TECHNICAL TRANSACTIONS | CZASOPISMO TECHNICZNE
MECHANICS | MECHANIKA

5-M/2016

DOI: 10.4467/2353737XCT.16.283.6115

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VOLCANIC TUFF AS AN INHIBITOR OF CORROSION IN AQUEOUS ENVIRONMENT

TUF WULKANICZNY JAKO INHIBITOR KOROZJI W ŚRODOWISKU WODNYM

Abstract

The aim of the studies was to examine the applicability of volcanic tuff as a corrosion inhibitor in aqueous systems and to identify the mechanisms owing to which the tuff is acting as an inhibitor of corrosion. The scope of research includes: examinations of the structure and selected properties of the tuff from Filipowice, including fractographic examination of the Filipowice tuff rocks, X-ray diffraction analysis, and thermal analysis; study of the corrosion resistance of DC01A low-carbon steel in aqueous systems without and with inhibitor, which is volcanic tuff.

Keywords: corrosion, inhibitors, volcanic tuff

Streszczenie

Celem badań było określenie możliwości zastosowania wulkanicznego tufu jako inhibitora korozji w środowiskach wodnych oraz określenie mechanizmów, które powodują, że tuf wulkaniczny działa jako inhibitor korozji. Zakres badań obejmuje: badania struktury i wybranych właściwości tufu z Filipowic, w tym faktograficzne badania tufu w postaci skał, analizy dyfrakcji rentgenowskiej i analizy termicznej; badanie odporności na korozję DC01A stali niskowęglowej w środowiskach wodnych bez oraz z inhibitorem, którym jest tuf wulkaniczny.

Słowa kluczowe: korozja, inhibitory, tuf wulkaniczny

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1. Introduction

Inhibitors are commonly used in the anticorrosion technology as agents reducing the rate of corrosion in metals and their alloys. Corrosion inhibitors can be divided into different groups, depending on the type of environment, the mechanism of action, the type of film (protective barrier) formed on the metal surface, and the type of material used in the inhibitor (organic, inorganic).

In terms of the type of environment in which they operate, the inhibitors can be divided into inhibitors active in aqueous solutions, in the air, and in organic liquids. The first and the largest group of inhibitors includes the inhibitors active in natural and industrial waters, and in solutions of salts, acids and bases [1].

In terms of the mechanism of the electrochemical action of inhibitors forming protective barriers on the metal surface, the inhibitors can be divided into the following types [2]:

- cathodic inhibitors – inhibit the cathodic process of depolarization,
- anodic inhibitors – inhibit the anodic process of metal dissolution,
- mixed inhibitors – affect both electrode processes, and are mainly adsorption inhibitors.

In terms of the nature of the protective barrier formed on the metal surface, adsorption inhibitors can be subdivided into inhibitors entering into reaction with metals by forces: chemical (chemisorption) or physical (physical adsorption) – due to the weak interaction, the latter type is not used in practice.

Corrosion inhibitors mainly operate through a mechanism called the anode passivation, although in their operation there are also other elements involved. As a result of an electrochemical process, inhibitors in the water with protecting liquid are guided to the anode and cathode, and are chemically absorbed on the surface. The resulting layer forms a barrier that effectively isolates the anode from the water in circulation and from contact with the cathode. This slows down the corrosion rate to a low level, usually about 100 or 1000 times lower than the corrosion rate in water without protecting liquid [3].

The passive layer undergoes continuous breaking and reconstruction and its presence depends on the continuous presence of the inhibitor in water, as its task is that of constant repair of the passive layer. With the lack of inhibitor, the protection against corrosion becomes immediately ineffective.

The value of pH – acidic or basic reaction of installation water – also plays a significant role in the corrosion of metals. For example, iron and steel corrode rapidly in an acidic environment, but not under alkaline conditions. The corrosion rate is affected by the type of corrosion product formed under various pH conditions. In an alkaline environment, iron and steel corrode to form Fe_3O_4 magnetite, which acts as a semi-protective layer on the metal surface reducing the rate of corrosion.

1. Silicates – inhibitors of cathodic-anodic type

Silicates have the general formula $\mathbf{Me_2OxSiO_2}$, where x is the molar silica-to-alkaline oxygen ratio. Sodium silicate solutions with a high modulus (high ratio of SiO_2 to Na_2O) contain the following particles [1]:

1) ions of Na^+, OH^-, SiO_3^{2-}, $n(Si_2O_5^{2-})$, $HSiO_3^-$
2) particles of Na_2SiO_3, $Na_2Si_2O_5$, H_2SiO_3, SiO_2nNaOH

3) complex compounds of $(SiO_3)x$, $(H_2SiO_3)x(SiO_2)x$, $(SiO_2)x$, $[(mSiO_3nSiO_2xH_2O)^m]^{2-}$ $(SiO_2xnH_2OySiO_3)$ and other compounds.

Silicates are cheap and popular inhibitors used primarily for the protection of water systems. The corrosion rate in the presence of silicate inhibitors is, however, higher than in the case of chromates [4]. On the other hand, silicates are not toxic in the concentrations normally used, do not confer to water taste, color or odor, eliminate the formation of "red water" and can be applied to systems already partially corroded. Like polyphosphates, silicates reduce the rate of corrosion not only in iron and its alloys, but also in other metals such as Al, Cu, Pb and Zn, in their respective alloys and bimetallic systems [5–7]. Silica concentration required to inhibit corrosion varies within wide limits depending on the type of metal and the composition of water, e.g.:

- crystalline silica – inhibits soft steel corrosion in a variety of cooling water types,
- sodium silicate – reduces the rate of corrosion in tap water by 82% [4],
- the ability of sodium silicate to move the corrosion potential in the negative and positive side, depending on the concentration, indicates that this inhibitor affects both the cathodic and anodic process; silicates added to the solution at higher concentrations result in inhibition of the anodic process, which means that the inhibitor may reduce the rate of the cathodic reaction of oxygen reduction and the anodic reaction of iron dissolution. So it is an inhibitor acting on both the anodic and cathodic process,
- due to their alkaline reaction in aqueous solutions, the effect of silicates does not mainly consist in the neutralization of CO_2 dissolved in water, but in spite of this, the adjustment of the solution pH using silicates provides a much better protection against corrosion than when the same pH value is obtained with the addition of a base alone, such as NaOH.

There is a general belief that silicates inhibit metal corrosion due to the formation of a protective layer on the surface of metals. There are two hypotheses regarding the formation of this layer in the presence of silicate:

- **First** – assumes a chemical reaction taking place between the metal ions or metal corrosion products and negatively charged ions of the silicate or colloidal silica particles, as a result of which iron silicates are formed [8, 9]. The role of silicates would thus consist in creating a protective layer on partially corroded iron, and so on iron on the surface of which there are iron oxides and hydroxides. The most widely accepted is the opinion that positively charged iron hydroxide removes water from negatively charged colloidal silica to deposit a protective film composed of both these substances.
- **Second** – assumes a neutralization of the oppositely charged particles of corrosion products and negatively charged silicate hydrolysis products. These particles undergo coagulation and a protective gel-like layer form on the metal surface [10] – according to this hypothesis, the mechanism of the protective film formation is not associated with the formation of iron silicates.

