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DUMITRU TSIULYANU,
OLGA MOCREAC

Scientific paper
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Hydrogen sensing behavior of tellurium thin films studied by A.C. measurements

For the first time it is pointed out that tellurium films exhibit sensitivity to H_2 at room temperature along with sensitivity to NO_2. The hydrogen gas sensing performance of tellurium thin films was investigated by method of impedance spectroscopy. The impedance spectra are strongly influenced by gaseous environment but the effect of target gas is mainly due to variation of resistance of the film. It is assumed that the sensitivity of tellurium films to H_2 arises because – of reducing effect of oxygen priory absorbed on the surface of the film from carrier (dry air) gas. The high concentration of oxygen in carrier gas promotes the formation of a catalytic gate, which can be removed by other gases including hydrogen. Removing of the priory-adsorbed oxygen results in decreasing of both, hole concentration and conductivity of the surface and intragrain regions of tellurium film. Due to impedance change in different direction, reducing H_2 may be distinguished from oxidizing NO_2, hence the effective, operating at room temperature H_2 sensors can be manufactured using tellurium-based films.

Key words: *Gas sensing, Tellurium, Hydrogen, A.C. measurements*

1. INTRODUCTION

Hydrogen (H_2) gas is a clean, naturally abundant energy resource and presently it has been widely implanted in household and transportation applications. To avoid damage to human life and infrastructures, a reliable sensor with accurate and fast H_2 gas detection is essential to safe H_2 gas production, storage and utilizations.

The development of hydrogen sensors concerns the research into the new materials that provide advanced sensitivity, selectivity, stability and low power consumption. So far, the metal oxide semiconductors, such as tin oxide [1] or tungsten trioxide [2] are the most studied materials for the H_2 gas detection. Although these materials exhibit good hydrogen sensing characteristic they require evaluated (100 - 600 ^{0}C) operable temperature. In the present study we rapport the possibility to detect H_2 at room temperature using tellurium thin films. It is known that a number of gases may be easily detected at room temperature using these films. First this possibility has been pointed out for NO_2 [3], then have been reported sensors operable at room temperature based on tellurium thin films to detected CO and propylamine [4] as well as NH_3 [5]. Although the cross sensitivity to mentioned gases is essential different, the distinguishing between them becomes important.

One of possibilities to obtain a selective detection of gases has been mentioned by Sbeveglieri [6] and consists in a fast sweeping of sensitivity of a single sensor at different frequencies. The sensitivity of sensor to different gases at different frequencies can be rather different. That is, by monitoring a.c. conductance at specific frequencies, the sensitivity to different gas components can be enhanced [7]. More over, a.c. measurements allow obtaining impedance or admittance spectra of a sensor, to calculate equivalent circuit and to distinguish between contributions from the surface, bulk or contacts to film conductivity [8].

In the present paper the impedance spectra of tellurium based thin films with interdigital electrodes have been investigated in gaseous media H_2 as well as NO_2 for comparison.

2. EXPERIMENTAL

Tellurium based thin films of $\approx 100nm$ thickness, were prepared by thermal vacuum evaporation of pure tellurium from tantalum boat onto ceramic substrates with a priory deposited platinum interdigital electrodes (Figure 1a). The electrode structure was structured at SIEMENS AG with electrode width of $15\mu m$ and interelectrode distances of $45\mu m$. The evaporation of tellurium was performed at the working pressure of $10^{-4}\,Pa$. The growing velocity of the film was in the order of 10 nm/s and the area of deposition around 10 mm^2. The surface morphology of the films was investigated, using a

Author's address: Technical University, bd. Dacia 41, Chisinau, MD-2060, Moldova

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VEGA TESCAN TS 5130 MM scanning electron microscope (SEM).

The film was encapsulated in a standard TO – 8 sockets and then the contacts were thermally bounded to socket pins, using the copper wires.

The sockets with thin film sensing devices were put into a test cell (of 10*ml* volume) in which the gases were injected with a flow rate of $100 ml/\min$, parallel to the film surface.

Hydrogen gaseous media, with concentration 1% by volume was obtained from cylinders (Linde, Germania). Nitrogen dioxide (NO_2) vapors with concentrations of *1,5 ppm* were obtained by using calibrated permeation tubes (Vici Metronics, USA), which were incorporated subsequent into the experimental set – up. Dry synthetic air was used as the carrier and reference gas.

Impedance measurements were carried out in frequency range of $5Hz$ to $13MHz$ using a HP 4192 A impedance analyzer.

3. RESULTS AND DISCUSSION

3.1 Impedance behavior under dry air

Before checking the effect of different harmful gases on a.c. conductivity the tellurium films were aged by 12 months in normal conditions and the measurements have been performed under synthetic dry air. Figure 1b shows the typical complex impedance diagram in Nyquist plot obtained in pure synthetic dry air from a thin film device at room ($22^{\circ}C$) temperature.

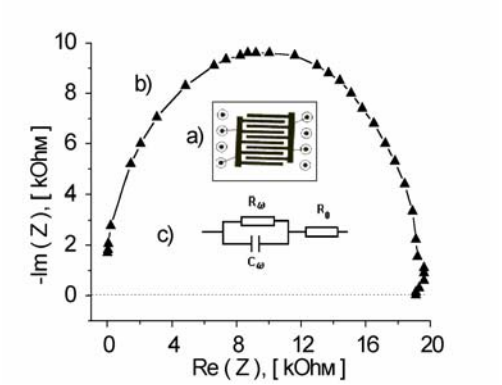

Figure 1 - a) Interdigital electrode structure used to measure the a.c. conductivity; b) Nyquist diagram of an aged at 22°C tellurium thin film in pure synthetic dry air; c) Suggested equivalent circuit

The diagram shows a slightly depressed semi – circular arc with a center displaced below the real axis, owing to presence of distributed elements in tellurium-based device [8]. A simplified equivalent circuit inserted in Fig. 1 (c) can interpret the Nyquist plot. The frequency independent serial resistance R_0 is assigned to a sum of Ohmic resistance due to electric connection, but resistance R_0 and capacity C_ω are distributed to others contributors, the grain boundary resistance and capacity being the main.

The circle of Nyquist – diagram shown in fig. 1b is depressed owing to the dependence of both C_ω and $R\omega$ on frequency. From the left and right intercepts of semi – circle with the $\mathrm{Re}(Z)$ axis the values of R_0 and $R_r = R_\omega + R_0$ can be estimated. Thus, R_0 was found to be very small, only about $5Ohm$. That is the arc practically passes through the origin and the right intercept gives the value of $R_r \approx 20kOhm$.

For a parallel R_ω C_ω circuit the impedance is given as:

$$Z(\omega) = \frac{1}{Y(\omega)} = \frac{1}{\frac{1}{R_\omega} + i \cdot \omega \cdot C_\omega} =$$

$$= \frac{R_\omega}{1 + i \cdot \omega \cdot C_\omega \cdot R_\omega} = \frac{R_\omega (1 - i \cdot \omega \cdot C_\omega \cdot R_\omega)}{1 + (\omega \cdot C_\omega \cdot R_\omega)^2} \quad (1)$$

where $Y(\omega)$ is the admittance, $i = \sqrt{-1}$ is the imaginary number, $\omega = 2\pi f$, f -the frequency.

Thus, the real and imaginary parts of the impedance are:

$$\mathrm{Re}(Z) = \frac{R_\omega}{1 + \omega^2 R_\omega^2 C_\omega^2} \quad (2)$$

and

$$\mathrm{Im}(Z) = \frac{\omega \cdot C_\omega R_\omega}{1 + \omega^2 R_\omega^2 C_\omega^2} \quad (3)$$

From these system of equations the values of R_ω and C_ω of the film can be evaluated as:

$$R_\omega = \frac{\mathrm{Im}^2(Z) + \mathrm{Re}^2(Z)}{\mathrm{Re}(Z)} \quad (4)$$

and

$$C_\omega = \frac{\mathrm{Im}(Z)}{\omega\left[\mathrm{Im}^2(Z) + \mathrm{Re}^2(Z)\right]} \quad (5)$$

From equations (4) and (5) the resistance R_m, capacitance C_m and time constant $\tau_m = (2\pi f_m)^{-1}$ of the film can be estimated at characteristic frequency f_m, that is the frequency at which the imaginary part - $I_m(Z)$ reaches its maximum value. Because of he-

terogeneity of the material-electrode system the relaxation time (time constant) τ_m, estimated from the complex impedance represents a mean value for the complete thin film device:

$$\tau_m = \omega_m^{-1} = \frac{1}{2\pi f_m} = R_m C_m \qquad (6)$$

where f_m - is the characteristic frequency at which the imaginary part – $I_m(Z)$ reaches the maximum value, R_m and C_m are the resistance and capacity of the film at characteristic frequency f_m. The characteristic frequency (f_m), impedance (Z) and estimated from equation (6) the time constant (τ_m) of the sample in dry synthetic air, are listed in Table 1.

Table 1 - Characteristic frequency, impedance and R-C values at different environments.

Environment	$f_m\,(kHz)$	$Z\,(kOhm)$	$\tau_m \cdot 10^{-7}\,s$	$R_\omega\,(kOhm)$	C_ω (pF)
Dry air	900	13,3	1,8	19,2	9,6
H_2 1% by vol.	600	19,8	2.7	31,7	8,5
1,5 ppm NO_2	1500	7,5	1,1	11,8	9,3

3.2. Impedance behavior under mixture of dry air with H_2 and NO_2

Figure 2 reports the complex impedance spectra of aged tellurium-based films upon exposure to different test gases that is NO_2 and H_2. It is seen that addition of these gases to dry synthetic air does not change the general shape of curve, i.e. they influences all elements of the equivalent circuit. The values of characteristic frequency, impedance and time constant τ_m of the film at this frequency, by indicated concentrations of NO_2 and H_2 at room temperature, are summarized in Table 1.

Listed in this table values of R_m and C_m (the resistance and capacity at characteristic frequency) have been obtained from Eq. (2) and (3) applied to the data of Figure 2.

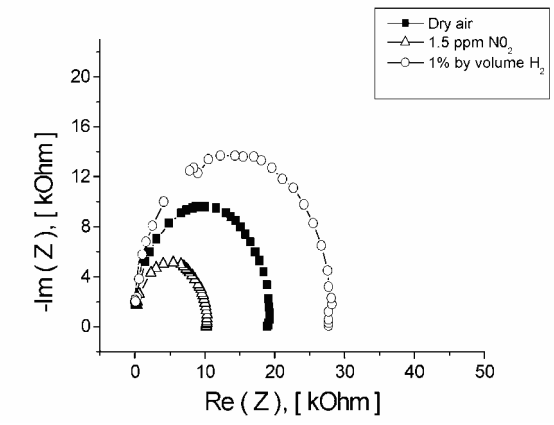

Figure 2 - Nyquist diagrams of tellurium thin films in different environmental conditions

From this table it is seen that as the environment is changed from dry air to its mixture with gases in question, the resistance R_m is mainly influenced and capacitance C_m does not very essentially. What is more the addition of NO_2 decreases both impedance and R_m (at characteristic frequency, which also is gas influenced) but addition of H_2 increases these parameters.

3.3. Real and imaginary parts of impedance for Te films in H_2 and NO_2 gaseous media.

Figure 3 reports the spectra of the real part of impedance of tellurium films upon exposure to different test gases. It is seen that addition of 1,5 ppm of NO_2 to dry synthetic air diminishes the real part of impedance by ~ 10 kOhm in the frequency range 1,0-10^3 kHz. On the contrary, the addition of 1 % of volume of H_2 to dry synthetic air enhances the real part of impedance by ~7,0 kOhm in the much shorter frequency range: 1,0 – 100 kHz.

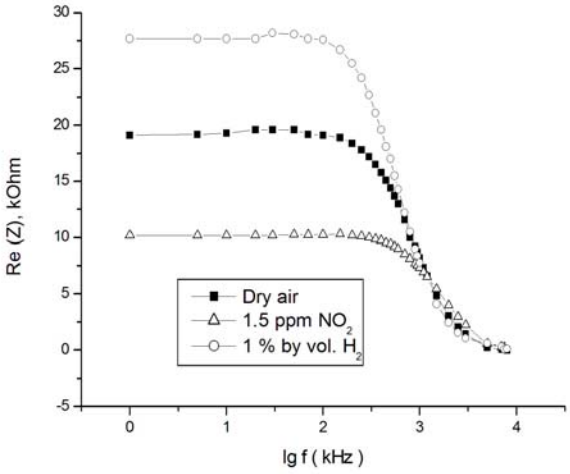

Figure 3 - Effect of target gas on the real part of impedance

The spectra of imaginary part of impedance exhibits the maximums strongly influenced by harmful gases species (Fig.4). The NO_2 vapors diminish

the peak of imaginary part of impedance shifting it to higher frequencies but the addition of H_2 vapors results in a vice-versa behavior. Analysis of these spectra help determining the influence of tested harmful gases on all elements of the equivalent circuit of the sample showed above in the Table 1.

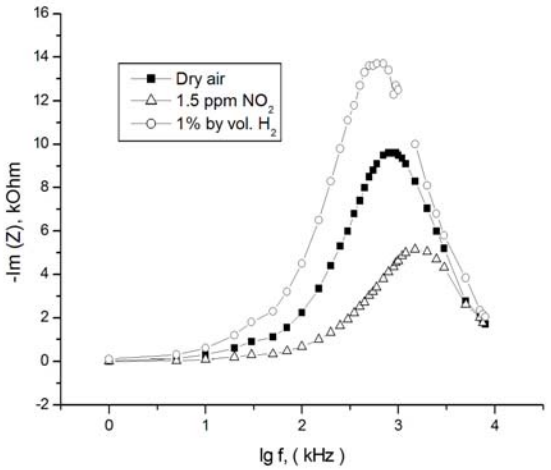

Figure 4 - Spectra of imaginary part of impedance upon exposure to different test gases

As the response to different gases strongly depends of applied frequency, it becomes interesting to analyze the frequency dependences of sensitivity to different target gases.

