

Corrosion of Cannon 75/27, model 1911. Déport, from the Collection of the Military Museum in Belgrade

Bore Jegdić

Scientific Associate
Institute Goša, Belgrade

Slavica Ristić

Principal Research Fellow
Institute GOŠA, Belgrade

Suzana Polić-Radovanović

Scientific Associate
Central institute for conservation, Belgrade

Ana Alilj

Research Assistant
Institute Goša, Belgrade

Vladana Rajaković-Ognjanović

Teaching Assistant
Faculty of Civil Engineering
University of Belgrade

This paper analyzes the state of the French Cannon 75/27 model 1911. Déport made of steel. The amount of non-corroded materials, the presence of cracks and other defects in the cannon were determined by the radiographic method. The composition of corrosion products were analyzed using diffraction of X-rays (XRD method). In addition to goethite $\alpha\text{-FeO(OH)}$, lepidocrocite $\gamma\text{-FeO(OH)}$ and magnetite Fe_3O_4 , the presence of akaganeite was observed in the corrosion products, $\beta\text{-Fe}_8\text{O}_8(\text{OH})_8\text{Cl}_{1.35}$ which indicates the accelerated corrosion of the base metal. With the ion chromatography method, the content of chloride, sulphate and other ions in corrosion products were examined. On the basis of conducted experiments, it can be concluded that it is necessary to treat the cannon in appropriate solutions, as quickly as possible, to remove chloride and sulphate ions.

Keywords: corrosion, akaganeite, XRD method, radiography, ion chromatography.

1. INTRODUCTION

Carbon steels without protective coatings, corrode in varying degrees when they are exposed to the external environment. A layer of corrosion products which is formed on the surface of steel is often porous, weakly adherent and easily cracked. These layers provide a little base metal protection from the effects of moisture and dissolved corrosion agents [1]. Cracks and destruction of the corrosion layers occur due to the formation of new corrosion products on steel surface whose molar volume is approximately three times higher than molar volume of steel [1-3]. Generally, carbon steels have a higher corrosion rate in the atmosphere than aluminium, copper, lead or zinc, particularly in industrial and coastal conditions [1].

A layer of corrosion products generally includes: the inner layer of black magnetite, Fe_3O_4 , which is electrically conductive and the outer layer of iron oxy-hydroxide, goethite, $\alpha\text{-FeO(OH)}$ and lepidocrocite, $\gamma\text{-FeO(OH)}$ with orange, red or brown colour of the corrosion steel products [1]. Besides the above mentioned compounds, significant amounts of amorphous materials are present in corrosive products [4-13]. Other corrosion products can be formed, depending on the ions present in the surrounding water. Dense compact layer of corrosion products is formed, on some types steel surface significantly slows corrosion rate of steel in comparison with ordinary carbon steels. The presence of small amounts of alloying elements (Cu, Mn, Cr and Ni) in steel has beneficial impact in the formation of the compact layer of corrosion products, which consist mainly of fine particles of goethite, $\alpha\text{-FeO(OH)}$ and

amorphous ferroxihite, $\delta\text{-FeO(OH)}$ [9,10,12]. This corrosion product was discovered by Misawa [4,5], and in his honour, it is called sometimes misavite [6,7]. This layer of corrosion products is a good barrier to prevent penetration of oxygen and water. The formation of a stable patina of corrosion products on the steel depends of the change cycles of wetting and drying and years may pass to form a compact patina [4-7,11, 14-17].

Chloride ions are easily transporting through the layer of corrosion products and they form as soluble iron chloride salts, and various complex compounds. These ions cause the formation of pitting and accelerated corrosion of steel and form an uneven surface. Sometimes, the chloride ions are incorporated into the layer of corrosion products and form iron oxy-hydroxide, akaganeite, $\beta\text{-FeO(OH)}$. Frequently, chemical formula of akaganeite that explicitly indicates the presence of chloride ions in the structure is $\text{Fe}_8\text{O}_8(\text{OH})_8\text{Cl}_{1.35}$ or $\text{FeO}_{0.833}(\text{OH})_{1.167}\text{Cl}_{0.167}$ [1,3,18,19]. The investigations have shown that during the corrosion of steel in solutions containing low concentrations of chloride ions, on the metal surface the layer of goethite $\alpha\text{-FeO(OH)}$ and lepidocrocite, $\gamma\text{-FeO(OH)}$ is formed. However, at higher concentrations of chloride ions, akaganeite precipitates [1-3].

