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CREVICE CORROSION OF STAINLESS-STEEL FASTENING COMPONENTS IN AN INDOOR MARINE-WATER BASIN

ŠPRANJSKA KOROZIJA PRITRDILNIH KOMPONENT IZ NERJAVNEGA JEKLA V NOTRANJEM BAZENU Z MORSKO VODO

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Equipment made from austenitic stainless steel corroded already after six months of the operation of an indoor marine-water basin. Two super chlorinations were performed during this period. Corroded stainless-steel components and different fastening components were investigated to detect the corrosion causes and improve the bathers' safety. Pitting corrosion was observed on flat surfaces, while crevice corrosion prevailed on the nuts and spring washers of bolted joints. The main reasons for the corrosion damages were: a high concentration of chlorides, a deficient control of sacrificial anodes, a lower corrosion resistance of spring washers and an inaccurate montage of some fastening components. The corrosion processes due to chloride ions can be reduced with frequent washing of all stainless-steel components with clear water and timely replacements of the sacrificing anodes.

Keywords: stainless steel, SEM, cathodic protection, chlorination, pitting corrosion, crevice corrosion

V notranjem bazenu z morsko vodo je vsa oprema, izdelana iz avstenitnega nerjavnega jekla, po šestih mesecih obratovanja začela rjaveti. V tem obdobju sta bili izvršeni tudi dve superkloriranji. Površine komponent in različni pritrdilni elementi iz nerjavnega jekla, prizadeti s korozijo, so bili preiskani zaradi ugotavljanja vzroka korozije in tudi zaradi varnosti kopalcev. Na ravnih površinah je prevladovala jamičasta korozija, špranjska korozija pa je prevladovala pri maticah, vzmetnih podložkah in pri vijačenih spojih. Glavni razlogi za korozijske poškodbe so bili kombinacija velike koncentracije kloridov, pomanjkljiva kontrola žrtvenih elektrod, slabša korozijska obstojnost vzmetnih podložk in nenatančna montaža drugih pritrdilnih komponent. Korozijske procese zaradi kloridnih ionov zmanjšamo s pogostim čiščenjem in spiranjem komponent iz nerjavnega jekla s čisto vodo in s pravočasno menjavo žrtvenih elektrod.

Ključne besede: nerjavno jeklo, vrstična elektronska mikroskopija (SEM), katodna zaščita, klorinacija, jamičasta korozija, špranjska korozija

1 INTRODUCTION

The atmosphere of the indoor basins is one of the most aggressive in a building environment. Under specific temperature conditions chlorine containing chemical species in the vapours of the pool water can condense onto the stainless-steel components and dry out. After several repetitions of this process very aggressive concentrations of chlorine-containing mixtures may build up. As the presence of marine water accelerates the chloride attack[1], the use of austenitic stainless steel alloyed with molybdenum is recommended. The situation is aggravated when the austenitic stainless-steel components are not regularly cleaned.

Galvanic or sacrificial anodes are often used for the corrosion protection of the basin equipment. Stainless-steel components are connected with wires to the sacrificing anodes absorbing the corrosion currents to the anodes as they are designed to have a more negative electrochemical potential than the equipment to be protected. A sacrificing anode[2] (made of Zn or Mg alloys) continues to corrode (sacrifice), being consumed until a replacement becomes necessary. If the anode is not replaced in time, the system loses the protective role and the corrosion processes on the components become more intensive.

Bathers also introduce contaminants into the water. Being added to the water, the chlorine hydrolyzes rapidly and produces hypochlorous acid (HOCl) and hydrochloric acid (HCl) as described by equation (1):

$$Cl_2 + H_2O \approx HOCl + HCl \quad (1)$$

Depending on the variation of the water pH the concentration of hypochlorous acid versus the concentration of hypochlorite (OCl^-) varies as well. Hypochlorous acid is weak and it ionizes at pH 7.5 and at 25 °C [3] by equation (2).

$$HOCl \approx H^+ + OCl^- \quad (2)$$

When nitrogen and HOCI combine, chloramines like monochloramine, dichloramine and nitrogen trichloride are formed according to the equations (3 to 5):

$$NH_3 + HOCl \approx NH_2Cl + H_2O \quad (3)$$

$$NH_2Cl + HOCl \approx NHCl_2 + H_2O \quad (4)$$

$$NHCl_2 + HOCl \approx NCl_3 + H_2O \quad (5)$$

The reactions (1) to (5) are in equilibrium and occur in the forward and reverse directions.

The chloramine causes the characteristic chlorine pool smell[4]. The nitrogen trichloride is more problematic in the case of a heated indoor basin because more nitrogen trichloride is vaporised[5].