On a clean surface of iron or steel, silica in water is not deposited [11]. A necessary condition for the formation of a protective film is the presence of iron oxides and hydroxides on the surface, and therefore to make it possible for the silica to act as an inhibitor, the metal must first undergo corrosion. Therefore, the inhibitory effect of silica is often observed after the lapse of several days from the time of the first contact between the steel and the solution

[12, 19]. The mechanism of the action of silicate inhibitors in water is a very complex one and has not yet been clearly explained. It is generally believed that this mechanism is associated with the formation of thin film on the surface of metal. The protective properties of the film depend on the nature of corrosion products present on the surface of metal. The products of corrosion, which are hydrated oxides, capture from the solution the negatively charged particles of hydrated silica sol. As a result of this process, the initial film of a gelatinous structure is formed, and on its surface, a portion of the mechanical suspension present in water may be adsorbed. In this case, since both water and the film have an alkaline pH, iron and components responsible for the water hardness are deposited on the film. The composition of the protective layer can change, but nevertheless, it will always contain variable amounts of silica. Its structure is close to a silica gel, which means that in a wet state it is semi-permeable, while in dry state it forms a thin film, usually of a brownish color or resembling graphite in appearance. The formation of protective film inhibits corrosion and at the same time reduces further growth of the film. In this way, the thickness of the film is self-regulated and is typically about 0.002 mm. The film is regenerated automatically in the event of a partial removal or damage. Metal undergoes corrosion, and in this place, a fresh film is formed, provided silicates in an appropriate concentration are present in the water. In terms of the physico-chemical phenomena, the mechanism of the film formation is complex – besides the effect of absorption, other mechanisms are operating like chemisorption, ion exchange and coagulation of the sol [13].

The time of formation of the protective film is relatively long, and depending on the concentration of silicate in water, it ranges from several days to several weeks. The protective effect is achieved only after some time.

2. Purpose and scope of research

The aim of the studies was to examine the applicability of **volcanic tuff** as a corrosion inhibitor in aqueous systems and to identify the mechanisms owing to which the tuff is acting as an inhibitor of corrosion.

The scope of research includes:

- examinations of the structure and selected properties of the tuff from Filipowice, including fractographic examination of the Filipowice tuff rocks, X-ray diffraction analysis, and thermal analysis,
- study of the corrosion resistance of DC01A low-carbon steel in aqueous systems without and with inhibitor, which is volcanic tuff.

3. Volcanic tuff – composition and properties

Volcanic tuff is porous rock belonging to the family of clastic rocks, which consist of pyroclastic material, often with admixture of other clastic materials, cemented with e.g. silica or clay binder. The characteristic feature of tuff is high porosity and the associated low specific gravity.

Tuff may be of crystaloclastic, lithoclastic or vitroclastic character. Crystaloclastic tuff is mainly composed of single pyrogenic minerals, like quartz, sanidine, biotite. Lithoclastic tuff is composed of effusive rock fragments of different sizes. Vitroclastic tuff consists entirely of glass. The most common is mixed crystalo – litho – vitroclastic tuff [14].

The Permian tuff from Filipowice characterized by a crystalo – litho – vitroclastic properties also contains impurities, i.e. fragments of sedimentary rocks mainly limestone. It occurs in the vicinity of Krzeszowice, among others, in Filipowice wherefrom its name derives. It is a pink-colored rock with bright spots, highly porous, with characteristic randomly arranged automorphic crystals of biotite. The fresh tuff is soft, when dry, it becomes hard and very brittle. It is easy to process and highly valued as a building material resistant to atmospheric conditions.

The tuff in the Sudeten Mountains has a composition similar to the tuff from Filipowice (it occurs frequently in the Rotliegend formations). Dark-colored basalt tuff occurs near Wałbrzych, Nowa Ruda and in Lower Silesia.

The tuff from Filipowice includes the following components: sanidine (the predominant component– Fig. 1, 2), kaolinite, biotite, illite, quartz, heavily modified feldspar, crushed alien rocks, opaque minerals, microcrystalline binder and carbonate binder.

Table 1

Composition of oxides in a sample of tuff from Filipowice used in the present studies

SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O	Other
56.04%	5.38%	16.73%	5.39%	0.60%	0.85%	9.16%	0.39%	5.46%

Fractography and EDS analysis of the Filipowice tuff rock

Structural and fractographic studies of the Filipowice tuff rock fragments were performed on a JSM-5510LV scanning electron microscope (made by Jeol Company) with (EDS) X-ray microanalyser. Quantitative analysis of the elemental composition was also conducted.

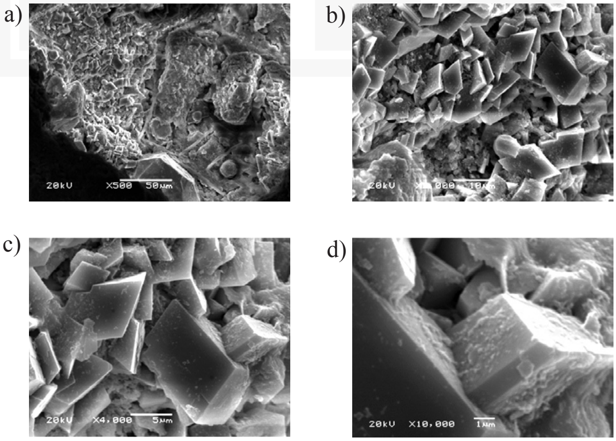
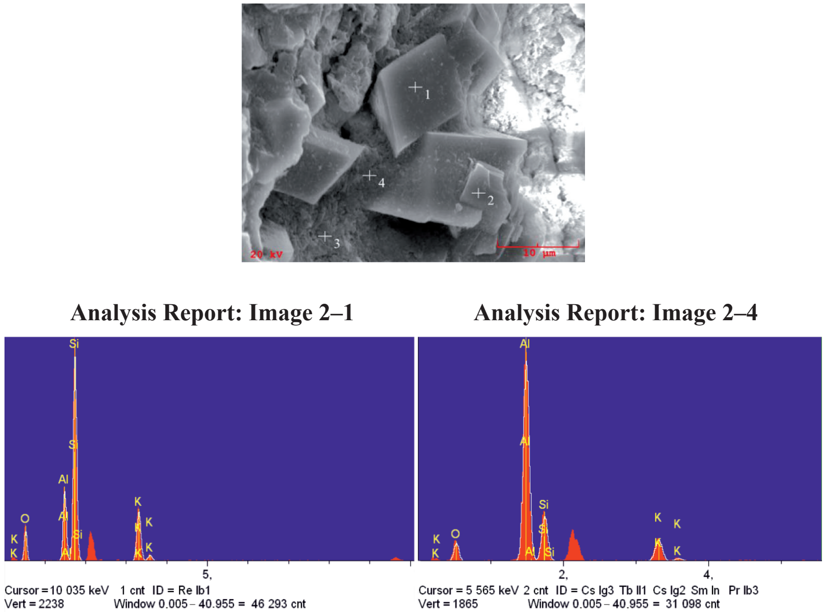


Fig. 1. Porous structure of Filipowice tuff – rhombohedral crystals of potassium feldspar:
a) – 500 x, b) – 2 000 x, c) – 4 000 x, d) –10 000 x



Analysis Report: Image 2–1

Analysis Report: Image 2–4

Fig. 2. Crystals of potassium feldspar embedded in a microcrystalline binder – EDS analysis

Studies by SEM and (EDS) X-ray microanalysis have shown that, besides sanidine, the tuff from Filipowice also contains quartz, kaolinite, illite, biotite and possibly allophane.

X-ray diffraction analysis

Phases present in the tuff were examined with X-PERT Philips PW 1830 X-ray diffractometer using tube with the following operating parameters: voltage = 40 kV, current = 30 mA.

The test product was pulverized natural tuff.

The X-ray diffraction analysis of tuff from Filipowice in natural condition revealed the occurrence of two main phases (Fig. 3):

- potassium aluminosilicate $K(AlSi_3O_8)$,
- silica SiO_2.