3.4. Sensor sensitivity versus applied frequency

3.4.1. Nitrogen dioxide

D. c. resistance of tellurium films is known to decrease reversibly in presence of NO_2 due to interaction of adsorbed species with lone – pair electrons, which from the upper part of the valence band [9]. Apparently, by changing from d.c. to a.c. technique the mechanism of interaction cannot be modified but the sensitivity (or selectivity) can be increased.

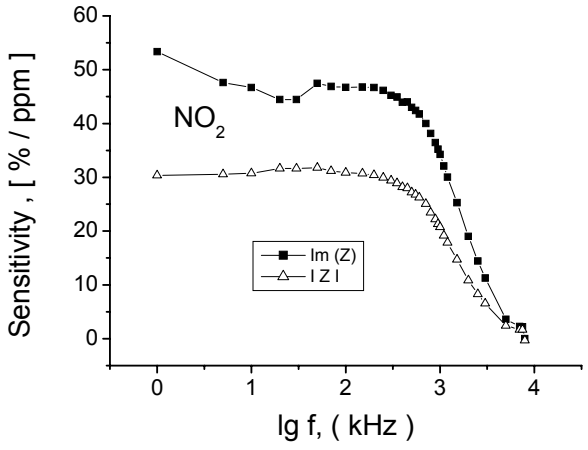

Figure 5 - Sensitivity to NO_2 for impedance and its imaginary part as a function of frequency

Figure 5 shows the sensor sensitivity as a function of the measurement frequency during the exposure to 1,5 ppm NO_2. The sensitivity (here and further) is defined as absolute variation of measured value (impedance or imaginary part of impedance) for a selected frequency in mixture of carrier gas with NO_2 divided by the measurement value in the carrier gas at the same frequency, in percents per ppm.

The response curves for either impedance or imaginary part are nearly independent on frequency until approximately 300 kHz, then go down, but sensitivity to NO_2 is maintained until 10 MHz. The sensitivity in d.c. and impedance measurements amounts to approximately 30 % / ppm, but evaluating the imaginary part as the sensor response results in an increasing of sensitivity until ~50 % / ppm. The high sensitivity, as well as the large frequency range of response to NO_2 supports the early-proposed mechanism of nitrogen dioxide interaction with chalcogenides [9], which involves ″strong″ chemisorption due to interaction between odd electrons of NO_2 molecules and lone – pair electrons of tellurium based chalcogenides.

3.4.2. Hydrogen

Figure 6 shows the sensor sensitivity as a function of measurement frequency using the hydrogen as a test gas. It is observed that sensitivity to hydrogen is by four orders of magnitude smaller that to NO_2, but also cover a large range of frequencies and can be clearly detected. Unlike exposure to NO_2 the impedance response spectra to hydrogen go down starting with approximately 150 kHz but at 1,0 MHz the sensitivity to H_2 practically disappears.

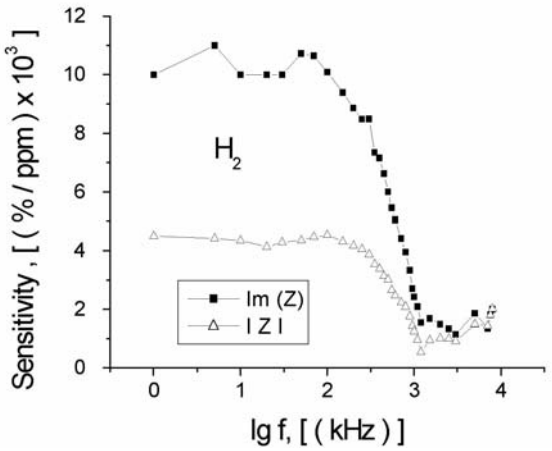

Figure 6 - Sensitivity to H_2 for impedance and its imaginary part versus frequency.

The last is valid also for the imaginary part taken as a sensor response, although the resulting value of sensitivity in this case is more than twice higher. These peculiarities suggest that mechanism of

hydrogen – tellurium film interaction essentially differs from interaction of these films with NO_2.

Elemental hydrogen occurs only as bi – atomic gas molecules at normal conditions. These molecules do not comprises unpaired (dangling) electrons, i.e. cannot be expected the strong chemisorptions of hydrogen on the surface or within the tellurium film. Perhaps the sensitivity of tellurium films to H_2 arise because – of reducing effect of oxygen priory absorbed on the surface of the film from carrier (dry air) gas. In our previous paper [9] was shown that ″weak″ chemisorptions of symmetric molecules of O_2 from carrier gas is accompanied by localization of holes near the surface, which results in decreasing the film resistance. Besides, the high concentration of oxygen in carrier gas promotes formation of a catalytic gate [10], which can be removed by other gases. That is why, assuming that molecular hydrogen removes a priory-adsorbed oxygen we can expect the decreasing of both, hole concentration and conductivity of the surface and intragrain regions of tellurium film.

4. CONCLUSIONS

Impedance spectra of tellurium thin films are strongly influenced by composition of gaseous environment. The effect of harmful gases on impedance is mainly due to variation of film's resistance but capacitance does not very essentially. Addition of H_2 increases impedance whereas addition of NO_2 decreases it in a large range of frequencies.

The response curves (sensitivity) for either impedance or its imaginary part strongly depend on target gas H_2 and NO_2 and frequency, because of different mechanisms of interaction between these gases with tellurium films.

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IZVOD

PROUČAVANJE PONAŠANJA VODONIKA NA OSETLJIVIM TANKIM FILMOVIMA OD TELURA POMOĆU AC MERENJA

Po prvi put je pokazano da su Telurovi tanki filmovi osetljivost na H_2 na sobnoj temperaturi uz osetljivost na NO_2. Reagovanje vodonika na Telurove tanke filmove ispitan je metodom spektroskopske impedanse. Spektri impedanse su pod jakim uticajem gasovitog okruženju, ali je efekat ciljanog gasa uglavnom zbog varijacija otpora filma. Pretpostavlja se da osetljivost Telurovih tankih filmova za H_2 nastaje zato - da se smanji dejstvo kiseonika apsorbovanog na površini filma od provodnog gasa (suv vazduh). Visoka koncentracija kiseonika u nosećem gasu podstiče formiranje katalitičkog kapije, koja može ukloniti druge gasove, uključujući i vodonik.

Uklanjanje apriori apsorbovanog kiseonika smanjenjuje koncentracije i provodljivosti na površinskim i intrgranularnim regionima Telurovih tankih filmova. Zbog promene impedanse u drugom pravcu, redukcija H_2 može se razlikovati od oksidacije NO_2, stoga efikasno, rad na sobnoj temperaturi H_2 senzora mogu biti proizvedeni pomoću telur osnovnih filmova.

Ključne reči: *vodonik, osetljivi tanki filmovi, telur, AC merenja*

Rad primljen: 18.02.2013.

Originalni naučni rad

IRINA FIERASCU[1]
RADU CLAUDIU FIERASCU[2]

Scientific paper
UDC:620.183.19

Research on the degraded artifacts for the development of new protection methods

The history of metals and metal artefacts is closely related to the history of mankind. The discovery of metals and metalworking are important factors that led to the development of human civilization. Even though the metals are considered stable materials, once in contact with the environment, they gradually deteriorate and the deterioration rate depends on every metal/alloys characteristic. That is why the restorer/conservator of metallic artefacts should have knowledge from diverse areas (metalworking techniques, history of metalwork, history of art, archaeology, corrosion of metals, scientific research methods and others). The paper presents some aspects regarding the steps involved in the restoration and conservation of some selected artifacts, from the point of view of researchers in the field of materials science and chemistry.

***Key words**: archaeometallurgy, artefacts, protection methods*

INTRODUCTION

Archaeometallurgy is considered to be the first well-developed area of archaeometry, appearing out of application of some physic-chemical methods in the area of cultural and historical research (Rehren, 2008). The born of a new scientific field can be traced back to 1958, when the journal *Archaeometry* established, and over the years, archaeometallurgy evolved in a recognized and important sub-field.

The metals and metal objects played a very important role in the development of human civilizations; its role is even reflected in the names of the archaeological periods (*Copper Age, Bronze Age, Iron Age*). Metallurgy can be traced back aprox. 8000 years ago, when the first gold objects were manufactured (Cramb, n.a.). From the metals known in our days, only 24 were known before 19th century, and 12 were discovered in the 18th century. Therefore, from the first use of metals (gold and copper) until the end of the 17th century, only 12 metals were known. From these metals, arsenic, antimony, zinc, bismuth and platinum, were discovered in the thirteenth, fourteenth and in the 16th century. The rest of the metals, known as *Metals of Antiquity* are: *Gold* (6000BC), *Copper* (4200BC), *Silver* (4000BC), *Lead* (3500BC), *Tin* (1750BC), *Iron* (1500BC) and *Mercury* (750BC) (Cramb, n.a.).

Author's address: [1]The National Institute for Research & Development in Chemistry and Petrochemistry – ICECHIM Bucharest & Politehnica University of Bucharest, Romania, [2]The National Institute for Research & Development in Chemistry and Petrochemistry – ICECHIM, Bucharest, Romania

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The history of metals is closely linked to that of coins. Nowadays, archaeologists and numismatics agree that the coins were invented independently at three different locations between 700-600 BC (Lydia, India and China), and then spread all over the Eurasian continent (Howgego, 1995).

The most threatening factors that can affect the metal artefacts are the atmospheric and mechanical factors (Curkovic et al., 2010). Even though metals seem to be protected from the action of biodeteriogens, the literature describes several fungi that are able to cause undesirable effects on metals (NPS, 1998) In our days, the main method of protecting the metal artefacts is the use of coatings (such as waxes, acrylic resins and other corrosion inhibitors); some biological treatments based on the capacity of fungal strains to create a stable layer on the surface of the artefacts are also studied (Joseph et al., 2012a; Joseph et al., 2012b).

Our goal in this paper is to present some aspects regarding the way we think a study on metal artefacts should be carried out, from the preliminary analysis to the selection of best-fitted coatings.

MATERIAL AND METHODS

Metal artefacts

All the analyzed coins are from private collections. The coins are presented in figure 1, and their characteristics in table 1.

Analytical methods

When speaking of rapid and non-destructive characterisation of any material (and especially materials with historic value), the most useful technique is XRF (X-ray Fluorescence), which is

widely employed for the analysis of elemental composition in materials.

The X-ray fluorescence analyses presented in this paper were performed using an EDXRF spectrometer, PW4025 MiniPal 2, PAnalytical.

The morphological characteristics of the analyzed coins were recorded with a metallographic microscope (IOR, Romania, x 20÷80). For the FTIR analysis we used a Tensor 37 FTIR spectrometer (Bruker).

Figure 1 - The analyzed coins (1 to 6)

Table 1. Characteristics of the analysed coins (the number in table corresponds with the number on fig. 1)

Coin	Inscriptions	Diameter (mm)	Weight (g)
1	50 BANI 1900/ Carol I rege al Romaniei (Carol I king of Romania), portrait	18	2.3942
2	10 BANI 1867/ Royal effigy	30	9.9363
3	Portrait (Dionysos right wreathed in ivy), Herakles standing left, holding club and lion's skin, Greek letters	33/30 (ellipsoidal)	16.6959
4	EIN KREUZER 1816/ Imperial arms surmounted by the Austrian imperial crown	26	7.7782
5	Diademed female head right, illegible	23	7.2868
6	10 BANI – illegible/illegible	22/4	3.9332

RESULTS AND DISCUSSIONS

Previously (Dumitriu et al., 2011) we proposed a synthetic approach for this type of artefacts, adapted in figure 2.

In the present paper we will discuss the results obtained on our artefacts in steps 1 and 2, and some solutions for step 5.

The first step involved the visual and microscopical (figure 3) examination of the artefacts. Those results are important both in therms of corrosion patterns (that can be observe) and in therms of surface characteristics of the coins (shape of the letters, a better image of the inscriptions on the coin and others).

After the visual investigation (table 1), two of the analysed coins presented illegible inscriptions. After the microscopical investigations, those inscriptions could be read, offering important information: on the surface of coin 5, we were able to distinguish the inscription *ΜΕΣΑΜ-ΒΡΙΑΝΩΝ* either side of Athena Alkidemos advancing left. On the front of coin 6, the year 1905 could be read and on the verso, the inscription *Romania*.

Step 2 of the process involved the identification of the metals (alloys) of the coins. The results obtained are presented in figure 4 and table 2.

