top layer. However, if an appropriate type of stainless steel is selected ex ante, we can remove the threat of corrosion altogether as long as the operation of the facility is performed in accordance with specified rules. The choice of high-grade stainless steel is associated with higher investment costs and lower operating costs. In the design and construction of sanitary engineering facilities, it is therefore necessary to think comprehensively about corrosion prevention, as the selection of appropriate steel types does not only provide structural strength; it can also ensure healthy drinking or bathing water, while reducing operational costs.

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