Two methods are used to eliminate chloramines[6,7]: break-point chlorination and super-chlorination. The later process is known as shocking because, with an addition of chlorine, the total chlorine in the basin water rises up to an amount ten times above the normal chlorine level. This operation is performed in a basin without any bathers. The basin can be used again when the level of chlorine is back down to around 5 μg/g. In general, the super-chlorination process is harmful to stainless-steel equipment and accelerates pitting- and crevice corrosions.

Chlorine is 100 % effective when the pH of water is 5.5. Such pH is too acidic for people to comfortably swim and it also accelerates the corrosion. At a higher pH, up to 7.0, algae will grow. The pH of 7.2 is the most comfortable for swimmers; however, having a pH of 7.2 chlorine is only 50-% effective and so a free-chlorine level should be increased to a minimum of 0.6 μg/g. The pH range of the pool water should be kept between 6.8 and 8 [8].

The latest research on super-chlorination revealed that the process is effective only for eliminating inorganic, ammonia-based chloramines. It was established that large doses of free chlorine react with organic contaminants and form a variety of disinfectants that are hazardous to the swimmers' health[9].

A new indoor basin with marine water was in operation for about six months. After that period traces of rust appeared around the screws and bolts, on all the surfaces of the equipment and on the stainless-steel decorative elements. The pillars holding the roof of the hall were decorated with vertical polished stainless-steel strips. The surface was covered with numerous speckles of rust, easily removable with a cloth. Corrosion pits were present on the steel surface under the rust. An in-situ control of all the basin components revealed rusted sites around the screws in the plastic inlets for fresh water (**Figure 1**), in the frames for the underwater lights and also on the joints connecting a step with a vertical holder tube (**Figure 2**). In fact, all stainless steel parts were more or less corroded.

The aim of this investigation was to reveal the reasons for general corrosion on all stainless-steel decorative and fastening components around and in the swimming pool. The safety of bathers was endangered also because of the rusted fastening joints of the vertical stairs.

2 EXPERIMENTAL PROCESS

After only six months of the operation corrosion products were observed on all the stainless-steel components. The rusted screws on the plastic frame of the fresh-water inlet, a nut, a spring washer and a bolt from the vertical stairs were removed and investigated.

An individual stair was fixed with a plastic inlet and a bolt on the vertical stair-holder tube. The rust was spread around the bolted connection (**Figure 2**), while no rust was observed around the direct contact of a longer bolt and the step holder. The removal of the step showed that the rust originated in the joint of the spring washer and the nut. The rust was concentrated around the spring washer, below the nut and spread around the bolted joints. The spring washer was heavily corroded.

A photograph of the rusted nut, the washer and the cross-head screw was taken (**Figure 3**) before further cleaning and the rust was removed from all the investigated samples in an ultrasound bath (**Figure 4**).

The surfaces damaged with the corrosion were examined with scanning electron microscopy (SEM) Jeol

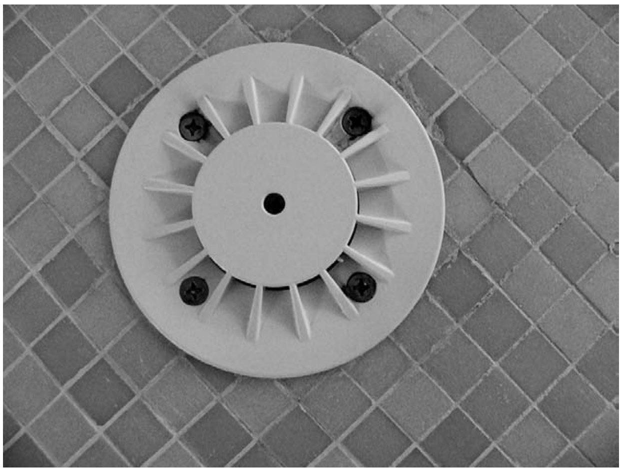

Figure 1: Rusted cross-head screws at the bottom of the pool
Slika 1: Rjasti vijaki s križno glavo z dna bazena

Figure 2: Rust on the vertical holder around the bolted-step connection
Slika 2: Rja na vertikalnem nosilcu okrog vijačenega spoja stopnice

Figure 3: A nut, a spring washer, a structural bolt of the stairs and a cross-head screw, all cowered with rust
Slika 3: Matica, vzmetna podložka, vijak stopnice in vijak s križno glavo, vsi pokriti z rjo

Figure 4: Corrosion-damaged structural components after cleaning with ultrasound
Slika 4: S korozijo prizadeti konstrukcijski elementi po čiščenju z ultrazvokom

JSM-6500F having a field-emission gun and analysed with energy dispersive X-ray spectroscopy (EDS).