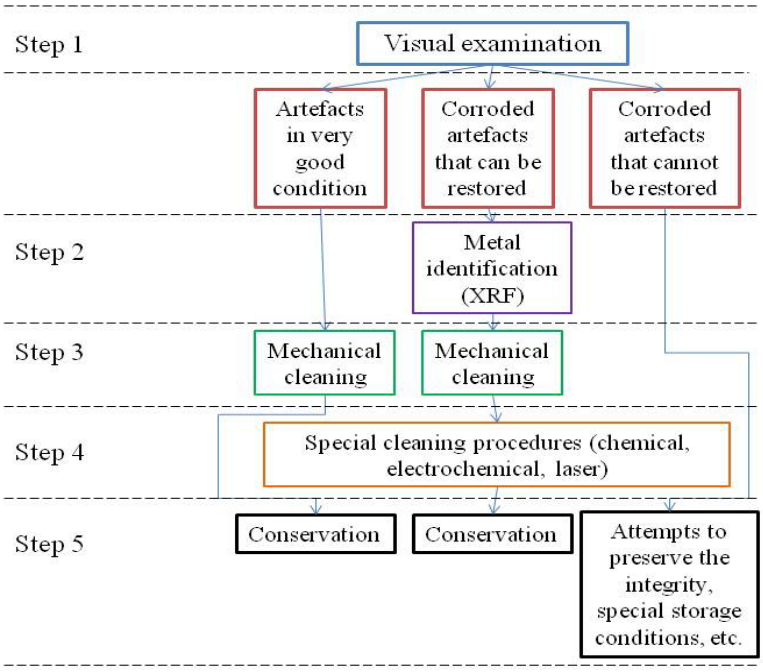

Figure 2 - Schematic representation of the approach on restoration/conservation of the coin artefacts (Dumitriu et al., 2011)

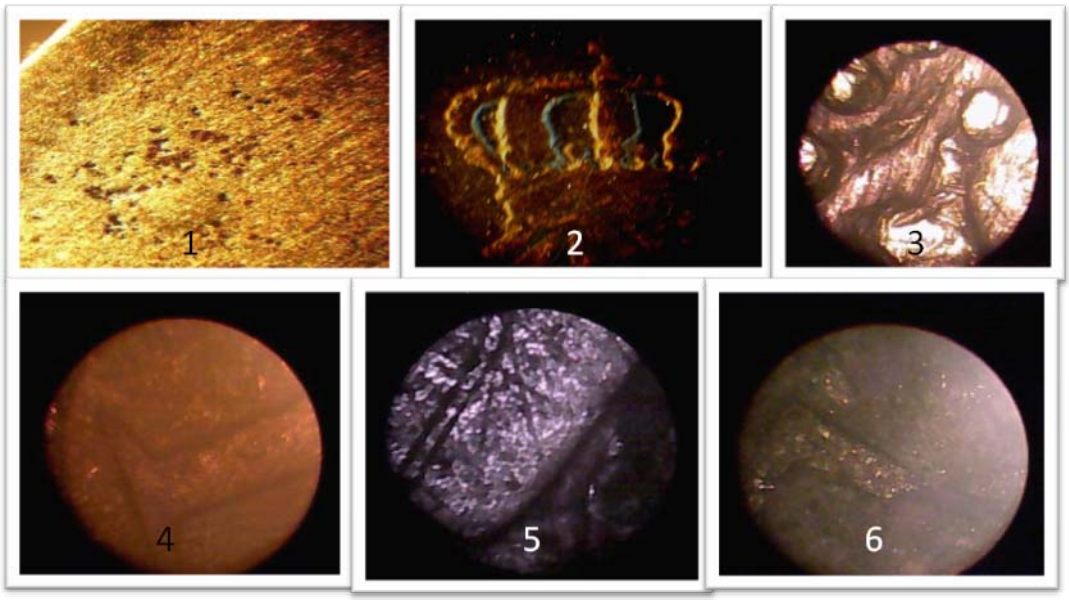

Figure 3 - Microscopical images of the analysed coins

Table 2 - Composition of the coins (XRF)

Coin	Composition (element) %					
	Cu	**Ag**	**Zn**	**Sn**	**Ni**	**Fe**
1	12.6	86.25	-	-	-	-
2	89.52	-	0.9	3.85	-	-
3	0.3	93.52	-	-	-	-
4	96.9	-	-	-	-	-
5	13,4	-	-	33,5	-	18.52
6	69.6	-	-	-	23.21	-

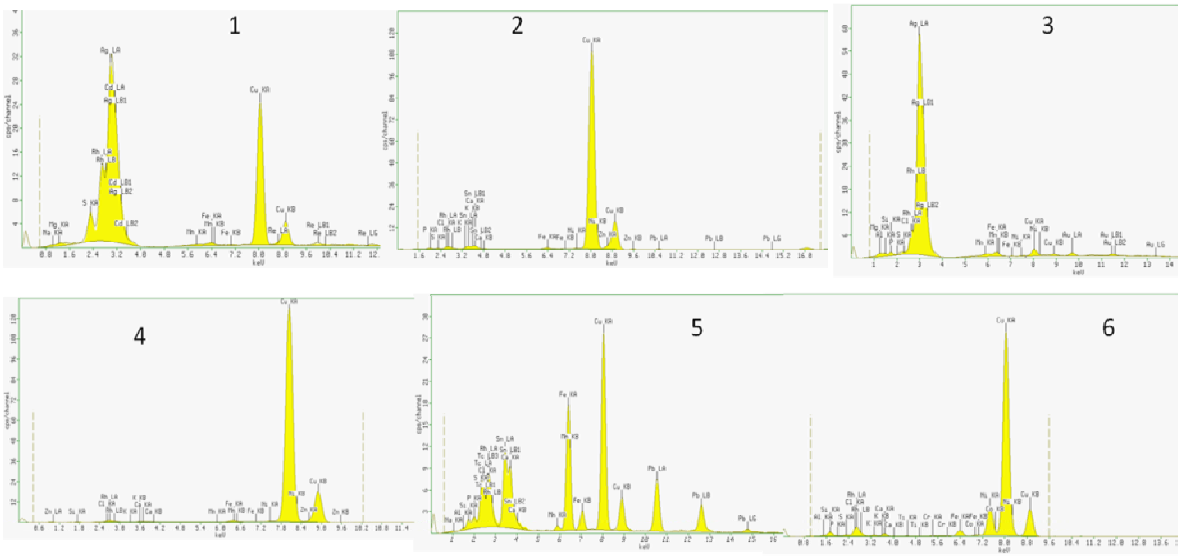

Figure 4 - EDXRF spectra of the analyzed coins

Traces of other elements were found on the surface of the coins (Fe, Co, S, Na, Ca and others). The presence of minor elements in the results can be explained either as corrosion products or as elements native in the ores from which the metals were extracted, as previously presented by our group (Ion et al., 2008; Fierascu et al., 2008; Fierascu et al., 2009, Dumitriu et al., 2011).

From steps 1 and 2 some conclusions can be drawn: coin 1 (Romanian coin) is made of silver, as it belongs to the *golden era* of the Romanian coin (a booming economic period); the other two Romanian coins (2 and 6) are made of copper alloys (Cu/Sn/Zn and respectively Cu/Ni) due to their low value (Fierascu et al., 2009); coin 4 (well-known in Romania) is the basic monetary unit of the Austrian Empire and is made of copper. The coin was issued up to 1852 wearing the same year (1816) (van Wie, 1999).

Coins 3 and 5 are, at first sight, Greek coins from the beginning of our era. Coin 5 is made of bronze and the alloy, the inscriptions and other details (diameter and weight) provides information on the authenticity of the coin. This seems to be a *Mesembria*, a Greek currency from 3rd-2nd century BC (Dumitriu et al., 2011).

Coin 3 is in a much better state of preservation (due the metal from which it was made, much less prone to oxidation). Diameter, weight, composition of the coin (silver) and details on the surface of the coin (blows on the coin, model of the letters) all lead to the conclusion that the currency is a *Tetradrahma* of Thasos (2nd-1st century BC) (Dumitriu et al., 2011).

Step 5 of the process requires the formation of transparent films in order to prevent contact with the atmosphere.

A coating suitable for coins (and other metal objects) should:

- be as inert as possible (will not react with the metal);
- be reversible (can be easily removed with solvents - so no mechanical action);
- be transparent, colorless, preferably as little gloss (matte)
- isolate the artefact from the rest of the environment;
- to age as hard as possible, without releasing corrosive products.

Our experience suggests some solutions:

- polyvinyl alcohol - water

The use of polyvinyl alcohol is hampered by the difficulty to form the film on the surface of the material and by the long evaporation time of the solvent used (water). These problems can be removed by evaporation to the point where the viscosity of PVA is very high, followed by formation of the film (the FTIR spectra of the film formed on the surface of the coin is presented in figure 5a). Removing the film can be done mechanically. Another disadvantage of the use of PVA is its biodegradability, the film needing restoration over time. The advantage of using PVA is the solvent (water), which poses no problems of toxicity.

Poly(methyl methacrylate), solvent acetone:toluene - 1:3, toluene or chloroform

The film can be very easily created, is a very good isolator and it is easy to remove using the proper solvents (figure 5b).

Polystyrene – solvent toluene

Coating (figure 5c) meets the requirements for conservation of metals and can be removed using toluene. However the last two solutions posses problems regarding the toxicity of the solvents used.

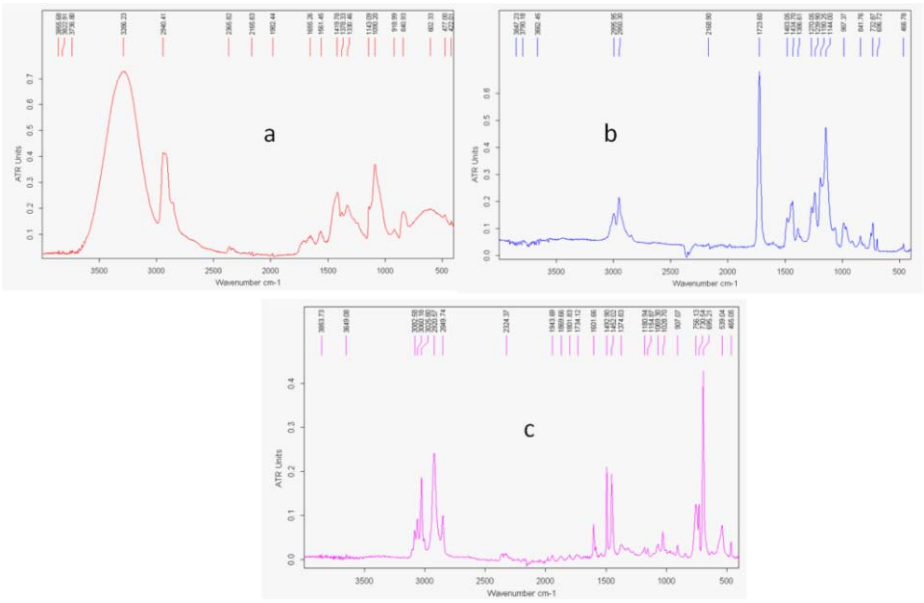

Figure 5 - FTIR spectra of the realized coatings

CONCLUSIONS

In the present work we presented some aspects regarding the preliminary analysis and the steps involved in the restoration and conservation of some metal artifacts (coins). In order to illustrate the principles involved in the process, six coins were selected, of various composition, ages and corrosion degrees.

Following the scheme presented any coin artifacts can be approached for the restoration and conservation. Also, using the visual examination (weight, dimensions, morphological characteristics), corroborated with the metal/alloy identification, some judgments regarding the authenticity of the coins studied can be made. If the alloys or the morphological characteristics (shape of the embossed letters and others) are not consistent with the known data, it is pretty safe to say the coins are not genuine.

The paper also suggests the use of some protective coatings, however this area of research will be further detailed in future papers.

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ANJA TERZIĆ[1], LJUBICA PAVLOVIĆ[2], LJILJANA MILIČIĆ[1]

Scientific paper
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Prevention of electrofilter ash toxic leaching by embbeding in composite materials

Disposal of the fly ash may pose a significant risk to the environment due to the leaching of hazardous pollutants. The only sustainable solution for the pollution-prevention is the reapplication of fly ash as one of the components in construction material composites. There is a risk of leaching even when fly ash is built-in the construction composites and the goal of this investigation was to prove that leaching concentrations of toxic elements is in range assigned by actual regulations. Fly ash was applied in several composits: mortar, concrete and asphalt. The leachability of the potentially toxic elements from the fly ash based products was investigated. The leaching behavior and potential environmental impact of the 11 potentially hazardous elements was tracked: Pb, Cd, Zn, Cu, Ni, Cr, Hg, As, Ba, Sb and Se. A detailed study of physico-chemical characteristics of the fly ash is included. The overall results showed that most of the elements are more readily leachable from the fly ash in comparison with the fly ash based composites.

***Key words**: leaching, toxic elements fly ash, reapplication, construction composites.*

1. INTRODUCTION

The request for the adoption of the „reusing" principle in construction materials industry and environmental protection is alerting. This principle refers to waste minimization through planning and design: the final product of the process is incorporated back into the same cycle without additional waste production. The reusing process also refers to the recovery of waste material and transferring it into secondary raw materials [1, 2]. Ash, the by-product of the coal combustion, is one of the hazardous environmental polluters. The annual global fly ash production is over 600 million tons which makes this by-product a serious problem with severe implications for the environment [3-5].

Regulations and contemporary investigations are focused on the recycling of the fly ash and reusing it as a component in construction materials [6]. Namely, the construction industry is the biggest "consumer" of recycled raw materials with reapplication rate of approximately 21 million tons of fly ash per year [5]. The high recycling rate is obtained mainly due to the fly ash pozzolanic behavior. Possibilities for fly ash reapplications are numerous: as bonding agent or aggregate in concrete/mortar [7-10], filler in road base [11], raw material in cement clinker production [12, 13], component in bricks and tiles [14, 15], as injection material, as geopolymers [16-18]. Even though fly ash has been utilized in cementitious materials for years, there is constantly increasing amount of the unused fly ash. Such occurrence highlights the necessity of developing new recycling methods and products where significant quantity of this waste could be reused.

In addition to the fly ash processing and reapplication in new products, there is also an environmental impact that needs to be evaluated. Namely, there is possibility of toxic metals leaching which could pass through the soil into the ground water, especially when fly ash is used as a construction material. Fly ash may contain some elements of environmental concern, such as arsenic, barium, chromium, cadmium, lead, selenium and mercury, which can limit the potential applications [19-22].