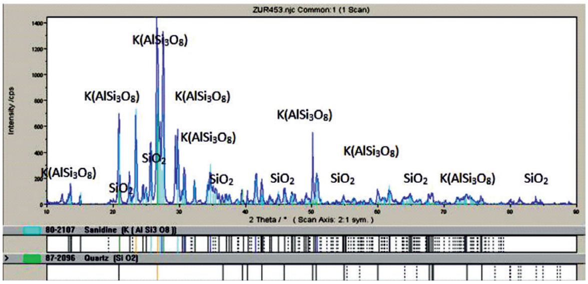


Fig. 3. The diffraction pattern of natural tuff powder

Thermal analysis

Thermal activation of aluminosilicates, conducted at low and high temperatures, leads to significant changes in both structure and texture. The increased temperature leads to dehydration, dehydroxylation and crystallization of new phases. For example, minerals from the kaolinite group, depending on their mineralogical nature and heating time, undergo dehydroxylation in the temperature range of 500–900^{o}C. Consequently, kaolinite is formed, the structure of which is composed of disturbed tetrahedral layer and deformed aluminum octahedra [15].

The differential thermal analysis (DTA) and thermogravimetric studies (TG) were performed. The analysis was carried out using a NETZSCH STA 409 CD QMS 403/5 Skimmer mass spectrometer (Fig. 4–6).

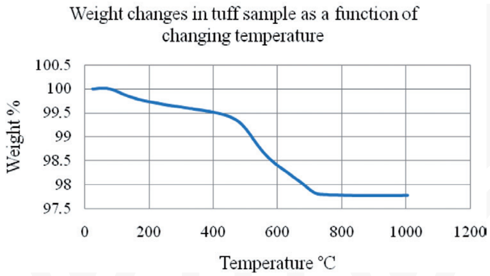


Fig. 4. The results of thermogravimetric studies

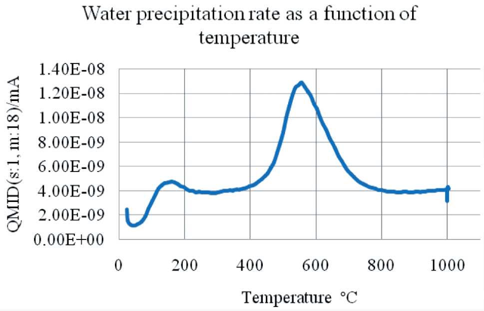


Fig. 5. The rate of water precipitation as a function of temperature

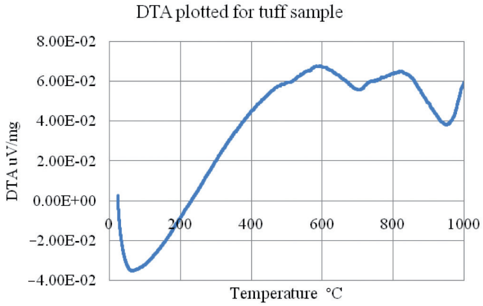


Fig. 6. Thermal effects accompanying transformations taking place in tuff under the effect of temperature

As shown by the thermographic analysis, biggest changes in the weight of natural tuff (powder) occur at a temperature of 702°C, and the weight loss is 2.3%. Water precipitates from the sample at temperatures ranging from 100 to about 820°C and the maximum precipitation rate occurs at about 550°C. It is a well-known fact [16–18] that in the process of thermal treatment, water is gradually removed from the aluminosilicate. In the temperature range from 105°C to 130°C, hydroscopic water is removed, at temperatures ranging from 180°C to about 500°C – water of crystallization, and at a temperature higher than 350°C – zeolitic water. In the case of tuff from Filipowice, the zeolitic water was removed in a temperature range of up to 820°C.

The differential thermal analysis has shown that phase transformations occur in the sample during heating at 468°C, 594°C and 818.7°C (exothermic transformations) and at 702°C and 949.3°C (endothermic transformations).

4. Testing the steel corrosion resistance in an environment of water and in 3% NaCl solution

The aim of the studies was to observe the behavior of DC01 low-carbon structural steel in accordance with PN-EN ISO 1514:2005 in aqueous systems with and without the addition of thermally activated volcanic tuff. The tuff was crushed and milled to an average particle size of 40. Thermal activation of Filipowice tuff was conducted at 850°C for 4h. Laboratory tests in liquids and solutions were carried out by the gravimetric method at ambient temperature. Tests were performed in the following media:

- water,
- 3% NaCl solution,
- water with 7 g of tuff per 1 dm^3 of solution at 20°C,
- 3% NaCl solution with 7 g of tuff per 1 dm^3 of solution at 20°C.

Studies were carried out on standard samples with dimensions of 50 × 40 × 0.8 mm, which, before the tests, were degreased with carbon tetrachloride, and then were placed in a measuring vessel with respective solution. Samples were placed in the vessels with solution in a hanging position. Measurements were going on for 60 days.

The samples, after removal from the solution and the subsequent washing and drying, were weighed and their surface was examined by SEM and EDS X-ray analysis. For comparison, the same examinations were also carried out on samples prior to immersing them in the solution.

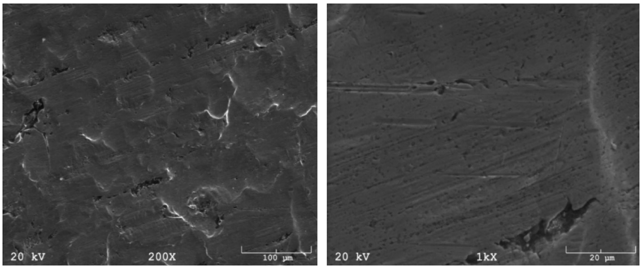


Fig. 7. Steel sheet surface before immersing in the solution

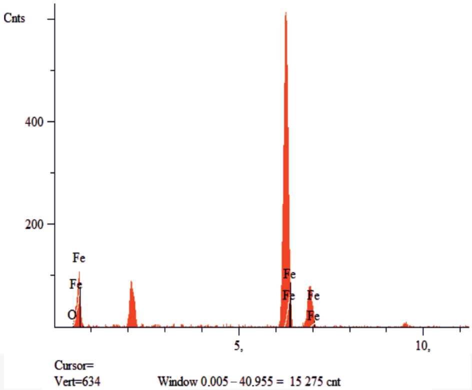


Fig. 8. EDS analysis conducted on sample before immersing in the solution

The EDS analysis (Fig. 8) has shown that the sample, which was not immersed in the solution, contained only iron, manganese and oxygen. The oxygen content ranged from 1.1 to 2.2%.

The results of corrosion tests in an aqueous environment

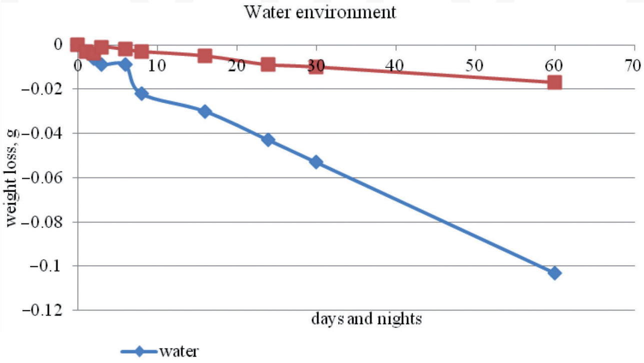


Fig. 9. The weight loss of samples in water – series 1 and in water with the addition of tuff – series 2

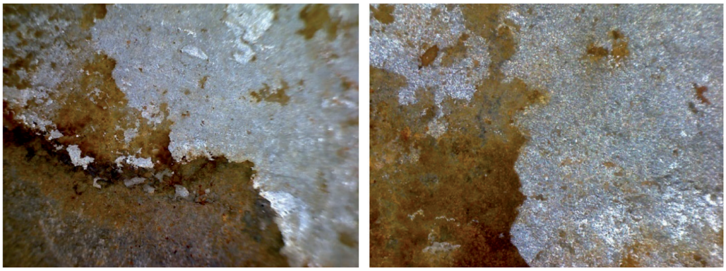


Fig. 10. Steel sheet surface after 60 days of exposure to water environment (40x and 200x)