3 RESULTS AND DISCUSSION

Inside the screw head we observed dip caverns (**Figure 5** and **6**) resulting from crevice corrosion. The basic conditions for the start of crevice corrosion are a wet environment with chlorides and a narrow crevice where a renewal of a damaged protective oxide layer on stainless steel is not possible due to the restricted oxygen diffusion in the crevice. Chloride ions from the salt water migrate into the crevice and increase the solution acidity accelerating the corrosion attack on the protective layer on the stainless-steel surface. The results of crevice corrosion are either deep corrosion caverns, as observed in

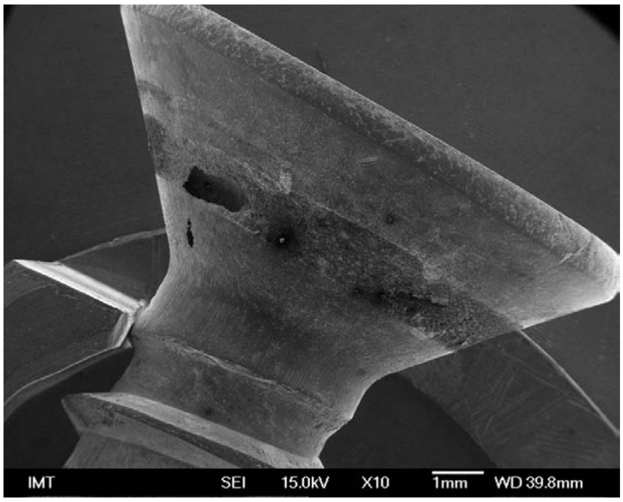

Figure 5: Screw damaged by crevice corrosion (SEM)
Slika 5: Vijak, poškodovan s špranjsko korozijo (SEM)

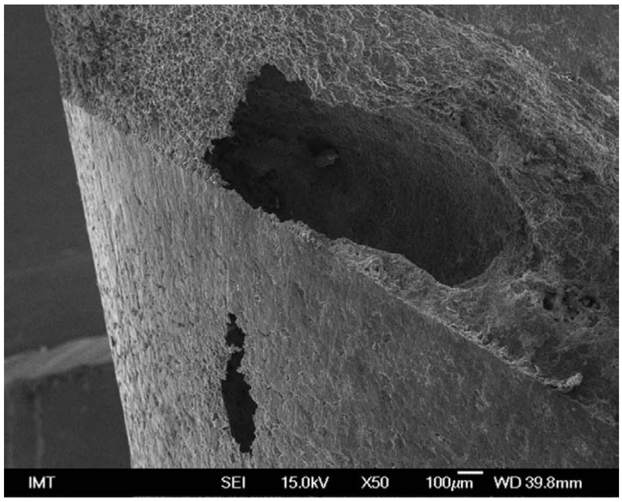

Figure 6: Detail from **Figure 5**: Crevice corrosion of a screw head (SEM)
Slika 6: Detajl s **slike 5**: špranjska korozija glave vijaka (SEM)

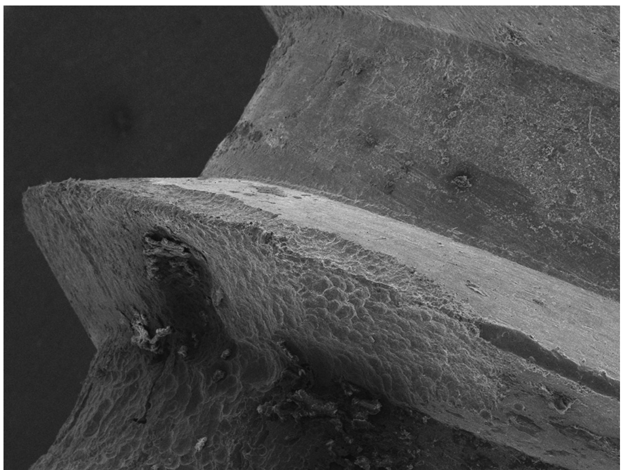

Figure 7: Corroded screw (SEM)
Slika 7: S korozijo poškodovan vijak (SEM)