In this study, fly ash based mortars were subjected to mechanical and structural analyses in order to investigate its preliminary characteristics and to evaluate its construction materials utilization potential and implementation safety.

2. MATERIALS AND METHODS

The investigated fly ash samples originated from the filter systems of five coal-fired power plants in Serbia: "Nikola Tesla - A", "Nikola Tesla - B", "Kolubara", "Kostolac - A" and "Kostolac - B". Fuels applied and power-plant regimes vary, therefore the fly ashes produced have different chemical and mineralogical compositions, as well as varieties in microstructure. Five types of fly ash are investigated (a sample from each power plant) and here subsequently labeled as FA_A, FA_B, FA_C, FA_D and FA_E.

The fly ash grain fraction content was analyzed by diffraction particle size analysis (Cyclo-sizer Warman International LTD, Australia). Grain size distribution of the fly ash samples is given in Figure 1.

Author's address: [1]Institut for Materials Testing, Voj. Mišića Boulevard 43, Belgrade, Serbia, [2]Institute for Techology of Nuclear and Other Raw Mineral Materials, Franchet d'Esperey st.76, Belgrade, Serbia

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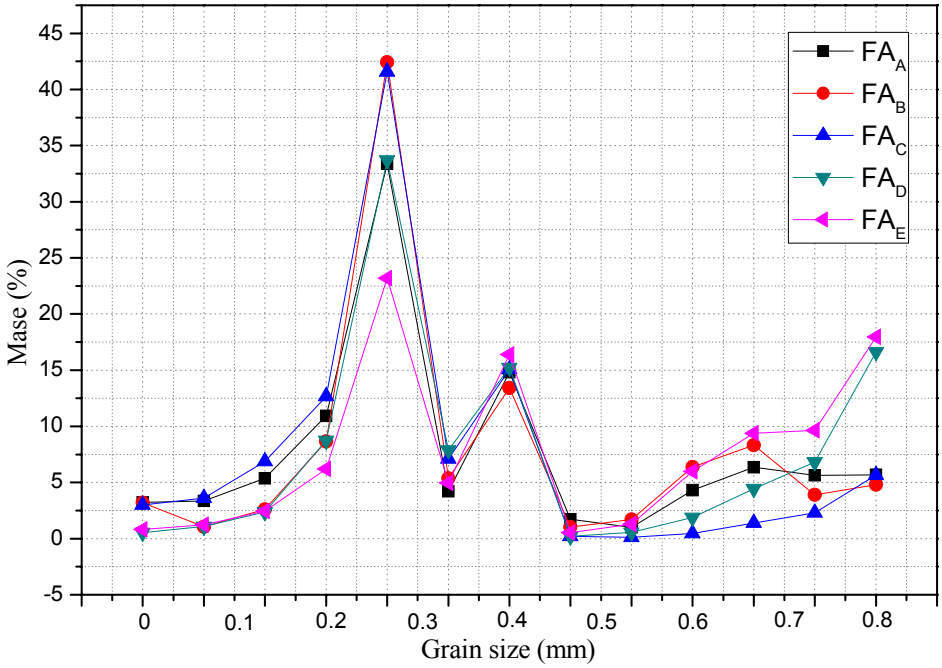

Figure 1 - Grain size distribution of the fly ash samples.

X-ray fluorescence (XRF) technique was used to conduct chemical element analysis. Analysis was performed on the XRF spectrophotometer ED 2000 - Oxford. Thermal stability of crystalline phases within fly ash samples and changes occurring with increasing temperature were investigated by means of the differential thermal analysis. The differential thermal analysis (DTA) of the fly ash was performed with a Shimadzu DTA – 50 apparatus. X-ray powder diffraction analysis was applied in investigation of mineral phases present in fly ash composition. Samples were analyzed by means of X-ray powder diffraction (XRD). The XRD patterns were obtained on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The microstructure of the fly ash samples and fly ash based composites was characterized by scanning electron microscopy method (SEM) using a JEOL JSM-6390 Lv microscope

Three different types of fly-ash based composites were prepared for the analyses: fly ash mortar, fly ash concrete and fly ash asphalt. Mix design of the composites was as follows:

- Mortar: binder - PC 42.5R "Lafarge"; aggregate - River aggregate - "Moravac", grain size fractions 0/4 mm; fly ash replacement coefficient – 35 %
- Concrete: binder - PC 42.5R "Lafarge"; aggregate - River aggregate - "Moravac", grain size fractions grain size fractions 0/4, 4/8, 8/16, 16/32 mm; fly ash replacement coefficient – 35 %
- Asphalt: binder Bitumen - BIT 60 "Pančevo"; aggregate - stone dust (4 %), fine fractions of crushed aggregate (grain size 0/4 mm, 68 %), and coarse aggregate (grain size 4/8 mm, 28%); fly ash replacement coefficient – 35 %

Each composite had five variations, i.e. each composite was prepared with different fly ash type (FA_{A-E}), mix-design remaining the same. Concrete, mortar and asphalt composites without addition of fly ash were also prepared. Such composites were "standard" samples, made for comparison with fly ash based composites. The green concrete and mortar mixtures were mixed for 10 minutes in laboratory RILEM-cem mixer and, afterwards, shaped in 10 cm cubic moulds. After 7 days of curing in a climate chamber at 20 ºC and humidity 60 %, the samples were demoulded and stored for another 21 days under the same conditions as in the climate chamber. For the asphalt samples, optimal mix design regarding assessment of bitumen as bonding agent was conducted according to the Marshall method: BIT = 6.2 % (m/m).

Trace elements mobility from the fly ash samples, fly ash based composites (concrete, mortar and asphalt samples) and "standard" composites was determined with batch leaching test (procedure conducted according to Standard EN 12457). Following the presumption that atmospheric water is the main resource of penetration through open fly ash landfill and building materials incorporated in exterior elements of structural objects or roads, the water was chosen as leachant. Composite specimens were milled in order to provide greater contact surface between the media and to ease the leaching of

present trace elements. The leaching test was performed at a liquid/solid ratio of 10 L/kg with a stirring time of 24 h and deionized water as the leachant. The content of the trace elements in the leachates were determined by means of inductively coupled plasma atomic emission spectrometer ICP-AES (Perkin-Elmer Optima 5300 DV). Results of the leaching test performed on the fly ash, fly ash based composites and "standard" composites were mutually compared.

3.RESULTS AND DISCUSSION

The fly ash samples chemical composition and physico-chemical characteristics are given in Table 1. and 2., respectively.

Table 1 - Chemical composition of the fly ash samples FA_{A-E}

Oxides (wt %)	FA_A	FA_B	FA_C	FA_D	FA_E
SiO_2	53.28	56.20	59.39	54.32	59.73
Al_2O_3	21.45	17.38	16.37	18.08	19.97
Fe_2O_3	7.16	9.33	9.48	6.98	7.55
TiO_2	0.51	0.50	0.52	0.57	0.57
CaO	7.61	7.96	6.96	9.71	4.83
MgO	2.74	2.28	1.98	3.3	2.21
P_2O_5	0.03	0.03	0.02	0.02	0.02
SO_3	0.78	0.85	1.06	1.29	0.48
Na_2O	0.44	0.4	0.31	0.5	0.41
K_2O	1.21	0.55	0.64	1.16	1.18
MnO	0.03	0.03	0.03	0.03	0.03
CO_2	0.25	0.28	0.09	0.11	0.07
LoI	4.51	4.21	3.15	3.82	2.95

Table 2 - Physico-mechanical characteristics of the fly ash samples FA_{A-E}

Sample	FA_A	FA_B	FA_C	FA_D	FA_E
Bulk density (g/cm^3)	2.20	2.32	2.19	2.18	2.18
Compressive strength (MPa)	16.1	10.4	12.5	13.5	15.2
Flexural strength (MPa)	4.6	3.5	4.2	4.1	4.7
Average grain size (mm)	0.118	0.112	0.143	0.089	0.067

Averaged values of main oxides of all five investigated fly ash samples are lying in the range of the values of the fly ashes typical for other origins (Table 3.), which in certain way approves applicability of Serbian fly ashes, since other counties already showed possibility of using fly ash in building products (SRPS CEN/TR 15677:2009).

Table 3 - Comparison of average chemical composition data for investigated fly ash and typical fly ashes from other origins

Average value (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO
Serbia	56.25	19.98	8.09	7.41
UK	50.09	28.10	11.70	1.62
USA	52.24	19.01	15.71	4.48
Netherlands	50.46	25.74	6.53	4.32
Spain	49.80	17.30	8.70	24.90
Poland	50.80	23.90	8.60	3.60

The heating process of the fly ash generally comprises three separate regions that are monitored by three individual peaks. All DTA curves showed a small peak at approximately 200 ºC. The first peak should be attributed to the evaporation of moisture. During temperature interval from 100 to 450 °C hydration water was completely removed. The second region occurring at the temperature range of 400–700 ºC incarnates polymorphic transition. Exact peak values are as follows: (FA_A) 530.85 ºC; (FA_B) 522.95 ºC; (FA_C) 520.74 ºC, (FA_D) 503.80 ºC; (FA_E) 535.25 ºC. Corresponding quantities of heat for each peak are: (Q_{FAA}) 2.77 kJ/g; (Q_{FAB}) 2.05 kJ/g; (Q_{FAC}) 4.13 kJ/g, (Q_{FAD}) 1.21 kJ/g; and (Q_{FAE}) 8.24 kJ/g. The third region represents the beginning of the fusion of fly ash. The peak at approximately 900 ºC which is endothermic is induced by presence of alumino-silicates. Exact peak values are as follows: (FA_A) 926.91 ºC; (FA_B) 928.41 ºC; (FA_C) 871.25-915.17 ºC, (FA_D) 928.53 ºC. Corresponding quantities of heat for each peak are: (Q_{FAA}) -1,57 kJ/g; (Q_{FAB}) -1,98 kJ/g; (Q_{FAC}) -0,14/-1,51 kJ/g and (Q_{FAD}) -2,78 kJ/g. Melting is not recorded at the temperature 1100 ºC for samples FA_{A-D}. This attributes to good thermal and refractory characteristics of fly ash as raw component material.

Major crystalline phases identified in the fly ash samples were: aluminosilicate glass, quartz and mullite. High amount of amorphous matter was present within all investigated fly ash samples. The main peaks on diffractograms relate to quartz. Magnetite, hematite, fluorite and anhydrite are present in relatively negligible amounts.

The water leaching trial gave closer picture of potential mobility of toxic elements existing in the fly ash composition (Cr, Ni, Cu, Zn, As, Se, Cd, Sb, Ba and Pb) in what can be called normal environment influenced only by atmospheric water – rain or snow. Results of the leaching test conducted on the fly ash,

fly ash based composites and "standard" samples are given in Tab 4-7., respectively. The results of the leaching trial performed on standard and fly ash based composites should be compared to the assigned toleration limits which are: 10 mg/l for Pb, 0.5 mg/l for Cd, 100 mg/l for Zn, 10 mg/l for Cu, 50 mg/l for Ni, 30 mg/l for Cr, 0.05 mg/l for Hg, 5 mg/l for As, 50 mg/l for Ba, 5 mg/l for Sb, and 5 mg/l for Se. Upper limit values for toxic metals found in leachate after leach test performed on potentially hazardous wastes used for reapplication/recycling here used are assigned by Serbian Standard EN 12457-(1-4)2002. Even though aluminium, calcium and iron are major constituents in the chemical composition of fly ash their leachability was not investigated due to following reasons: (1) aluminium is element which is poorly leached; (2) calcium is not regarded as an element of concern; (3) iron is mainly present as magnetite mixed in various proportions with hematite, although a minor proportion can be assimilated in the glassy matrix and iron releases are of little significance in relation to the concentration in the fly ash.