Corrosion occurs in the crevice of any complex metal construction in the atmosphere. The rate of diffusion of oxygen in the crevice is limited, the oxygen concentration cell is formed and the area within the crevice is rapidly corroded. This area is anodic compared to the area outside the crevice. The acidity and concentration of dissolved metal ions in the crevice increase, causing a significant rising in steel corrosion rate [1].

2. SUBJECT OF RESEARCHING

The cannon 75/27, a model from 1911, designed by French Colonel Déport, belongs to the collections of the Military Museum in Belgrade. This model, at the time

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Correspondence to: Bore Jegdić

Institute Goša, Belgrade

Milana Rakića 35, 11 000 Belgrade, Serbia

E-mail: borejegdic@yahoo.com

of construction, was one of the most original and the most effective artillery weapons at the beginning of the twentieth century. The cannon 75/27 was the first artillery weapon with a bifurcated mount whose legs can spread. The cannon had two cradles with anti-recoil mechanism which did not follow the pipe elevation. The lower cradle remained fixed and horizontal during firing, while the top remained horizontal, but participated in the tube recoil. The return spring, as high, semicircular structure over the pipe, aided the pipe back to its original position. The great advantage of this design was in that it didn't come to overheating of recoiled mechanism (Fig.1).



Figure 1. Cannon 75/27, model 1911. Déport, shoed extraordinary results during the First World War [20].

The cannon 75/27 was the main field cannon in Italian army. Mass production was during the World War I. It was used in the Spanish Civil War too, and during World War II. A large number of copies of this artillery weapon during World War II were seized by the People's Liberation Army units.

3. EXPERIMENTAL RESEARCHES

3.1 Ultrasound and radiographic methods

By visual inspection of the cannon, covered with a layer of corrosion products, it is not possible to estimate how much metal, without corrosion, is left and if cracks and other defects are present in the material. Radiographic method [21-23] is the most reliable method to estimate the amount of core iron without corrosion products, and the types and forms of its damage [23]. That method was used in this paper.

The photo of cannon barrel was taken before the radiographic examination, and barrel wall thickness was measured by ultrasound method. It makes easier the performance of radiographic examinations. Ultrasound testings are among the most commonly applied non-destructive techniques (NDT), applying to determine the size of cracks or other defects in the metal, as well as to determine the local wall thickness of the barrel wall Cannon 75/27. For ultrasonic barrel wall thickness measurements, Krautkramer DM4 Demeter a probe 401 was used.

Radiographic method is sensitive to any discontinuities in the material, which may affect the absorption properties of the material [24,25]. Radiographic testings were carried out by using γ -rays

on defectoscope SU 50 with radioactive isotope Iridium 192. Radiographs were analyzed by placing them on an intensive source of light, which is a standard procedure. In this paper, the original radiographic images were scanned and displayed in the form of photos; so that much important information can not be seen.

3.2 XRD method

X-ray diffraction is the most frequently applied method of testing the composition and concentration of crystalline phases in the corrosive products [4-7,10,12,17-19]. Each crystal compound has a characteristic reflection spectre, obtained by measuring, which can be identified [26]. Standard data on the structure of crystalline compounds are found in databases such as the JCPDS (Joint Committee on Powder Diffraction Standards) database standard.

Samples of corrosion products, brought into the form of powder, were tested by diffractometer PHILIPS PW 1710 under the following conditions: operating voltage $U = 40$ kV, current $I = 30$ mA, X-ray radiation from anticathode copper (Cu), the wavelength of $\text{CuK}\alpha = 1.54178$ Å, graphite monochromator, the range of testing $4 - 70^\circ 2\theta$, 2θ step of 0.02, 0.5 s time constant (per step).

The data position of diffraction maximum 2θ ($^\circ$), distance d_{hkl} from inter plane values (Å) for all hkl reflections, and the corresponding relative intensities I/I_{max} are presented graphically and in the table. Besides the usual graphical charts, the other important experimental results obtained by XRD method, such as the Miller index of crystal planes of reflection (hkl) and inter plane distance (d) are presented in the table. Based on the values of I/I_{max} and d , crystalline phases are identified by comparison with JCPDS standards. Small differences of calculated values in the diagram and in the table appeared because of different algorithms for finding the diffraction peaks that are used in embedded applications. The tests were performed in the laboratory of Mining and Geology Faculty, University of Belgrade.