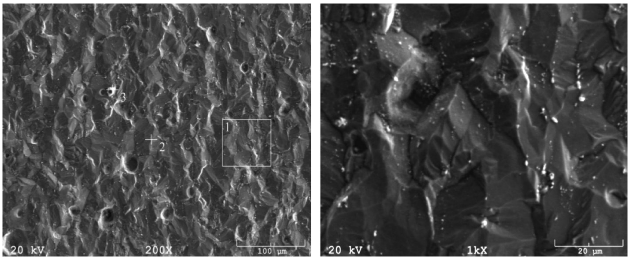


Fig. 11. Steel sheet surface after 60 days of exposure to water environment – sample taken out from water and washed

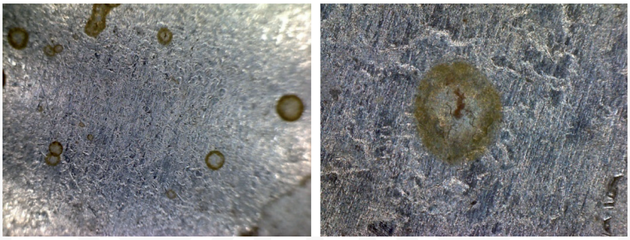


Fig. 12. Steel sheet surface after 60 days of exposure to water + tuff environment – sample taken out from water (40x and 200x)

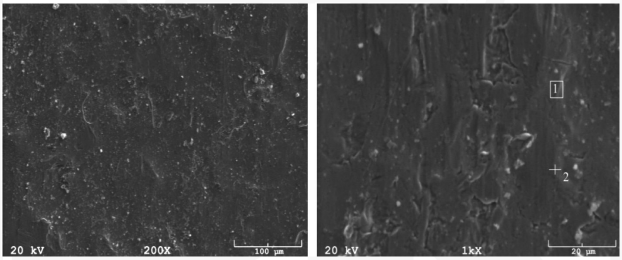


Fig. 13. Steel sheet surface after 60 days of exposure to water + tuff environment

The results of corrosion tests in a seawater environment

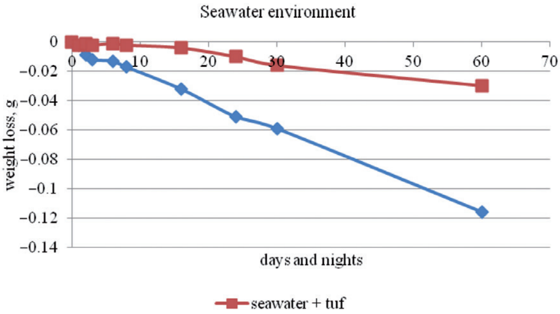


Fig. 14. The weight loss of samples in seawater – series 1 and in seawater with the addition of tuff – series 2

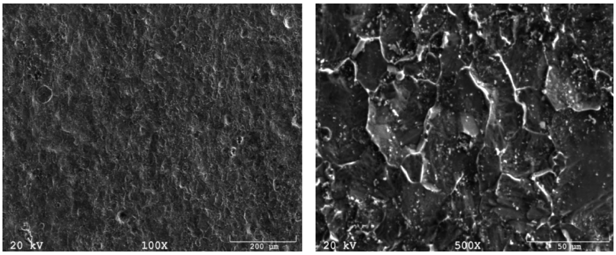


Fig. 15. Steel sheet surface after 60 days of exposure to the effect of 3% NaCl solution – sample taken out from the solution and washed

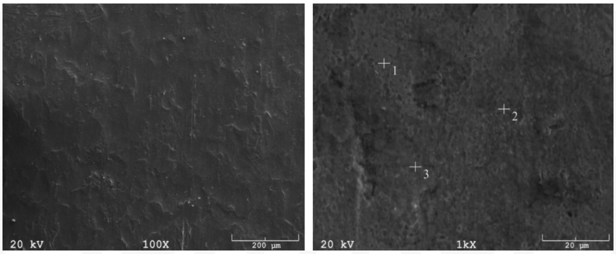


Fig. 16. Steel sheet surface after 60 days of exposure to the effect of 3% NaCl solution+ tuff – sample taken out from the solution

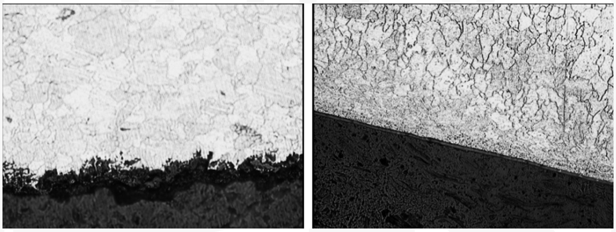


Fig. 17. Steel sheet immersed in 3% NaCl solution with the addition of tuff, the exposure period – 60 days; transverse metallographic section, 100x, specimens etched with 4%HNO_3

In water with the addition of tuff (Fig. 9–13), samples of low-carbon steel showed an average weight loss six times lower than the samples placed in water without tuff. In 3% NaCl solution with the addition of tuff (Fig. 14–17), samples showed an average weight loss four times lower than the samples placed in seawater without tuff.

As a result of tuff addition to water and 3% NaCl solution where samples of the low-carbon structural steel were placed, the appearance of the samples changed as well as the depth of corrosion layer from the developed with deep pitting to a flat silver-colored surface with visible coating of protective layer. Examinations made on transverse metallographic sections of these samples revealed the presence of a protective layer. On the metal surface exposed to the effect of water with the addition of tuff and to the 3% NaCl solution, minor signs of corrosion were observed. Examinations carried out under a stereoscopic microscope showed that this was due to microcracks formed in the protective layer.

Surface examinations by SEM and EDS X-ray microanalysis

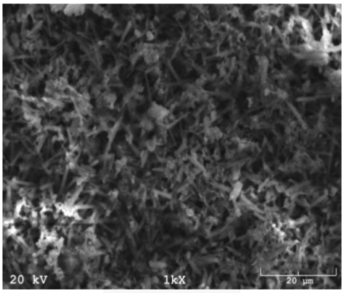
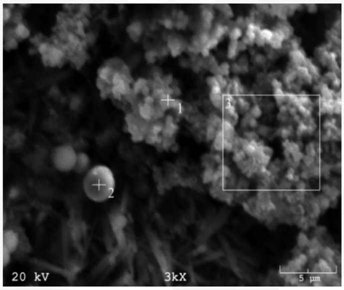
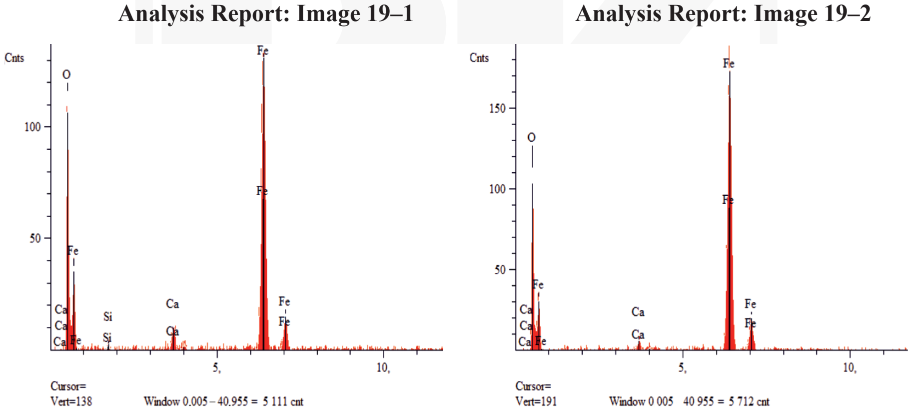


Fig. 18. A layer of film deposited on the steel sheet surface after 60 days of exposure to water environment



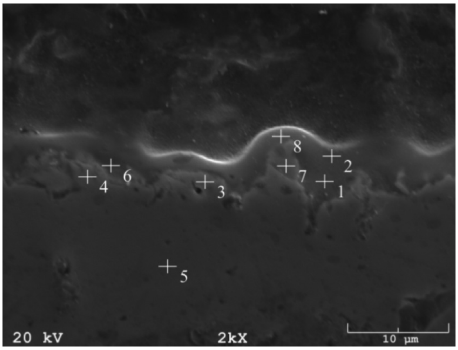


Analysis Report: Image 19–1

Analysis Report: Image 19–2

Fig. 19. A layer of film deposited on the steel sheet surface after 60 days of exposure to water environment – EDS analysis

Figures 18 and 19 show a layer of film deposited on the steel sheet surface after 60 days of exposure to water environment.