Table 4 - Results of water leaching trial performed on raw fly ash samples

Toxic element (mg/l)	FA_A	FA_B	FA_C	FA_D	FA_E
Pb	0.04	0.05	0.04	0.07	0.03
Cd	-	-	-	-	-
Zn	0.679	0.66	0.674	0.693	0.964
Cu	0.008	0.005	0.009	0.01	0.009
Ni	0.18	0.175	0.185	0.187	0.196
Cr	0.133	0.127	0.129	0.139	0.128
Hg	-	-	-	-	-
As	0.004	0.003	0.009	0.002	0.004
Ba	-	-	-	-	-
Sb	0.038	0.003	0.004	0.001	0.003
Se	0.004	0.004	0.006	0.007	0.005

Table 5 - Results of water leaching trial performed on standard and fly ash based mortars

Toxic element (mg/l)	$FA_{A\ mortar}$	$FA_{B\ mortar}$	$FA_{C\ mortar}$	$FA_{D\ mortar}$	$FA_{E\ mortar}$	Standard mortar
Pb	0.09	0.04	0.12	0.08	0.06	0.04
Cd	-	-	-	-	-	-
Zn	0.647	0.955	0.647	0.656	0.667	0.662
Cu	0.005	0.002	0.007	0.006	-	0.012
Ni	0.178	0.148	0.189	0.179	0.172	0.173
Cr	0.132	0.08	0.127	0.133	0.085	0.151
Hg	-	-	-	-	-	-
As	0.003	0.008	0.008	0.003	0.001	0.001
Ba	-	-	-	-	-	-
Sb	0.01	0.086	0.012	0.005	0.004	0.01
Se	0.004	0.013	0.005	0.008	0.006	0.007

Table 6 - Results of water leaching trial performed on standard and fly ash based concretes

Toxic element (mg/l)	$FA_{A\ concrete}$	$FA_{B\ concrete}$	$FA_{C\ concrete}$	$FA_{D\ concrete}$	$FA_{E\ concrete}$	Standard concrete
Pb	0.09	0.17	0.15	0.08	0.19	0.17
Cd	-	-	-	-	-	-
Zn	0.701	0.693	0.667	0.729	0.699	0.677
Cu	0.015	0	0.014	0.017	0.002	0.015
Ni	0.199	0.153	0.182	0.222	0.172	0.186
Cr	0.145	0.122	0.143	0.155	0.145	0.151
Hg	-	-	-	-	-	-
As	0.019	0.007	0.018	0.009	0.005	0.006
Ba	0	0	0	0	0.086	0.09
Sb	0.008	0.009	0.032	0.008	0.005	0.008
Se	0.009	0.011	0.005	0.015	0.004	0.005

Table 7 - Results of water leaching trial performed on standard and fly ash based asphalts

Toxic element (mg/l)	$FA_{A\ asphalt}$	$FA_{B\ asphalt}$	$FAC_{\ asphalt}$	$FA_{D\ asphalt}$	$FA_{E\ asphalt}$	Standard asphalt
Pb	0.08	0.15	0.16	0.1	0.19	0.17
Cd	-	-	-	-	-	-
Zn	0.795	0.701	0.683	0.741	0.695	0.682
Cu	0.013	0	0.001	0.017	0.002	-
Ni	0.208	0.134	0.166	0.202	0.152	0.16
Cr	0.134	0.136	0.141	0.133	0.146	0.142
Hg	-	-	-	-	-	-
As	0.01	0.009	0.005	0.005	0.011	0.004
Ba	-	-	-	-	-	-
Sb	0.01	0.007	0.007	0.023	0.007	0.008
Se	0.018	0.007	0.015	0.018	0.001	0.004

Results of the leaching test conducted on raw fly ash samples (Tab 4.) showed that level of all investigated leached toxic elements was beneath its upper limit value. Content of Zn was higher than content of other toxic elements. Certain toxic elements, precisely Cd, Ba and Hg, were not detected in leachate of tested fly ash samples. Absence of cadmium in fly ash leachate is in accordance with assumption that Cd present in fly ash is consistently immobile while in neutral environment. At the other hand mercury can condensate on surface of fly ash particles and as the water soluble it might pose a risk for groundwater contamination and barium in fly ash forms sparingly soluble compounds with carbonates and sulphates. However, Ba and Hg were not present in investigated fly ash leachates. Concerning other detected elements, lead originates from sulphides found in coal and it is placed within the internal glassy matrix of fly ash and therefore not readily leached. Zink is in sulphide association in the coal and its mobility in fly ash is high. The level of Zn in fly ash and fly ash based composites leachate was high in comparison to level of other investigated toxic elements, but still under upper level of toleration. Copper is assimilated within the glassy phase and not easily leached. Nickel is distributed between the silicate fraction and the magnetic fraction of fly ash during combustion process and most of the leachable Ni is solubilised from the non-magnetic fraction. Chromium leaching generally poses high threat to the environment since it is recognized as potentially carcinogenic matter. However, Cr quantity in investigated samples was significantly beneath level of tolerance. Selenium shows high solubility in water which makes Se as an element of major concern in ash due to its mobility. However, detected level of Se was rather low and did not represent any concern for environment. Antimony in coal occurs in sulphides along with pyrite. The leaching behavior has been scarcely covered in the literature, although it is known that Sb is insoluble in all types of leachant. Amount of Sb found in leachate of investigated composites is low. Arsenic is associated with As-bearing pyrite from coal, which is decomposed during the combustion process. Arsenic condenses on the surface of fly ash as sparingly soluble. The leachability varies widely depending on the nature of the fly ash. In investigated ashes and fly ash composites As was not readily leachable.

Leaching test performed on "standard" cement-mortar and fly-ash based cement-mortar (Tab 5.) showed no presence of Cd, Ba and Hg which was expected due to the lack of theses toxic elements in raw fly ash leachate. Mean values of all toxic elements, except Cu and Cr, found in fly ash based mortar leachate are higher than content of adequate element found in standard mortar leachate. Namely, addition of fly ash slightly increased level of most of toxic elements present in mortar composition. However quantities of toxic elements found in fly ash mortar leachate do not exceed upper limit of toleration. The comparison of results of batch leaching test performed on raw fly ash and fly ash based mortar did not show significant differences between level of toxic elements found in leachate, pointing out to the fact that addition of 30 % of fly ash did not cause any unpredicted or unwanted chemical reactions during cement hydration nor additional toxic and/or harmful chemical products were made.

Table 6. gives the results of batch leaching test conducted on samples of fly-ash based concrete and standard concrete. As in case of raw fly ash and fly ash based mortar, test showed no presence of Cd and Hg. However, small quantity of Ba (< 0.1 mg/l) was detected in leachate of FA_E-concrete, probably originating from "standard" concrete whose leachate also contained certain small quantity of Ba. Ba was not found in other investigated samples, probably because its content was beneath detection level. Ba was probably "carried in" as chemical compound found in composition of a component used in concrete design, presumably aggregate which contained some impurity (possibly $Ba(SO_4)$ originating from sedimentary rocks). Quantity of all investigated toxic elements found in concrete leachate was beneath the upper limit values. Same as in case of mortars, the comparison of results of batch leaching test performed on raw fly ash and fly ash based cement did not show significant differences between levels of toxic elements found in leachates. Thus, addition of 30 % of fly ash did not cause formation of any undesired additional toxic chemical product.

Results of the leaching test conducted on samples of fly-ash based asphalt and "standard" asphalt, given in Table 7., pointed out to the fact that there was no Cd, Hg and Ba found in leachate. Cu was in non-detectable quantity in samples FA_B–asphalt and "standards" asphalt. In other samples, Cu originates from fly ash addition. Quantity of all investigated toxic elements was beneath the upper limit values. The results of leaching test did not show any significant change in toxic leaching of the fly ash based asphalt samples in comparison with adequate results of toxic leaching of raw fly ash and "standard" asphalt.

Results obtained from laboratory leaching trial tests performed on three different types of fly ash composites show relatively small environmental risk in these composites are used in building construction. Namely, content of harmful toxic elements is low and not easy leachable. Level of all toxic pollutants found in leachate of both fly ash and investigated composites is significantly lower than assigned level of toleration. This highlights the possibility of fly ash application in construction materials industry. Namely, there is low environmental risk posed by the presence of contaminant trace elements in the fly ash if the fly ash is applied in a construction composite included in either building or road constructive element and exposed to the action of rain and snow. However, it should be stated that wider environmental impact should be investigated only after application of composites in construction element, building or road – namely during a real-time scale researches.

Microstructural analysis of all fly ash samples was performed, however the microstructure of fly ashes FA_{A-E} is rather similar, thus the FA_A was chosen as representative sample and its microstructural elements are presented as original SEM microphotograph in Figure 2.

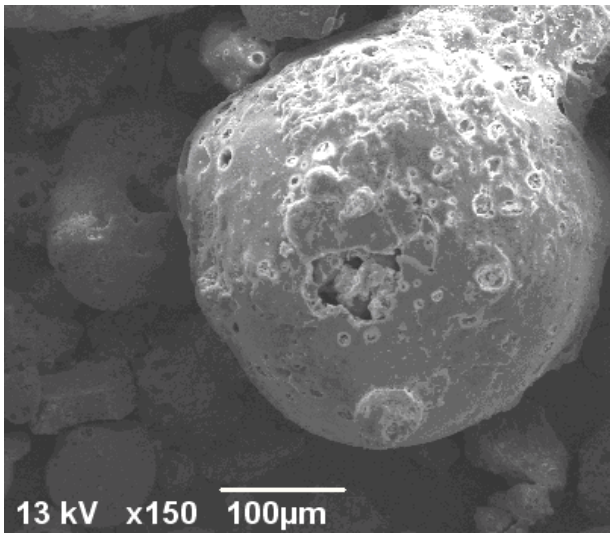

Figure 2 - Microphotograph of FA_A fly ash.

The fly ash samples were mainly composed of unbounded glassy spherical hollow particles, even though certain amount of grains of different size and irregular shape was present. Differently sized and shaped particles belong to different mineral phases which were previously detected by means of XRD. One of the characteristic spherical fly ash particles in Fig. 2. It can be noted that superficial porosity of fly ash grain is high. High porosity of grains leads to elevated water demands when composite mixture is prepared. Also, grain porosity might induce higher apparent porosity of the final product (mortar, concrete or asphalt), which might in return enable easier leaching in natural surroundings. However, the leaching test performed on fly ash and fly ash based composites showed no possible toxic leaching threat, since all toxic elements in leachates proved to be assigned limits. Larger particles which may be either spherical or slightly irregular usually contain variable amounts of the "bubbles" and other differently shaped crystalline minerals.

Microstructure of fly ash based composite FA_A-concrete is given as SEM microphotograph in Fig.3. Microphotographs of other sub-types of composites are not provided here because due to application of same raw materials – same bonding agents and aggregates and only varying the type of fly ash, there are no significant visible differences between them.

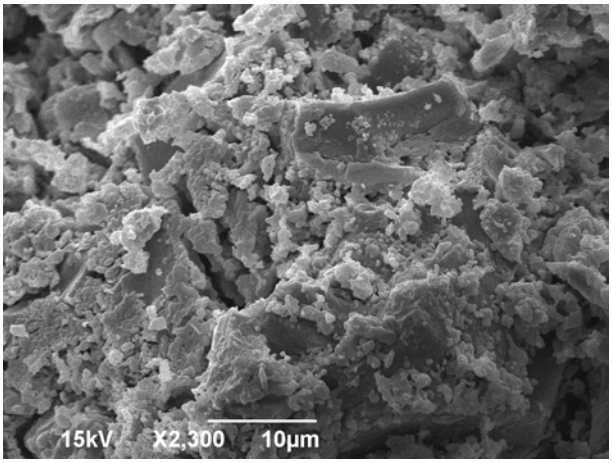

Figure 3 - Microphotograph of FA_B-concrete.

In Figure 3. fly ash particles are incorporated in "cementing zone" between aggregate grains. The fly ash which is merged with cement during process of setting and afterwards hardening of the concrete behaves like standard puzzolanic material. Namely, cement and fly ash together form hardening bonding-agent paste locking the aggregate grains together in stone-alike composite structure. In such structure, fly ash porous grains are being interlocked in the space between particles of bonding agent and/or filler making internal barriers within pore channels, "cutting" the path of the water and preventing the larger scale toxic leaching. Also, fly ash particles, due to its spherical shape, improve the "packing" of the concrete microsturcture and fill in potentially left structural voids. Namely, fly ash acts like super-plasticizer making the concrete stucture more compact and decreasing the level of porosity. The role of the fly ash is same in all composites: conrete, mortar and asphalt.

4. CONCLUSIONS

The investigation performed on the fly ash originating from electro-filters of five different power plants and fly ash based composites - asphalt, concrete and mortar led to the conclusion that investigated fly ash can be considered as non-hazardous in terms of its reapplication as raw material in building materials. The conventional powder processing of lignite coal fly ash, which did not include additional thermal or chemical activation, allowed the formation of relatively high density/low porosity building materials (mortars, concretes and asphalts) which proved to have optimal composition regarding prevention of toxic leaching. The toxic element leaching obtained for experimentally designed ash based composites was comparable to that of commercially produced engineering composites - standard mortars, concretes and asphalts. Potential toxic and/or leachable elements in leachates of investigated fly ashes and fly ash based building composites were under upper limit of toleration assigned by official regulative. The following potential pollutants – Pb, Cd, Zn, Cu, Ni, Cr, Hg, As, Ba, Sb and Se proved to be of low concern when fly ash is exposed to standard environmental conditions approximated by laboratory batch water leaching test. As the leaching tests carried out on the fly ashes and fly ash based composites dismissed the possibility of potential larger scale transition of toxic elements from the building material in contact with water, fly ash reapplication might be regarded as safe process.

5. Acknowlegements

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JELENA PJEŠČIĆ[1], DARKO VUKSANOVIĆ[1], DRAGAN RADONJIĆ[1], VESELINKA GRUDIĆ[1], REFIK ZEJNILOVIĆ[2]

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Ispitivanje efekta inhibitora na koroziono ponašanje austenitnog manganskog čeličnog liva u vodenim rastvorima

Za izradu rezervnih djelova mlinova i drobilica kao nezamjenljiv materijal koristi se austenitni manganski čelični liv. U toku rada ovaj materijal je izložen abrazivnom habanju i udarnom opterećenju. Osim ove primjene austenitno manganski čelici mogu biti korišćeni i kao materijali u uslovima vodene korozione sredine.

Abrazivno habanje je često uvećano prisustvom korozionih materijala, među kojima se može ubrajati i voda, obzirom da je djelovanje korozije znatno izraženije mehaničkim odnošenjem materijala.

Najčešće proizvodi korozije imaju malu otpornost na habanje. Iz prakse je poznato da je brzina habanja obloga kod mlinova za mokro mljevenje cementa mnogo veća u odnosu na brzinu habanja obloga kod suvog mljevenja.

Cilj ovog rada je da pokaže uticaj različitih inhibitora na koroziono ponašanje austenitnog manganskog čeličnog liva, koji u svom sastavu ima različit odnos aluminijuma i molibdena. Dobijeni rezultati će pokazati efekat korišćenih inhibitora.

Ključne reči: *inhibitori, korozija, austenitni manganski čelični liv, vodeni rastvori*

UVOD

Izbor načina kojim će se produžiti vijek trajanja opreme koja radi u uslovima agresivne sredine predstavlja stalan izazov za inženjere svih struka. Tehnološki razvoj opreme većih dimenzija i težina, a samim tim i kapaciteta, stvorio je potrebu za razvojem novih poboljšanih materijala koji su u stanju da podnesu često rigorozne uslove rada.