3.3 Ion chromatography (IC)

Ion chromatography is an analytical method used to determine of anions and cations in the aqueous solutions (drinking water, wastewater, surface water, etc.). This method is usually used for anion determination: F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , etc. The method is very sensitive, very quick and requires no additional samples preparation.

The sample of corrosion products in the form of powder, 1.362 g weight was put into demineralised water. After thirty days (to allow diffusion of chloride and other anions into water), the concentration of anions in solution was determined by the ion chromatograph Metrohm, type 861 Advanced Compact IC MSM II. The characteristics of the instrument are: PC - Compact controlled ion chromatograph for anion analysis, the detector conductivity with chemical suppression, controlled flow of 0.2 to 2.5 $\text{cm}^3 \text{min}^{-1}$, the maximum pressure of 35 MPa. The column characteristics are: Metrosep A Supp 5-150 (for anion

analysis), anionic eluent: 3.2 mmol Na₂CO₃/1.0 mmol NaHCO₃, solution for suppressor: 50 mmol H₂SO₄. All samples were filtered before analysis through a 0.45 microns filter and degassed into the ultrasonic bath, Elmasonic, type S100. Standards solutions were prepared from demineralised water and ion standard solutions. Signal and noise ratio was 3:1. The detection limit of IC columns used for fluoride, chloride, nitrite, bromide, nitrate and sulphate is 10 ppb and 30 ppb for phosphate (mg cm⁻³). The samples were analyzed in the laboratory of the Faculty of Civil Engineering in Belgrade.

4. RESULTS AND DISCUSSION

Figure 2 shows the photo of the cannon barrel during the preparation, prior to radiographic examinations. The wall thickness (in the areas where radiographic recording was done) was measured by ultrasonic method.



Figure 2. The cannon barrel preparation before the radiographic recording.

The radiogram of the upper side of the pipe shutter (Figure 3a) shows the visible grooves-vertical lines on the inner wall of the pipe. The corrosion destructions, unevenly distributed over the surface, are visible, too, as contrast differences in the radiogram. The radiogram of the lower side of the cannon barrel shutter (Figure 3b), also shows the visible-vertical line grooves on the inner surface of the pipe. It can be determined where the material is lacking and where intense corrosion damages exist.

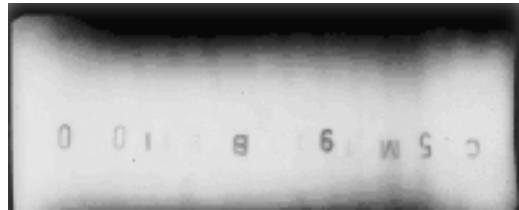
Figure 4 shows the cannon barrel fractured surface, and figure 5, the radiogram of that position. Cracking the cannon tube is probably due to an explosion in the pipe when it's firing. This is indicated by the location of the occurrence and spread of crack characteristic lines, which are still quite visible on the fracture corroded surface.

In figure 5, vertical lines can be observed on the inner surface of the pipe. The places where material is lacking or where there has been intense corrosion damage are notable, too. It is evident in the central part. In general, the cannon barrel has not been damaged so much that after the desalination treatments, removal of

corrosion products and by subsequent preservation it couldn't be in a state suitable for displaying this heratologic important exhibit.



a)



b)

Figure 3. The shutter of French cannon, a) radiograph of upper side, b) lower side.



Figure 4. Photo of section in which there was a fracture of pipe.

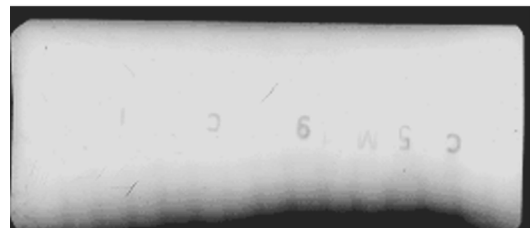


Figure 5 Radiogram of upper pipe side on the fracture position.