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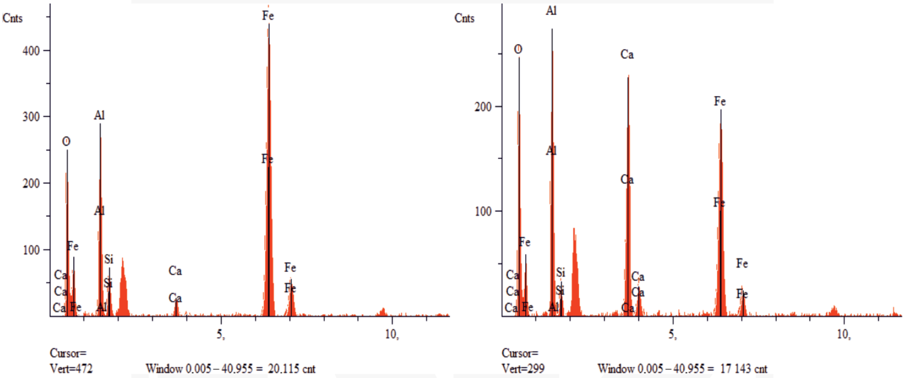

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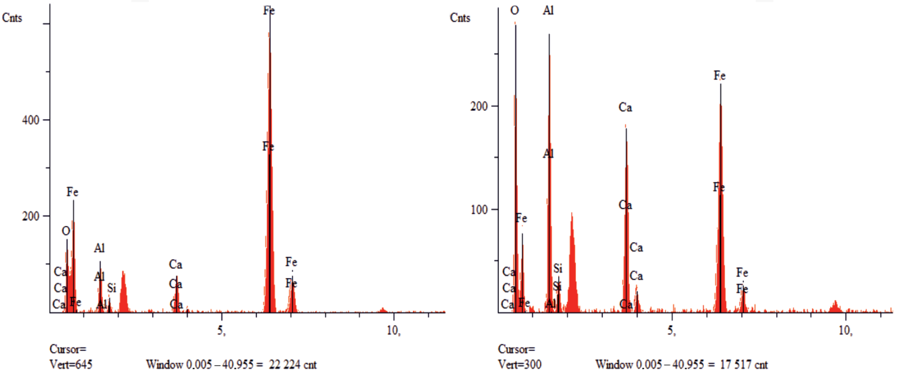
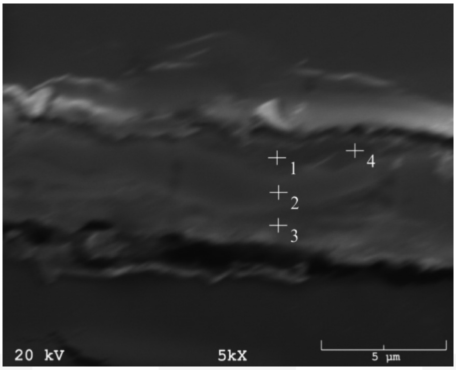
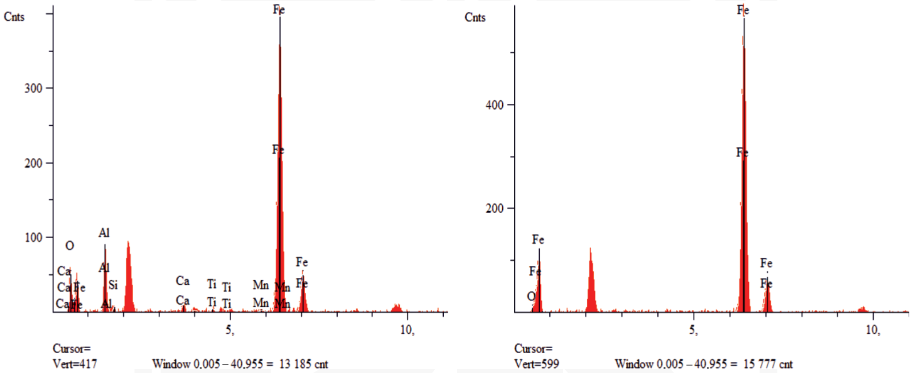


Fig. 20. Steel sheet immersed in water with the addition of tuff, the exposure period in water – 14 days; transverse metallographic section. Visible is the layer of thickness from 2 to 4 µm. EDS analysis