Pouzdano se može reći da od svog otkrića 1882. godine od strane R.A.Hadfilda, nijedna vrsta čelika i čeličnog liva nije toliko mnogo i na toliko mjesta u svijetu istraživana, kao austenitni manganski čelični liv sa sadržajem mangana od 11-13% i ugljenika od 1,0-1,3% (1).

I pored određenih poboljšanja u proteklom periodu, najveći dio manganskog čeličnog liva koji se u svijetu danas proizvodi, istog je hemijskog sastava kakvog ga je R.A.Hadfild prvi put proizveo.

U ovom radu, pokušaće se kroz dodatno legiranje aluminijumom i molibdenom uraditi poboljšanje kvaliteta odlivaka od austenitnog manganskog čeličnog liva. Takođe, izvršiće se ispitivanje korozionog ponašanja austenitnog manganskog čeličnog liva u vodenim rastvorima bez prisustva i uz prisustvo neorganskih inhibitora ($NaNO_2$, Na_2CO_3 i K_2CrO_4), na osnovu čega će biti utvrđena njihova koroziona postojanost i sam efekat inhibitora.

Adrese autora: [1]Metalurško-tehnološki fakultet Podgorica, [2]Farmaceutski fakultet Podgorica, Crna Gora

Rad primljen: 14.02.2013.

EKSPERIMENTALNI DIO

Svi odlivci austenitnog manganskog čeličnog liva dobijeni su u livnici Instituta za crnu metalurgiju u Nikšiću. Kao osnovni uložak poslužile su šipke ø 40 mm od valjanog ugljeničnog čelika. Potreban sadržaj mangana i ugljenika dobijen je legiranjem sa Fe-Mn(C). Sadržaj silicijuma i molibdena dobijen je korišćenjem Fe-Si i Fe-Mo. Za legiranje sa aluminijumom korišćena su užad od aluminijuma, čistoće 99,9%.

Livenje legura vršeno je loncem kapaciteta 100 kg. Temperatura čeličnog liva kod svih šarži iznosila je 1520^{o}C, a prosječno vrijeme livenja 15 sekundi. Livenje je vršeno u pješčane kalupe, pri čemu su odlivci nakon livenja hlađeni u njima 18-23 časa.

Koroziona i elektrohemijska istraživanja vršena su na opremi za ubrzana ispitivanja-sistem PAR koji čine: potenciostat-galvanostat model 273, diferencijalni elektrometar, koroziona ćelija K0047, standardna zasićena kalomel elektroda, pomoćne elektrode-valjkasti elektrografit, računar sa korozionim softverom SOFTCORR 352 II i štampač.

Eksperimentalni dijagrami dobijeni su korišćenjem metoda:

- metoda polarizacionog otpora, Rp;
- potenciodinamička metoda.

REZULTATI ISTRAŽIVANJA

Hemijski sastav ispitivanih legura dat je u tabeli 1.

Tabela 1 - Hemijski sastav ispitivanih legura u masenim %

Leg.	C	Si	Mn	P	S	Cu	Cr	Ni	Mo	Al
1(1)	1,14	0,67	13,01	0,051	0,01	0,26	0,33	0,15	0,14	0,06
2(4)	1,19	0,78	11,90	0,052	0,01	0,24	0,38	0,14	0,27	0,46
3(7)	1,18	0,64	11,30	0,052	0,01	0,24	0,38	0,15	0,30	1,33
4(9)	1,20	0,63	11,90	0,055	0,01	0,23	0,40	0,13	0,37	2,78
5(11)	1,22	0,65	12,44	0,054	0,009	0,22	0,39	0,14	0,44	3,67

Iz tabele 1 se vidi da se radi o austenitnim manganskim čelicima, kod kojih je mijenjan prvenstveno sadržaj aluminijuma i molibdena, pri čemu je odnos aluminijuma i molibdena bio najveći kod legure 5 (8,34).

Zbog slabe mehaničke obradivosti rađena su samo mjerenja tvrdoće dobijenih legura austenitnog manganskog čeličnog liva.

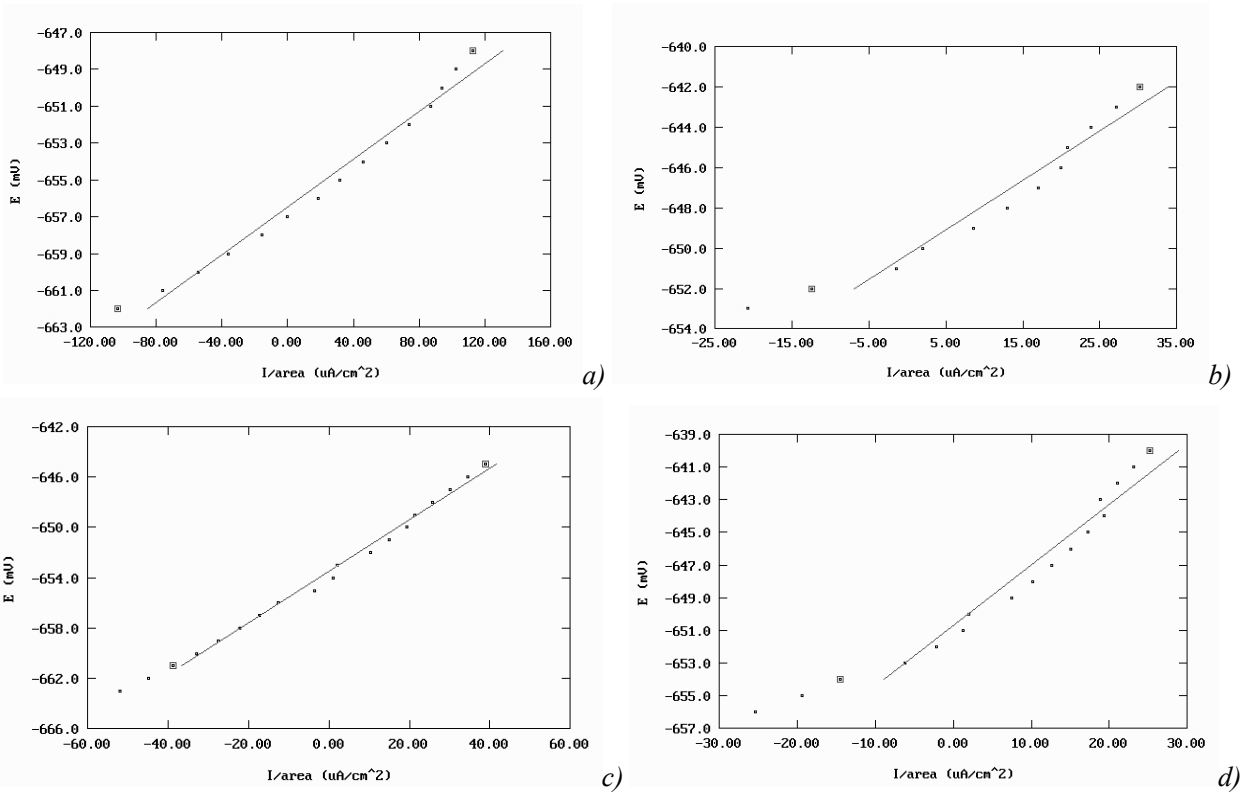
Rezultati ispitivanja tvrdoće u livenom stanju prikazani su u tabeli 2.

Rezultati ispitivanja tvrdoće u livenom stanju austenitno-manganskih čeličnih livova pokazuju da sa porastom odnosa aluminijuma i molibdena opada tvrdoća u livenom stanju.

Na slici 1 prikazani su eksperimentalno dobijeni dijagrami metodom polarizacionog otpora za leguru 5 u 0,51M rastvoru NaCl bez inhibitora i sa dodatkom tri neorganska inhibitora koncentracija 10^{-4} M.

Tabela 2 - Rezultati ispitivanja tvrdoće u livenom stanju

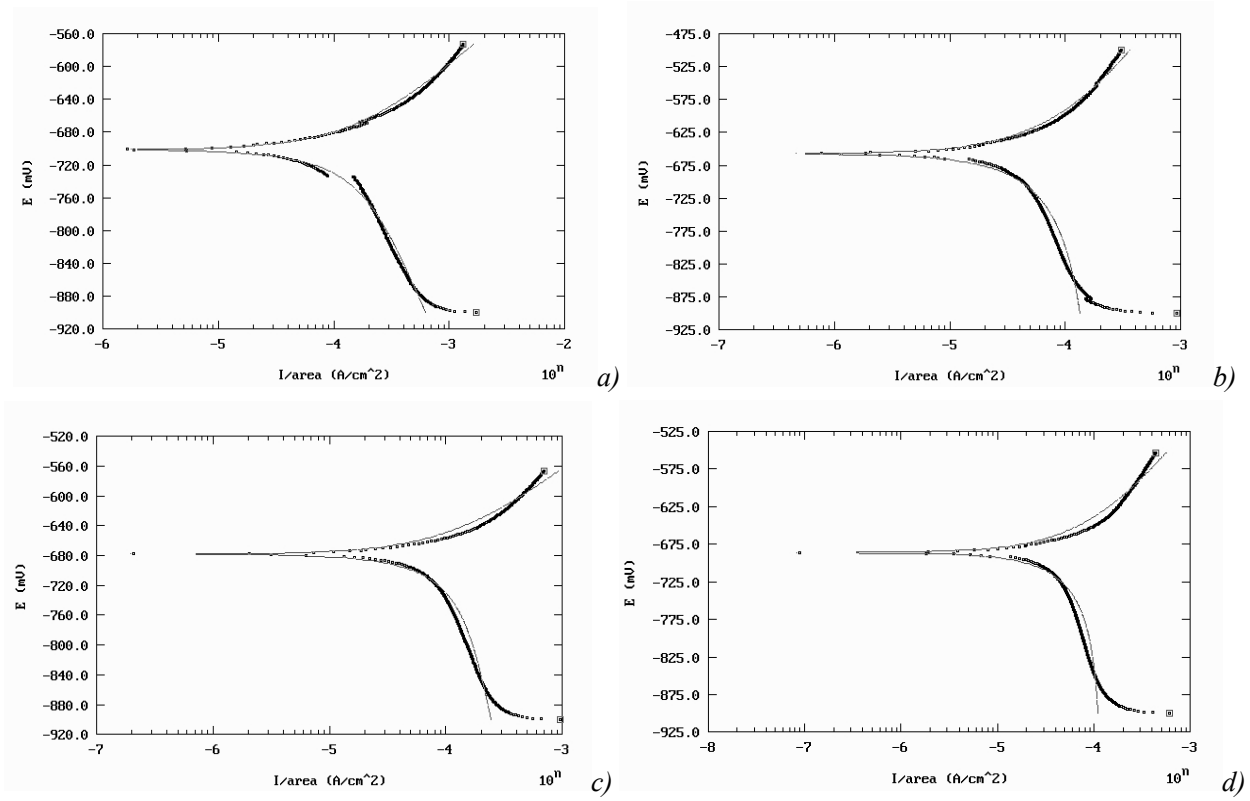
Broj legure	I mjerenje tvrdoće (HB)	II mjerenje tvrdoće (HB)	III mjerenje tvrdoće (HB)	Srednja vrijednost tvrdoće (HB)
1	241	241	255	246
2	269	255	241	255
3	255	255	255	255
4	241	229	229	233
5	217	229	229	225



Slika 1 - Linearne polarizacije legure 5: a) bez dodatka inhibitora, b) u prisustvu 10^{-4}M Na_2CO_3, c) u prisustvu 10^{-4}M $NaNO_2$, d) u prisustvu 10^{-4}M K_2CrO_4

Dijagrami linearne polarizacije (slika 1) su pomjeraju ka pozitivnijim vrijednostima u prisustvu neorganskih inhibitora korozije, u odnosu na dijagram bez dodatka inhibitora. Prema tome, inhibitori utiču na usporavanje brzine korozije, što je i njihova uloga u ispitivanom sistemu hloridnih rastvora.

Na slici 2 date su potenciodinamičke katodne i anodne polarizacione krive za leguru 5 u 0,51M rastvoru NaCl bez inhibitora i sa dodatkom tri neorganska inhibitora koncentracija 10^{-4} M.



Slika 2 - Potenciodinamičke katodne i anodne polarizacione krive legure 5: a) bez dodatka inhibitora, b) u prisustvu 10^{-4}M Na_2CO_3, c) u prisustvu 10^{-4}M $NaNO_2$, d) u prisustvu 10^{-4}M K_2CrO_4

Na dobijenim katodnim i anodnim polarizacionim zavisnostima za leguru 5 (dijagrami su dati na slici 2), jasno se pokazao pozitivan efekat svih inhibitora na brzinu korozije ispitivane legure. Vrijednosti e(j=0) su pomjerene ka pozitivnijim vrijednostima, u odnosu vrijednost e (j=0) koja je dobijena potenciodinamičkim praćenjem legure 5 u rastvoru bez dodatka inhibitora.

Svi rezultati eksperimentalnih istraživanja (sa i bez dodatka inhibitora) na legurama 1-5 dati su u sljedećim tabelama.