The corrosion products for XRD analysis were taken from the surface of the cannon tube, near the fracture place. The corrosion products were red-brown in colour. In table 1, crystalline phase detected in the corrosive products, the values of Bragg's angle (2θ), corresponding Miller indices of crystal planes (hkl), interplane distance (d) and X-ray intensity ratio (I/I_{\max}) are listed during the examination of corrosion products. It can be seen that the iron oxy-hydroxide, goethite is the most present, although akaganeite is present significantly, too.

Table 1. The values of Bragg's angle (2θ), Miller indices of crystallographic planes (hkl), interplane distance (d) and X-ray intensity ratio (I/I_{max}) obtained during the examination of corrosion products by XRD method.

	2θ (°)	Crystal plane	d _{hkl} (Å)	I/I _{max} (%)
α-FeO(OH)	17.775	020	4.986	47.62
	21.160	110	4.195	100.00
	36.705	111	2.447	66.67
	69.920	260	1.344	47.62
Fe ₃ O ₄	41.150	400	2.192	47.62
	53.195	422	1.721	47.62
	62.920	440	1.476	47.62
γ-FeO(OH)	14.035	020	6.305	47.62
	26.900	021	3.312	47.62
	33.705	130	2.513	57.14
β-FeO(OH)	11.695	101	7.561	85.71
	26.900	301	3.312	47.62
	33.310	400	2.688	47.62

Figure 6 shows XRD diagram of the crystalline phases identified in the corrosion products. The present crystalline phases are identified, based on the values of I/I_{max} and d_{hkl} and in comparison with JCPDS standards. Based on the data given in Table 1 and in Figure 6 it can be concluded that in the examined sample of steel corrosion products, the most frequent (70%) is weakly crystallized iron oxy-hydroxide, goethite, α-FeO(OH) (JCPDS 29-0713). The second phase (10%) is the iron(II,III) oxide, magnetite, Fe₃O₄, (JCPDS 19-0629). In small quantities (less than 10%) are present iron oxy-hydroxide, lepidocrocite, γ-FeO(OH) (JCPDS 44-1415) and iron oxy-hydroxide-chloride, akaganeite, β-Fe₈O₈(OH)₈Cl_{1.35}, (JCPDS 42-1315). Weak crystalline degree of the sample of corrosion products could be due to the presence of the tiny little particles goethite, α-FeO(OH), and misavite (amorphous iron oxyhydroxide, feroxyhite), δ-FeO(OH) that could not be identified by the XRD method.

The presence of akaganeite in the corrosion products indicate that they contain a significant amount of chloride ions and that the corrosive environment was acidic, which lead to active corrosion of the base metal [1-5,8,11,15,16,27-29]. On the surface of the cannon barrel a very thick layer of the corrosion products is present, consisting of easily separated sub layers. During exploitation, on the cannon surface, under a layer of the corrosion products, anodic corrosion reaction (dissolution) of steel ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$) takes place. Diffusion of atmospheric oxygen into the metal surface was difficult due to the existence of physical barriers (layers of corrosion products), so that the cathodic reaction of the oxygen reduction occurs only in the layer of corrosion products that are electrically conductive (typically magnetite). Reactions of Fe²⁺ ions with water (hydrolysis) form local acidic environment and produce the H⁺ ions. In this way, the separation

between anodic reactions (metal dissolution) and cathode oxygen reduction reaction occurred. In order to establish an electrical balance with the positive ions produced on the surface of metals (Fe²⁺ and H⁺ ions), the negative Cl⁻ ions diffuse from the surrounding environment into the layer of corrosion products, where its accumulate [1-3,15,16]. High concentration of chloride ions in the corrosion products stimulates the formation of akaganeite [1-3].

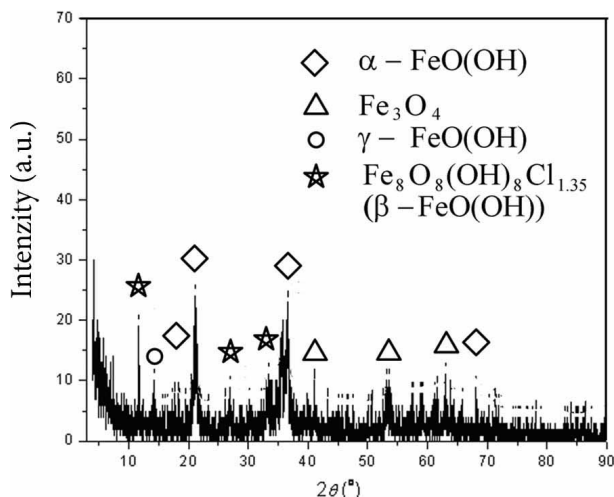


Figure 6. XRD diagram of the corrosion products taken from Cannone 75/27.