Analysis Report: Image 21–1 **Analysis Report: Image 21–2**



Analysis Report: Image 21–3 **Analysis Report: Image 21–4**

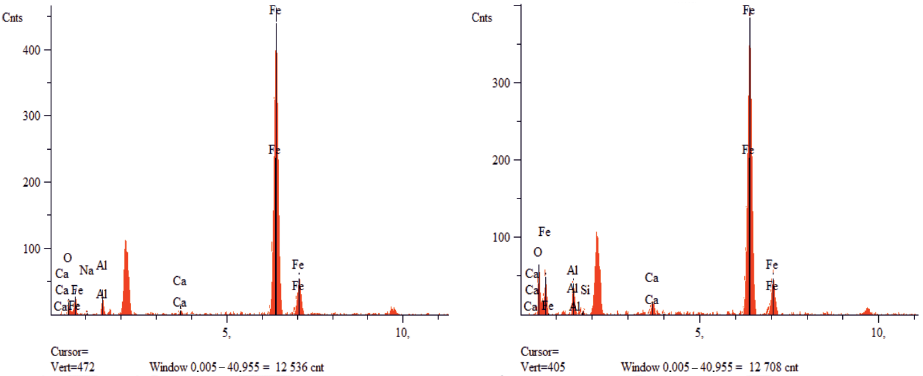
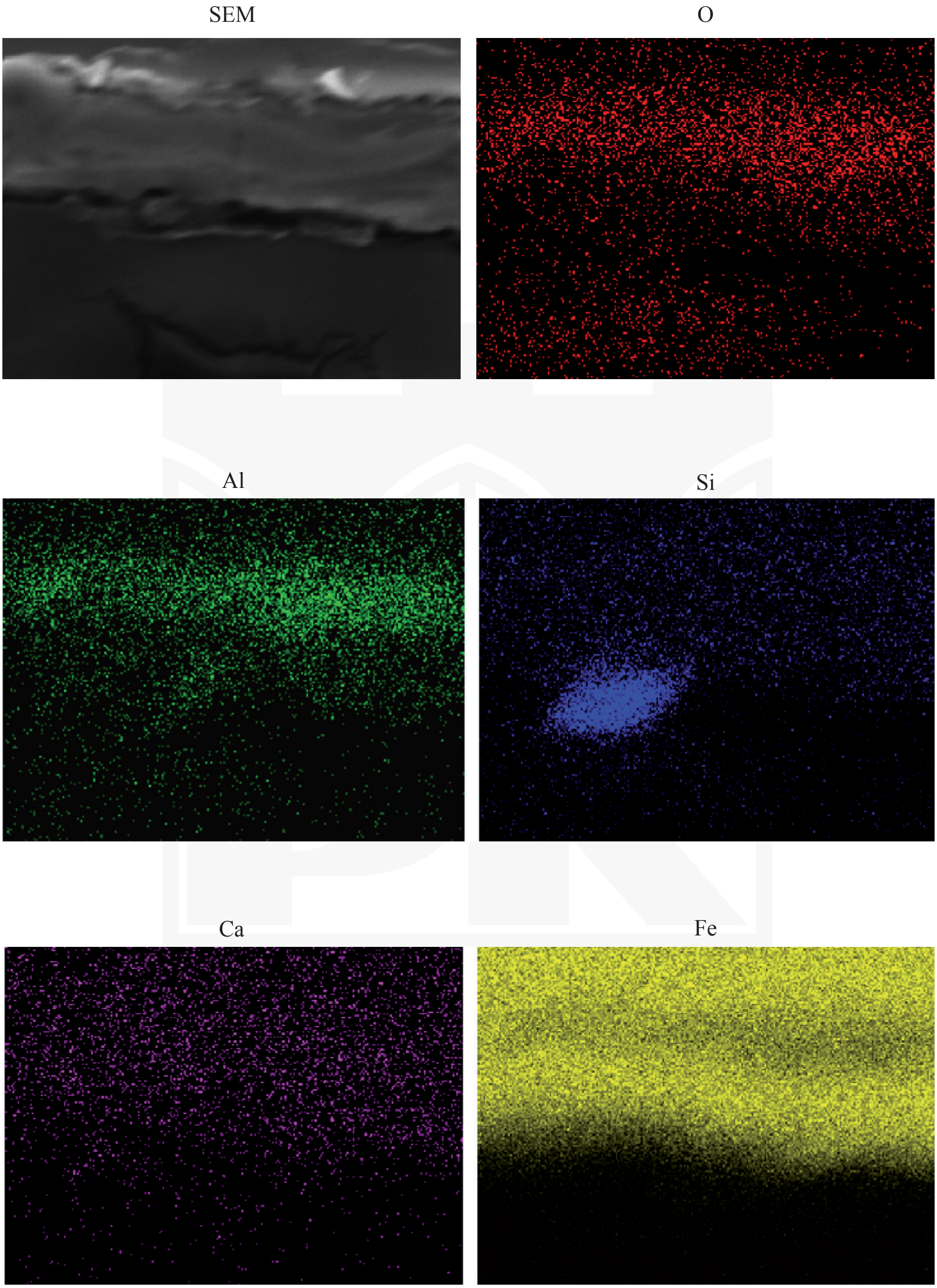


Fig. 21. The cross section of water + tuff sample (after 60 days). EDS analysis



SEM

O

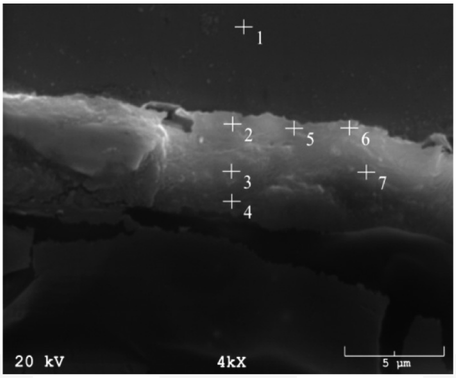
Al

Si

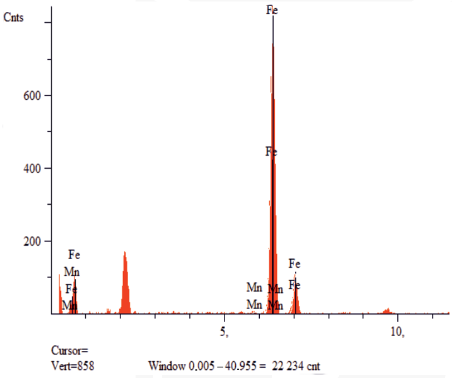
Ca

Fe

Fig. 22. The cross section of water + tuff sample (after 60 days) – the distribution of elements: O, Al., Si, Ca, Fe



Analysis Report: Image 23–1



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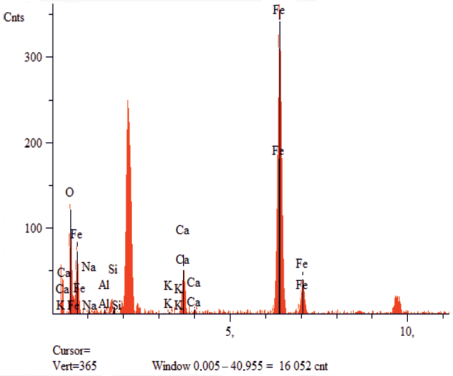

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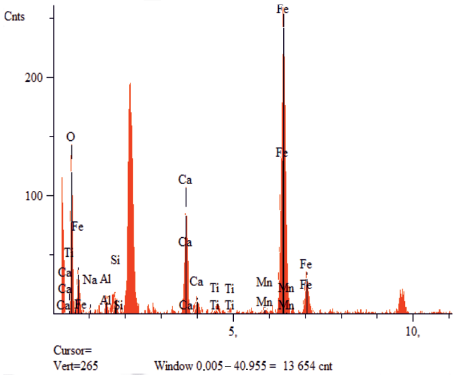


Analysis Report: Image 23–4

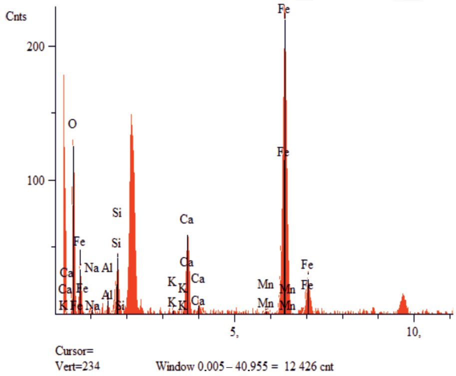


Fig. 23. Steel sheet – 3% solution of NaCl + tuff (after 14 days), the transverse metallographic section. EDS analysis

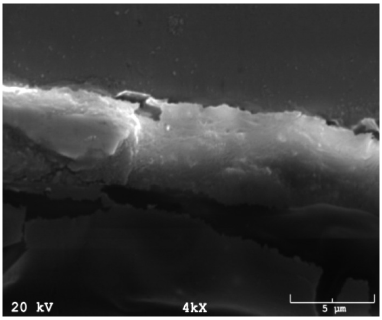


Fig. 24. Steel sheet –3% solution of NaCl + tuff (after 14 days), the transverse metallographic section