Tabela 3 - Vrijednosti Rp, j_{corr} i e(j=0) dobijene metodom polarizacionog otpora u prisustvu inhibitora Na_2CO_3

Legura	Bez inhibitora			10^{-4} M Na_2CO_3		
	e(j=0) [mV]	Rp [Ω]	j_{corr} [μA/cm^2]	e(j=0) [mV]	Rp [Ω]	j_{corr} [μA/cm^2]
1	-674,2	110,4	196,7	-611,1	147,5	147,3
2	-627,0	270,5	80,28	-624,6	272,2	79,79
3	-650,4	65,17	333,2	-640,6	240,6	90,25
4	-668,0	214,5	101,2	-653,3	301,1	72,11
5	-656,5	64,88	334,7	-650,3	245,4	88,48

Tabela 4 - Vrijednosti Rp, j_{corr} i e(j=0) dobijene metodom polarizacionog otpora u prisustvu inhibitora $NaNO_2$

Legura	Bez inhibitora			10^{-4} M $NaNO_2$		
	e(j=0) [mV]	Rp [Ω]	j_{corr} [μA/cm^2]	e(j=0) [mV]	Rp [Ω]	j_{corr} [μA/cm^2]
1	-674,2	110,4	196,7	-625,9	180,2	120,5
2	-627,0	270,5	80,28	-623,6	280,5	77,42
3	-650,4	65,17	333,2	-646,2	174,0	124,8
4	-668,0	214,5	101,2	667,1	266,0	81,65
5	-656,5	64,88	334,7	-653,5	205,2	105,8

Tabela 5 - Vrijednosti Rp, j_{corr} i e(j=0) dobijene metodom polarizacionog otpora u prisustvu inhibitora K_2CrO_4

Legura	Bez inhibitora			10^{-4} M K_2CrO_4		
	e(j=0) [mV]	Rp [Ω]	j_{corr} [μA/cm^2]	e(j=0) [mV]	Rp [Ω]	j_{corr} [μA/cm^2]
1	-674,2	110,4	196,7	-635,6	177,9	122,1
2	-627,0	270,5	80,28	-626,8	289,0	75,15
3	-650,4	65,17	333,2	-649,6	336,6	64,51
4	-668,0	214,5	101,2	-661,8	319,0	68,08
5	-656,5	64,88	334,7	-650,7	371,4	58,46

Vrijednosti polarizacionog otpora i gustine struje korozije iz tabela 3-5 može pokazuju da korišćeni inhibitora snižavaju brzine korozije ispitivanih legura u 0,51M rastvoru NaCl, na bazi povećanja vrijednosti Rp i smanjenja vrijednosti j_{corr}. Efikasnost zaštite na osnovu podataka iz tabela računa se prema jednačini:

$$\eta = \frac{j_{corr} - (j_{corr})_{inh}}{j_{corr}}$$

gdje je j_{corr} gustina struje korozije u neinhibiranom, a $(j_{corr})_{inh}$ u inhibiranom rastvoru. Izračunate vrijednosti efikasnosti zaštite date su u tabeli 6.

Tabela 6 - Efikasnost zaštite ispitivanih legura u prisustvu neorganskih inhibitora

Legura	10^{-4}M Na_2CO_3	10^{-4}M $NaNO_2$	10^{-4}M K_2CrO_4
1	25,11%	38,74%	37,93%
2	0,61%	3,24%	6,39%
3	72,91%	62,55%	80,64%
4	28,75%	19,32%	32,73%
5	73,56%	68,39%	82,78%

Eksperimentalni rezultati iz tabela 7-9 daju jasnu sliku o pozitivnom uticaju sva tri korišćena inhibitora na brzinu korozije kod svih korišćenih legura, upoređujući vrijednosti e(j=0) u rastvoru 0,51M NaCl bez inhibitora i u tri rastvora 0,51M NaCl u koji su dodati neorganski inhibitori. Najznačajnije pomjeranje potencijala uočeno je kod legure 2 uz dodatak $NaNO_2$ kao inhibitora.

Tabela 7 - Vrijednosti e(j=0) dobijeni potenciodinamičkom metodom u prisustvu inhibitora Na_2CO_3

Legura	Bez inhibitora	10^{-4} M Na_2CO_3
	e(j=0) [mV]	e(j=0) [mV]
1	-706,5	-684,6
2	-726,2	-667,7
3	-708,0	-695,3
4	-699,3	-678,7
5	-701,4	-657,4

Tabela 8 - Vrijednosti e(j=0) dobijeni potenciodinamičkom metodom u prisustvu inhibitora $NaNO_2$

Legura	Bez inhibitora	10^{-4} M $NaNO_2$
	e(j=0) [mV]	e(j=0) [mV]
1	-706,5	-680,4
2	-726,2	-663,1
3	-708,0	-658,8
4	-699,3	-694,5
5	-701,4	-678,1

Tabela 9 - Vrijednosti e(j=0) dobijeni potenciodinamičkom metodom u prisustvu inhibitora K_2CrO_4

Legura	Bez inhibitora	10^{-4} M K_2CrO_4
	e(j=0) [mV]	e(j=0) [mV]
1	-706,5	-675,4
2	-726,2	-693,8
3	-708,0	-661,7
4	-699,3	-694,5
5	-701,4	-685,9

ZAKLJUČAK

Dobijeni rezultati ispitivanja austenitnih manganskih čelika pokazuju:

- Koroziona stabilnost ispitivanih austenitno manganskih čeličnih livova isključivo je zavisna od hemijskog sastava, kao i strukture koja se formira prilikom njihovog očvršćavanja.
- Rezultati ispitivanja korozionih osobina svih ispitivanih legura pokazuju da se svi ispitivani čelici (legure) ne ponašaju stabilno u vodenim rastvorima hlorida bez prisustva inhibitora.
- Efekat inhibitora je značajan posebno kod čelika kod kojih je povećan odnos sadržaja aluminijuma i molibdena. Na osnovu ovoga najveću efikasnost zaštite u prisustvu neorganskih inhibitora imao je čelik broj 5, a od korišćenih inhibitora najefikasniji je bio K_2CrO_4 (efikasnost 82,78 %).

Zahvalnost

Autori se zahvaljuju Ministarstvu nauke Crne Gore na sredstvima dodijeljenim za naučno-istraživački projekat „Ispitivanje uticaja inhibitora na brzinu korozije materijala na bazi željeza i aluminijuma u vodenim rastvorima“.

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ABSTRACT

INVESTIGATION OF THE INHIBITORS EFFECT ON THE CORROSION BEHAVIOR OF AUSTENITIC MANGANESE STEEL CASTINGS IN AQUEOUS SOLUTIONS

Production of spare parts for mills and crushers as an indispensable material is austenitic manganese steel casting. In the course of this material is subjected to abrasive wear and impact load. In addition to the application of austenitic manganese steels can be used as materials in aqueous corrosive environment conditions.

Abrasive wear is often increased by the presence of corrosive materials, among which counts water, since the corrosion effects are much more pronounced mechanical removal of material.

Corrosion products usually have a low resistance to abrasion. Practice has shown that the wear rate of coating mills for wet grinding of cement is much higher compared to the rate of wear of lining dry milling.

The aim of this paper was to investigate the influence of different inhibitors on the corrosion behavior of austenitic manganese steel, which is composed of different relationships aluminum and molybdenum. The results will show the effect of the used inhibitors.

Key words: *inhibitors, corrosion, austenitic manganese steel castings, aqueous solutions*

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Scientific paper

JADRANKA MALINA[1]
ANITA BEGIĆ HADŽIPAŠIĆ[1]
ŠTEFAN NIŽNIK[2]

Scientific paper
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Electrochemical corrosion and hydrogen diffusivity in dual phase steel

Due to application in automotive industry, dual phase (DP) steels have received enormous attention over the last three decades. They show superior mechanical properties when compared to conventional high strength low alloyed (HSLA) steels, but their susceptibility to hydrogen embrittlement need to be explored in a greater extent. Therefore, in this study diffusion properties of hydrogen absorbed in steel were investigated in order to quantify the parameters of H-migration through complex microstructure of DP.

Electrochemical experiments have shown that exposure of DP steel in 2M H_2SO_4 under free corrosion potential at room temperature led to the evolution of hydrogen atoms in amount high enough for diffusion through the metal.

The values obtained for diffusivity and solubility of atomic hydrogen in DP steel suggest that permeability depends primarily on fine-grained microstructure of ferrite and martensite. Such heterogeneous polymorphic structure enables a high solubility of hydrogen within a network of numerous grain boundaries which act as reversible hydrogen traps. At ambient temperatures, these traps cannot retain hydrogen permanently and therefore the net result of trapping is low diffusion rate of hydrogen.

Key words: *DP steel, electrochemical corrosion, hydrogen diffusivity, ferrite, martensite*

1. INTRODUCTION

Dual-phase (DP) steels belong to a group of modern multi-phase steels (DP, TRIP, TWIP) characterized by ferrite matrix containing one or more phases (martensite, bainite and residual austenite) [1-3]. The coexistence of soft/hard phases and their interaction in working conditions allow both high strength and ductility to be achieved.

DP steels consisting of soft ferrite and hard martensite show superior mechanical properties compared to conventional HSLA steels. That has led the researchers to explore their suitability for different structural and constructional purposes [4-7]. Although a lot of papers were published regarding very good combination of mechanical properties in DP steels [8-13], further investigations are necessary to find the effect of phase constituents on the corrosion resistance properties [14,15]. The synergies of crystal structure of these materials with the hydrogen evolved and entrapped during corrosion is also a matter of a great concern and should be investigated in relation to the hydrogen embrittlement phenomena (HE) known as the most dangerous problem in HSLA steels exploitation [16-19].

In view of the above, the present research is undertaken to understand the electrochemical behaviour of commercial DP steel immersed in 2M H_2SO_4 solution, as well as diffusion properties of H-atoms migrating in dual phase steel during spontaneous corrosion process.

2. EXPERIMENTAL

2.1. Material

Specimens were cut from the commercial DP-sheet produced with 3 mm in thickness by the compact strip production (CSP). This is an advanced manufacturing technology in the present iron and steel industry, which is widely adopted for hot strips production from a continuous cast slab in order to save energy and improve the productivity of steels [20]. Compared to the low carbon steel produced by conventional hot-rolling process, CSP is characterized by high strength and fine grain size. For the corrosion experiments the specimens of original thickness were used, while those in hydrogen permeation experiments were thinned mechanically from both sides to 1.5 mm.

2.2. Microstructural analyses

The microstructure of steel before and after hydrogenation was analysed by optical microscope Olympus GX 51. SEM images were recorded by detection of signals from the secondary electrons (SE) using Scanning Electron Microscope TESCAN

Author's address: [1]University of Zagreb, Faculty of Metallurgy, Sisak, Croatia, [2]Technical University of Košice, Faculty of Metallurgy, Košice, Slovakia

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VEGA LSH (Czech Republic) equipped with energy dispersive x-ray spectrometer (Oxfords' Instruments INCA system with software and detector technology for EDS microanalysis).

2.3. Corrosion testing

Round specimens with surface of 0.384 cm2 were taken for electrochemical studies of corrosion. Prior to the experiment, each specimen was polished up to 600 emery paper followed by washing in distilled water and degreasing in ethanol. The experiments were conducted using PARSTAT 2273 potentiostat, interfaced with personal computer. Electrochemical polarization studies were performed in electrochemical cell in deaerated condition by N2-purging. The potential of the working electrode was measured against saturated calomel reference electrode (SCE) in the Luggin capillary placed close to the working electrode. Pt-mesh was used as a counter electrode. The potentiodynamic polarization studies were carried out at the open circuit potential (Eocp). The scan rate used was 5 mV/s. The corrosion rate was determined using Tafel's extrapolation method, as per ASTM standard. The Tafel's slope, cathodic (βc) and anodic (βa) and the corrosion current densities (icorr) were estimated from the Tafel plots. The corrosion rates were obtained from the corrosion current density using Faraday's law incorporated in Parstat software PowerCorrTM.

2.4. Hydrogen permeation

Electrochemical hydrogen permeation has been a well established experimental technique for more than forty years [21]. In the hydrogen permeation experiment two individual electrolytic cells are separated with a membrane made from the steel to be investigated. On the entrance side (cathodic compartment filled with 2M H_2SO_4 and deaerated) the hydrogen is produced spontaneously by corrosion reaction. The hydrogen is then adsorbed on the sample surface and atomically absorbed into the material of the membrane. A constant potential (+ 200 mV vs SCE) is applied to the output side (anodic compartment filled with 1M NaOH) using a potentiostat. The hydrogen which diffuses through the membrane is oxidized on this side and the resulting oxidation current is registered.

For the purposes of the electrochemical H-charging, the commercial DP strip was cut in the form of membrane with dimensions 80mm×50mm×1.5mm. Both sides of the steel membrane were ground up to 600 grit paper, and the detection side of steel membrane was electroplated with Ni in order to ensure the surface passivity and reliability of the hydrogen oxidation current [22]. After cleaning the specimen surface with ethanol, the steel membrane was mounted between two electrochemical cells. An area of 3.14 cm^2 was exposed to each electrolyte inside the cells.

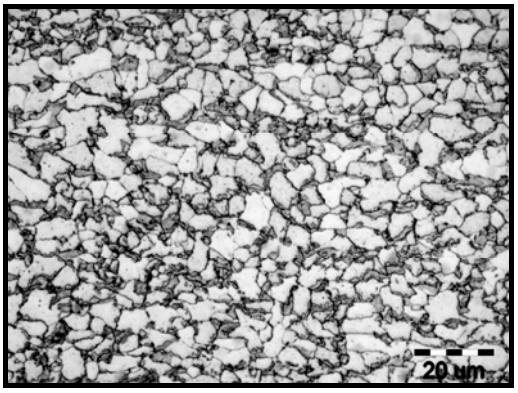
All the measurements were done in triplicate, at room temperature (T = 20 °C).