Figure 7 shows the akaganeite structure, where it the presence of chloride ions in its structure can be noticed. Chloride ions are placed in akaganeite tunnels, stabilizing its structure. Depending on the quantity of chloride ions in the corrosive products, their concentration in the akaganeite are from 2.28 to 6.4 wt.% [2.8], although Reguer et al. [18] and Stahl et al. [19] reported that content of chloride ions in akaganeite goes to the 12 wt.%.

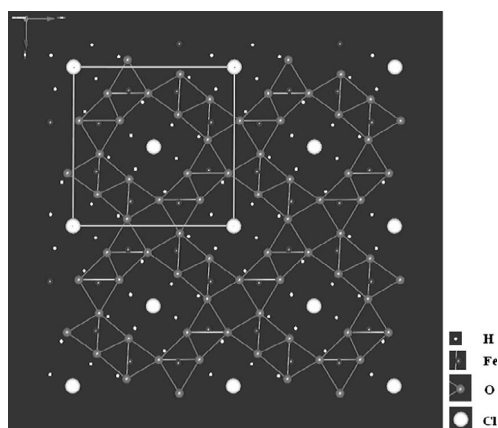


Figure 7 Structure of akaganeite (Fe₈O₈(OH)₈Cl_{1.35}) [18].

In order to determine the content of chloride ions that can be easily separated from the corrosion products, and possibly other present ions, which can be corrosion-aggressive, the method of ion chromatography was applied. This method can accurately determine the concentration of ions present in the solution obtained after their dissolution from the corrosion products. The concentration of chloride ions in the solution obtained was 2.228 mg dm⁻³ (Fig. 8), which was calculated in the mass of corrosion products is ~ 0.05 wt.%. In

addition to chloride ions, corrosion products contained a high concentration of sulphate ions (9.951 mg dm⁻³, and was calculated in the mass of corrosion products of ~ 0.18 wt. %).

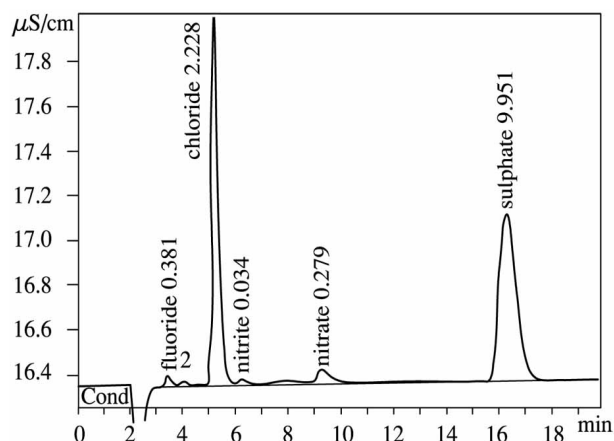
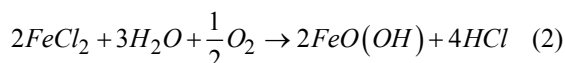
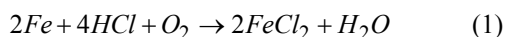


Figure 8. The results of determination the anions in corrosion products by IC method.

Ashey [30] proposed a corrosive cycle that directly shows how much chloride ions take part in the cycle of "acid regeneration" and increase the corrosion of steel:



A similar cycle of corrosion, but with the regeneration of sulphuric acid, H₂SO₄ that accelerates corrosion processes is proposed by Graedel et al. [31]. Unlike chloride ions, sulphate ions are gradually separated from the corrosion cycle, because they form insoluble iron (III) hydroxy sulphate [2,31,32].

Several formulas were proposed for estimating the corrosion resistance of the corrosion product layer, formed on steel, on the basis of its composition i.e. corrosion resistance index [11,16,17]. The most general formula is proposed by Kamimura et al. [17]. This index takes into account all the crystal phases that are formed on the surface of steel. It is the ratio of content phase weights that have protective properties (α -FeO(OH)) and phases that support the corrosion process (β -FeO(OH) + γ -FeO(OH) + Fe₃O₄). The investigated corrosion products, taken from the cannon, satisfied this criterion (Tab.1 and figure 6).