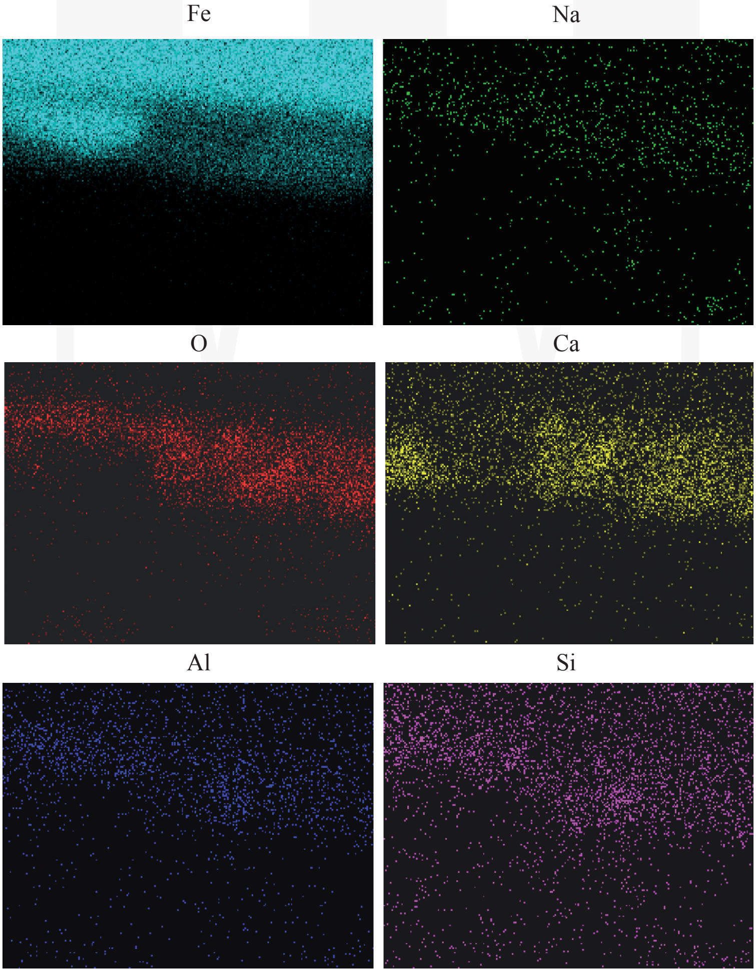
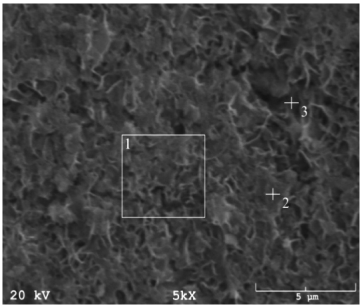


Fig. 25. The cross section of sample immersed in 3% solution of NaCl + tuff (after 14 days) – the distribution of elements: Fe, Na, O, Ca, Al, Si



Analysis Report: Image 26–1 **Analysis Report: Image 26–2**

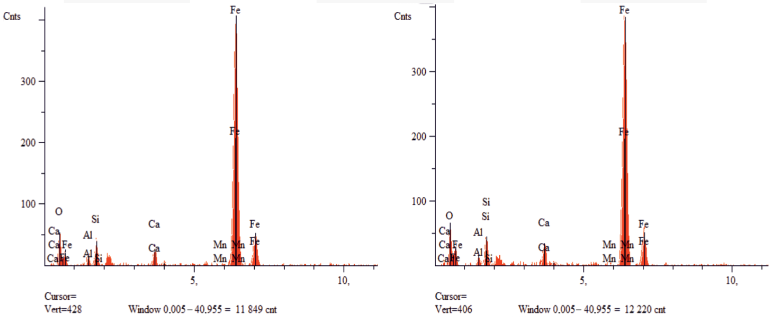
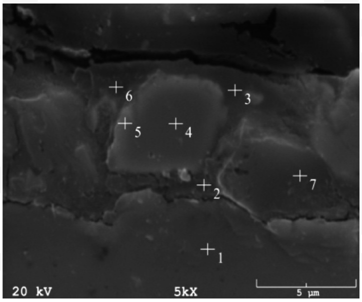
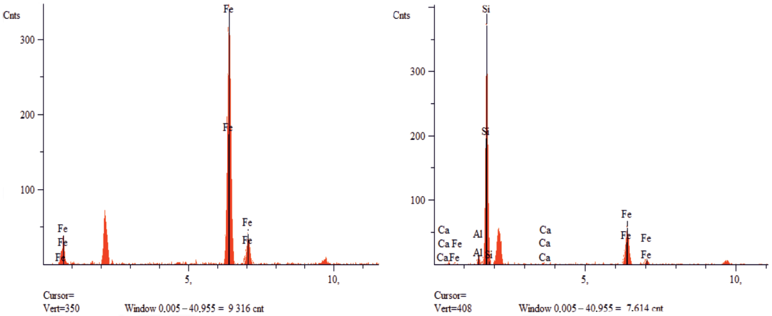


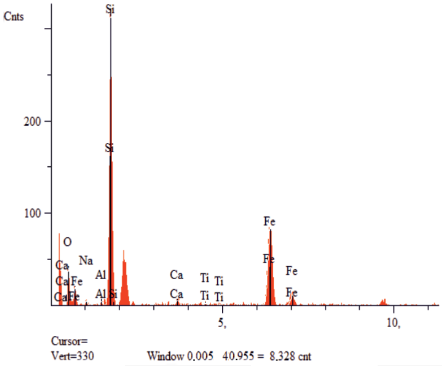
Fig. 26. Steel sheet surface – 3% solution of NaCl + tuff (after 60 days). EDS analysis



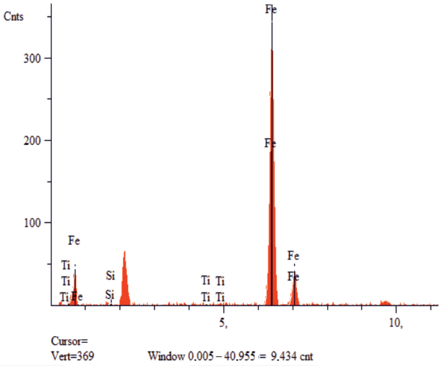
Analysis Report: Image 27–1 **Analysis Report: Image 27–2**