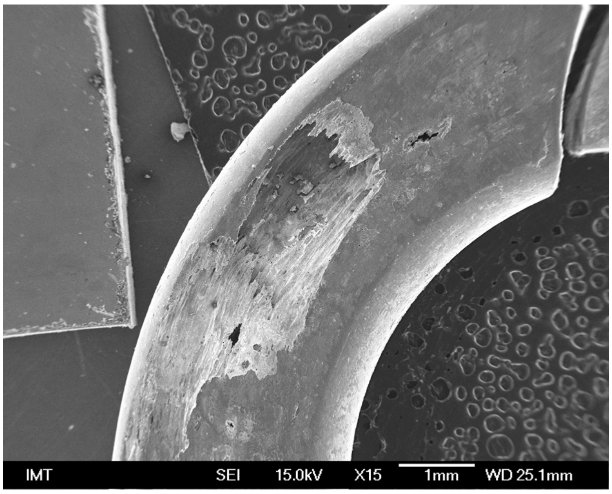

Figure 8: Crevice corrosion of a spring washer (SEM)
Slika 8: Špranjska korozija vzmetne podložke (SEM)

the screw head, or shallow pits, as observed on the screw body (**Figure 7**).

Corrosion caverns were also observed in the spring washer (**Figure 8, 9**), taken from the connection step of the vertical holder. A test of the spring washer with a magnet revealed slight magnetism in the cold-formed spring washer, probably due to the presence of deformation-induced martensite in the washer. This martensite in the austenitic stainless steel is magnetic and has a lower resistance to corrosion[9]. Deformation-induced martensite can be transformed back to austenite by heating at the temperature of 1 050 °C and by water rapid cooling. In the examined case, the spring washer was in the cold deformed state to keep the spring properties and for this reason the spring washer was the most sensitive component to corrosion. In general, there are two possible causes for the corrosion of a spring washer in a chloride environment: either crevice corrosion[10,11] due to geometrical reasons (the presence of a crevice) or stress corrosion[12] due to internal stresses in deformation-induced martensite of cold deformed steel. In the examined case it is supposed that the first cause prevailed because of the presence of corrosion caverns in the spring washer.

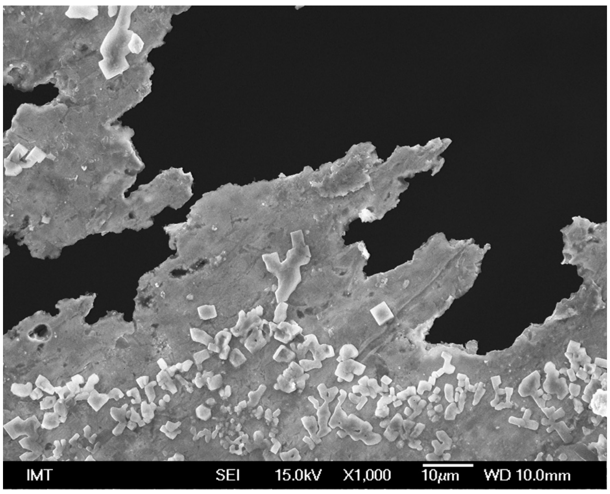

Figure 9: Remains of NaCl around a crevice-corrosion cavern (SEM)
Slika 9: Ostanki NaCl okrog izjede, povzročene s špranjsko korozijo (SEM)

The nut was from austenitic stainless steel, it was non-magnetic and after the removal of the rust the shallow pits were observed on the surface only. Comparing the corrosion damages on the nut and the spring washer, it looks that most of the rust originated from the spring washer.

The rust from the spring washer was spread also on the bolt and the bolt surface was coloured by the rust. No corrosion damages were observed on the bolt surface after being cleaned in the ultrasound bath.

An EDS analysis confirmed that the nut and the spring washer were made of austenitic stainless steel AISI 316 with 2 % to 3 % of molybdenum added to increase the corrosion resistance of stainless steel in a chloride environment.

The cross-head screw from the bottom of the basin did not contain molybdenum and was, thus, made of AISI 304 austenitic stainless steel that is less corrosion resistant in a chloride environment.

Stainless-steel components are usually corrosion protected with sacrificing electrodes made of Mg or Zn alloys. An in-situ control revealed that the sacrificing electrodes that were dissolved had neither been periodically checked nor replaced. For this reason, the austenitic stainless-steel stairs and fences were more serious attacked by corrosion.

4 CONCLUSIONS

Examinations revealed that after six months of the operation, severe corrosion damages appeared on all the stainless-steel components in the hall and in the basin with marine water.

Decorative bands, fences, the steps of vertical stairs and other austenitic stainless-steel components were damaged either by pitting or by crevice corrosion.

The spring washers and nuts were the most sensitive structural elements to corrode in the examined chloride environment.

The super-chlorination performed twice over a short period additionally increased the corrosion processes within the basin and the basin hall.

The corrosion processes due to chloride ions can be reduced with frequent cleaning of all stainless-steel components with clear water and timely replacements of the sacrificial anodes.

For the bathers' safety sake, all the vital joint connections in the vertical stairs need to be checked periodically and, if necessary, replaced in time.

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