When the alloying elements during the process of corrosion cross in the border layer, they have a strong catalytic effect for the formation of compact corrosion products, even if it is moderately acidic environment [15]. In the tested cannon, a layer of corrosion products was not compact, but it was in the form of layers, which are relatively easily separated and the whole corrosion layer easily separates from the base metal. It means that the cannon metal is probably not alloyed with these alloying elements. The corrosion products also contain a significant amount of corrosion aggressive chloride and sulphate ions (Fig. 8).

All the above analyses suggest that it is necessary, as soon as possible, perform a chemical treatment for this cannon in the proper cleaning solution - desalination and removing the chloride and sulphate ions from the

corrosion products. In conservation practice, the procedures most applied are dipping in chemical solution NaOH with concentration of 0.1 to 0.5 mol dm⁻³, at room temperature [3,9,21,33-35] or in alkaline solution of Na₂SO₃ [3,8], where the duration of treatments is several weeks. Also, cathode electrochemical treatment [3,9,28] or thermal desalination treatment is sometimes used usually in an inert atmosphere at moderately high temperatures [36], with additional washing in alkaline solutions. During the desalination processes in solution, the concentration of separated chloride ions is continuously measured by potentiometric titration with AgNO₃, using as an indicator the Ag electrode, potentiometric titration with use of ion selective electrode or ion chromatography method [37]. The results presented in this paper were obtained using the ion chromatography method, because it has the highest accuracy of all the aforementioned methods and allows with only one experiment to determine the presence of practically all the anions present in solution.

Figure 9 shows the photo of the cannon, of the same series, after all cleaning phases and conservation.



Figure 9. The French cannon of the same series after preservation.

5. CONCLUSION

In this paper is analyzed the state of Cannon barrel 75/27, model 1911. Deport, made of steel from the collections of the Military Museum in Belgrade. The amounts of non corroded materials as well as the presence of cracks and other defects in the cannon were determined using radiographic method. The composition of corrosion products was analyzed using X-ray diffraction (XRD method). The presence of chloride and other anions in corrosion products were determined using ion chromatography (IC method).

In addition to the common corrosion products of steel, goethite, α -FeO(OH), lepidocrocite, γ -FeO(OH) and magnetite, Fe₃O₄, the presence of akaganeite, β -Fe₈O₈(OH)₈Cl_{1.35}. was observed on the object. The presence of akaganeite in the corrosion products is usually a sign of active corrosion of the base metal. Also, the corrosion products had low degree of crystallinity, indicating that the amorphous phases were present as iron oxy-hydroxide, feroxyhite, δ -FeO(OH), which can not be identified using XRD method.

The fracture of the cannon barrel was probably due to an explosion of the barrel when its firing. This is indicated by the location and characteristic line of the crack spread, which is still visible on the fracture surface.

Based on the presented experiments, it can be concluded that the cannon can be still restored. It is necessary to put it in the appropriate treatment solution as soon as possible to remove chloride and sulphate ions. Also, after removing the remaining corrosion products, it is necessary to perform its conservation.

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**КОРОЗИЈА ТОПА 75/27, МОДЕЛ 1911. ДЕПОРТ
ИЗ КОЛЕКЦИЈЕ ВОЈНОГ МУЗЕЈА У
БЕОГРАДУ**

**Боре Јегдић, Славица Ристић, Сузана Полић-
Радовановић, Ана Алил, Владана Рајковић-
Огњановић**

У овом раду анализирано је стање француског топа 75/27 модел 1911 Déport израђеног од челика. За одређивање количине некородиралог материјала, присуства прелина и других дефеката у експонату коришћена је радиографска метода. Састав корозионих продуката је анализиран методом дифракције рендгенских зрака (XRD). Поред гетита, α -FeO(OH), лепидокрокита, γ -FeO(OH) и магнетита, Fe₃O₄, на експонатима је уочено присуство акаганита које указује на активну корозију основног метала. Методом јонске хроматографије је одређен садржај хлоридних и других аниона у корозионим продуктима. На основу изведених експеримената намеће се закључак о неопходности третмана топа у одговарајућим растворима што је могуће пре у циљу уклањања хлоридних и других корозионо активних јона.