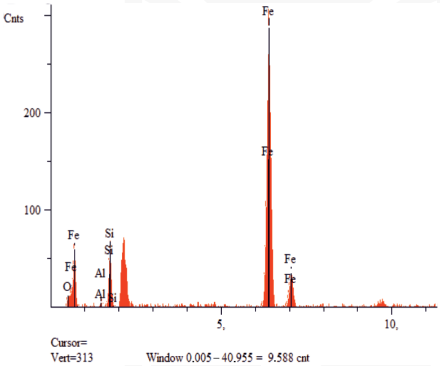
Analysis Report: Image 27–3



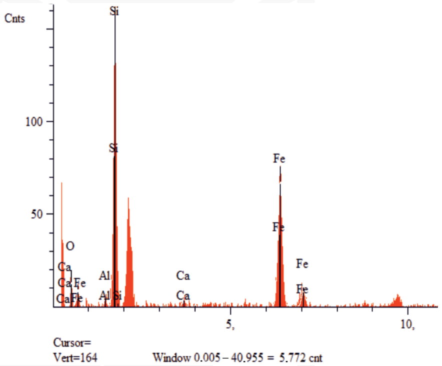
Analysis Report: Image 27–4



Analysis Report: Image 27–5



Analysis Report: Image 27–6



Analysis Report: Image 27–7

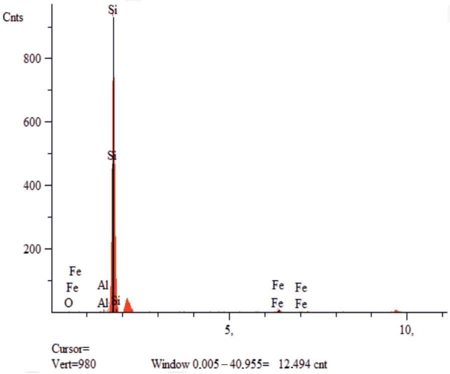
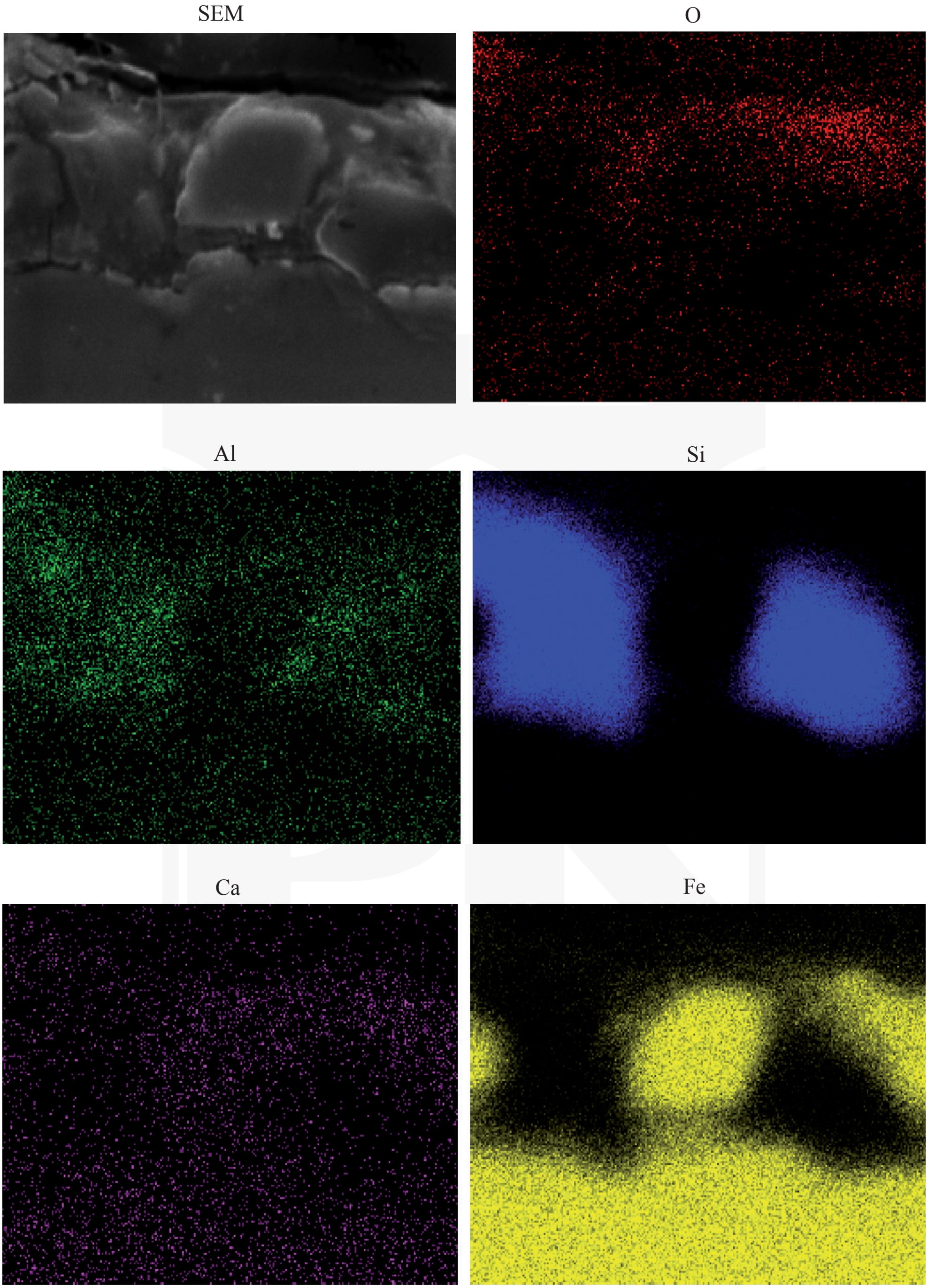


Fig. 27. Steel sheet –3% solution of NaCl + tuff (after 60 days), the transverse metallographic section. EDS analysis



SEM

O

Al

Si

Ca

Fe

Fig. 28. The cross section of sample – 3% solution of NaCl + tuff (after 60 days) – the distribution of elements: O, Na, Al, Si, Ca, Fe

Studies carried out by SEM and EDS showed that in the case of steel samples immersed in water with the addition of tuff, after 14 days of exposure in the solution (Fig. 20), the protective coating 2 to 5 μm thick was formed. The protective coating had a laminated structure. In the coating area directly contacting the steel surface, the presence of a layer comprising Fe, Al, Si and O was observed. The upper part of this layer contained Al, Ca, Fe, Si and O.

In the case of samples immersed for 60 days in water with the addition of tuff (Fig. 21, 22), the thickness of protective coating was approximately 6 to 7 μm. The coating had an obviously layered structure. Near the steel surface, there was a layer containing Fe, Al and O, the next layer contained Fe, and again there was a layer containing Fe, Al and O. The concentration of Ca and Si was uniform across the entire thickness of the coating. The results of EDS test have indicated that oxygen concentration in individual layers of the film was correlated with the concentration of Al. Elemental distribution analysis has confirmed that high oxygen concentrations were present in areas with the high concentration of aluminum, while in areas with the high concentration of Fe, virtually no oxygen was present.

In samples immersed for 14 days in 3% NaCl solution with the addition of tuff (Fig. 23–25), the thickness of protective coating amounted to about 55 μm. Also in these coatings, similar as in coatings exposed to water, a layered structure was observed. The coatings contained Fe, O, Na, Ca, Al and Si. In areas with the high concentration of Fe, a marked reduction in the oxygen concentration was noticed. In areas with the low concentration of Fe, high concentrations of Ca, Si and O, and increased concentrations of Al and Na occurred.

In samples immersed for 60 days in 3% NaCl solution with the addition of tuff (Fig. 26–28), the thickness of protective coating was 7 to 8 μm. The structure of these coatings was observed to differ from the structure of coatings exposed to the effect of water with the addition of tuff. It consisted of two types of complexes (areas) – the first type of complex with high concentration of Fe and very low concentration of oxygen, and the second type of complex with high concentration of Si, high concentration of Al and very low concentration of oxygen. The complexes were embedded in the matrix composed mainly of Si, Fe and O, with low concentration of Al and Ca.

5. Conclusions

1. Tuff in aqueous solutions inhibits steel corrosion by forming a protective film (coating) composed of the steel corrosion products and products of the volcanic tuff hydrolysis.
2. The formation of protective layer on the steel surface is a multi-step process and consists of the process of tuff hydrolysis (preparation of the sol solution), the deposition of coating in the form of sol on the steel, the formation of cross-linked gel by polymerization of the sol particles, the formation of amorphous or crystalline coating during drying.
3. Tuff particles introduced to an aqueous environment are undergoing the processes of hydration and hydrolysis. As a result of these processes, the most easily soluble mineral components are dissolved and washed out. Ions of Si^{2+} and Al^{3+} Ca^{2+} are the most mobile cations, while in the grains of tuff remain the less mobile components. The decomposition products are transported as suspensions, colloidal solutions and real

solutions. The synthesis of sols of hydroxides of Al, Si, Ca, Fe and of other components to which the tuff is decomposed takes place. Under certain conditions, hydroxides mutually coagulate and precipitate in the form of gel.

4. The transition between the state of sol and complete gel is running continuously as a result of advancing parallel processes of hydrolysis and condensation, which are highly beneficial for the coating adhesion.
5. Gel is formed when, in a colloidal system, the number of colloidal particles is so high that they contact or communicate with each other at many points, forming a space lattice system. During drying, the excess water is removed. The end result of this process is the amorphous or crystalline material.
6. The complex composition of the resulting layer formed on the steel surface is most likely due to the sorption by gels, from which it arises, of additional elements from the aqueous solution. As a result of this process, on the steel surface, a protective layer is formed, and it consists of the steel corrosion products and tuff hydrolysis products.
7. Introducing properly prepared tuff formulations to protective coatings (including protective paints) is expected to improve the corrosion resistance while maintaining the sufficiently high mechanical strength properties of the coating.

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