3. RESULTS AND DISCUSSION

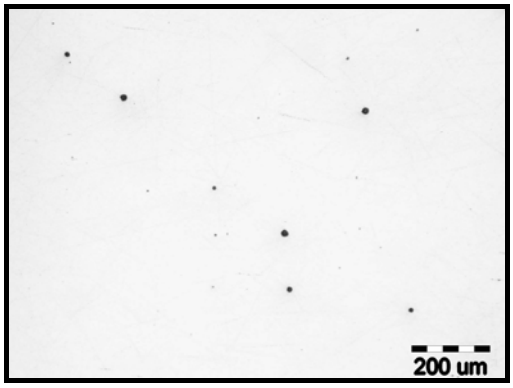
Table 1 and Figure 1 show the chemical composition and the microstructure of the tested steel, respectively. It can be seen that commercial DP strip is characterized by high purity since the content of carbon and sulfur is very low.

Table 1 - Chemical composition (mass. %) of DP steel

C	Mn	P	S	Si	Cu	Mo	Al	Cr	Ni	Sn	Nb	N
0.05	1.23	0.012	0.003	0.42	0.16	0.01	0.033	0.66	0.05	0.008	0.002	0.0085 ppm



a)



b)

Figure 1 - Optical micrograph of DP steel showing (a) the islands of martensite (dark phase) in ferrite matrix (light phase) and (b) globular particles of different size

Microstructure of as-received strip shown in Figure 1 reveals that the steel consists of fine and uniformly distributed polyhedral ferrite grains with diameter of about 5-15μm, and martensite islands (~10 %) embedded in a ferrite matrix. The presence of these two phases in contact with 2M H2SO4 significantly influenced the corrosion behaviour of DP steel during polarization studies and permeation experiments, as presented in Figure 2.

From experimentally obtained cathodic and anodic polarization curves in Figure 2a, corrosion potential and corrosion current have been derived using Tafel's linear extrapolation method. The data are shown in Table 2.

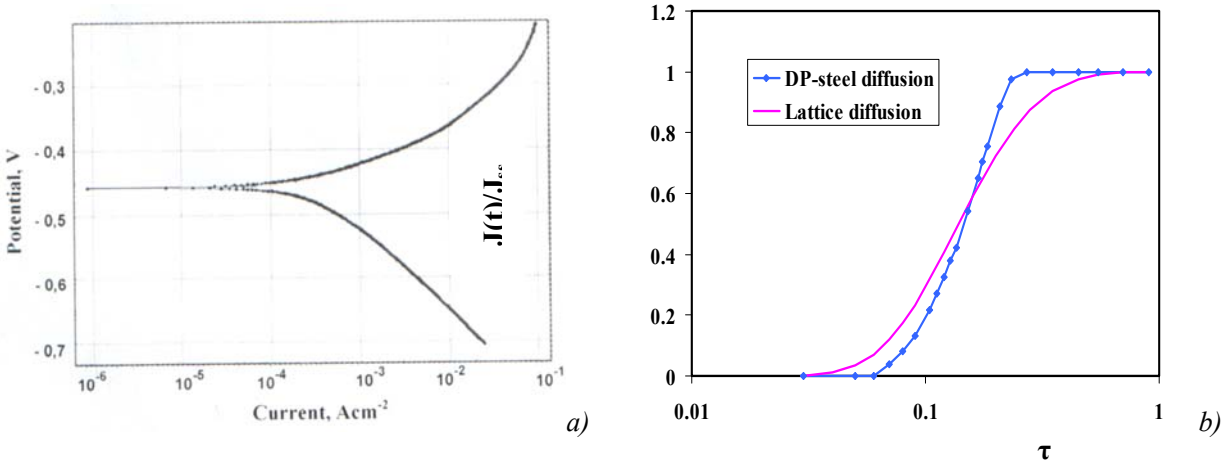


Figure 2 - Polarization curves of DP steel in H_2SO_4 (a); normalized hydrogen flux in DP steel (b)

Table 2 - Corrosion characteristics of DP steel in 2M H_2SO_4 solution

E_{corr} /mV vs SCE	**I_{corr}**/μAcm^{-2}	**βa**/mV	**βc**/mV	**Corrosion rate**/mma^{-1}
-455.6	736.7	56.7	122.8	8.55

Corrosion rate value is comparable to the one [23] for structural carbon steel in 1M H2SO4, and Tafel's coefficients βa and βa suggest that corrosion of tested dual-phase steel in acid solution is dominated by the hydrogen-ion reduction. When DP steel corrodes in H_2SO_4, the following reactions occur on the steel surface, with ferrite phase acting as anode:

Fe -2e→ Fe 2+ (anodic)

2H+ + 2e → H2 (cathodic).

Very fine-grained structure of DP steel is characterized with number of the interfacial areas between ferrite (anode) and martensite (cathode) offering significant corrosion activity. Therefore, H-atoms evolved at the surface enter the metal and start their diffusion through the steel membrane. Because of the continuous oxidation of hydrogen at the output side and constant incoming flux of hydrogen from the input side of steel, the oxidation current is directly proportional to the amount of hydrogen penetrating through the membrane.

At a steady state, a constant concentration gradient through the DP-membrane is established. As a result, the evolution of hydrogen flux with time exhibits a sigmoid relationship shown in Figure 2b: the rate of hydrogen permeation rises after a certain break-through time and then approaches asymptotically to the steady state permeation rate. Normalized flux of hydrogen atoms through α-Fe is also presented in Figure 2b, for easier comparison with the theoretical (Fick's second law) lattice diffusion [22]. A permeation curves provide various informations on the hydrogen diffusion and trapping in the steel membrane, such as diffusivity (Dapp), permeability (Jss·L) and solubility (Sapp). Dapp represents the apparent lattice diffusivity of dissolved and reversibly trapped hydrogen, L is membrane thickness, Jss is H-flux in stationary state and the Sapp corresponds to the hydrogen in lattice and reversible traps. These values were calculated from the experimental curves and diffusion theory using tlag-method [22]. The data are listed in Table 3.

Table 3 - Hydrogen permeation data for DP steel

t_{lag}	**i_{ss}**	**$J_{ss} \times 10^{11}$**	**$J_{ss} \times L \times 10^{11}$**	**$D_{app} \times 10^{7}$**	**$S_{app} \times 10^{6}$**
s	μA cm^{-2}	mol cm^{-2} s^{-1}	mol cm^{-1} s^{-1}	cm^2 s^{-1}	mol H/cm^3
6600	2.07	2.15	0.32	5.68	5.66

From the hydrogen transients in Figure 2b, it is obvious that break-through time required for H-atoms to reach the exit site of DP-membrane is longer than that in α-iron. However, the diffusion coefficient D becomes about 100 time lower (Table 3) in comparison with the value for lattice diffusivity in α-Fe (DFe = 6.2 × 10-5 cm2 s-1) [24]. It is known [25] that the decrease in diffusivity and increase in solubility of hydrogen in steel strongly depend on trapping of H by various defects like dislocation, grain boundaries, matrix-particle interface etc. SEM/EDS analyses performed on the tensile fracture surfaces of DP steel have shown (Figure 3) the presence of characteristic inclusion particles with Ca, Al and O as the main constitutive elements.

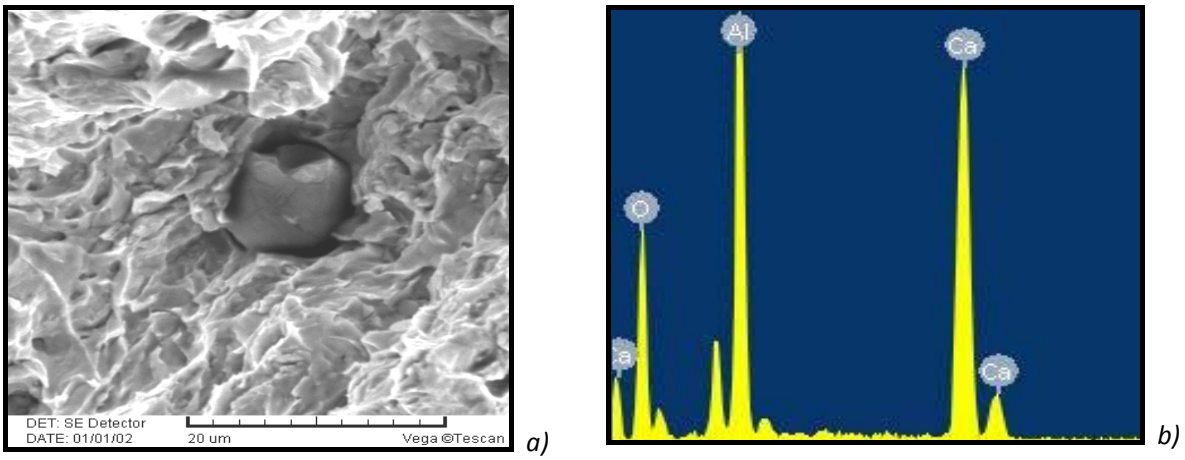


Figure 3 - SEM micrograph and EDS spectrum of inclusion particle on the tensile fracture surface of tested DP steel

It is obvious that particles identified are Ca, Al-oxides registered also by optical metallography. Their random distribution and globular shapes are presented in Figure 1b.

Hydrogen atoms trapped by such strong traps are released only if heated to very high temperatures and do not contribute to diffusivity at ambient temperature.

Hence, most of the traps present in DP steel would be of low binding energy like grain boundaries and dislocations. Very fine ferrite-martensite structure of DP-strip provides extremely high density of such traps, especially that of grain boundaries. At ambient temperatures, these traps cannot retain hydrogen permanently and therefore the net result of trapping is the decrease in diffusion rate of hydrogen, which in turn results in an apparent increase in the solubility.

4. CONCLUSION

- Electrochemical corrosion of dual-phase steel in 2M H2SO4 solution is dominated by the hydrogen-ion reduction and results in Fe-ion release.
- The exposure of DP steel to the electrolyte solution under free corrosion lead to the evolution of hydrogen atoms which enter the crystal lattice.
- The lower permeability and diffusivity of atomic hydrogen in DP steel compared to α-Fe is the consequence of heterogeneous polymorphic structure with different traps in which H-atoms may be captured.
- Most of the traps present in DP steel are of low binding energy like grain boundaries and dislocations although some globular Ca, Al-oxides, known as strong traps are detected in DP steel.

Aknowledgment

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IZVOD

ELEKTROHEMIJSKA KOROZIJA I DIFUZIJA VODONIKA U DVOJNOJ FAZI ČELIKA

Zbog primjene u automobilskoj industriji, dvofazni čelici (DP) pobudili su tijekom protekle tri dekade izuzetno zanimanje. U usporedbi s konvencionalnim visokočvrstim niskolegiranim čelicima (HSLA) imaju superiorna mehanička svojstva, ali njihovu sklonost krhkosti potaknutoj vodikom (HE) treba posebno ispitati. Stoga su u ovom radu proučavana difuzijska svojstva vodika apsorbiranog u čeliku, s ciljem da se odrede parametri karakteristični za H- migraciju kroz kompleksnu mikrostrukturu DP-a.

Elektrokemijski eksperimenti pokazali su da tijekom kontakta DP čelika s otopinom 2M H_2SO_4 u uvjetima spontane korozije pri sobnoj temperaturi nastaju vodikovi atomi u količini koja je dovoljna za difuziju u metalu.

Vrijednosti izračunate za topljivost i difuziju atomarnog vodika u DP čeliku sugeriraju da permeabilnost prvenstveno ovisi o izrazito sitnozrnatoj mikrostrukturi ferita i martenzita. Takva heterogena polimorfna struktura omogućava dobru topljivost vodika zahvaljujući brojnim granicama zrna koje djeluju kao reverzibilne zamke za vodik. Pri sobnim temperaturama ovakve zamke ne mogu vodik trajno zadržati, ali ga usporavaju tako da je brzina difuzije smanjena.

***Ključne riječi**: DP-čelik, elektrokemijska korozija, difuzija vodika, ferit, martenzit*

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Scientific paper

ANDREJ ČEŠNOVAR[1],
MARTINA SALOVA[2]

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Appearance, management and prevention of corrosion in the brewing industry

In the food industry, the brewing sector is one of the most severely affected by corrosion. The process uses large quantities of water for beer production, bottling, storage and cleaning. The beer itself is acidic and aggressive to low carbon steel. Furthermore, it contains live microorganisms, which can cause biocorrosion. The cleaning agents used in the plant are also known to cause corrosion problems. Corrosion causes significant expenses, in terms of equipment damage. Moreover, corrosion products dissolved in the beer can cause impairment of its quality.

This paper deals with the appearance of corrosion in different stages of the brewing process, as well as with the methods of management and prevention of corrosion. Different types of materials used in breweries are analyzed, regarding their corrosion resistance. Also, the conditions of the process which may cause corrosion are considered. The corrosion control and prevention are reviewed through controlling the process parameters and selection of improved materials.

***Key words**: brewing industry, corrosion, causes and solutions*

1. INTRODUCTION

Production of beer is a process that involves different operations while processing raw materials, such as malt, water, hops and yeast, as well as adjuncts. The equipment cleaning is done by the use of various cleaning agents: sulphuric and phosphoric acid, caustic soda and chlorine and iodine for sterilization. For utility services, coal, fuel oil and ammonia are used. The brewing process consists of batch processing of different materials and it is conducted in strictly defined and controlled conditions [1].

Regarding the equipment, brew making is heterogeneous as well; the following materials are used: copper, stainless steel, coated mild steel and, in some cases, aluminum. Considering the fact that the process of brewing is complex, that the auxiliary operations are inevitable and the materials used for equipment production, there is general conclusion that in various points of the process there could be appearance of corrosion.

2. PRODUCTION OF BEER

Brewing is the production of beer through steeping a starch source (commonly cereal grains) in water and then fermenting with yeast. The process consists of few steps:

Malting is the process of preparing barley for brewing. It is comprised of three steps: steeping, germination and kilning.

Milling is cracking of the malted grains.

Mashing, which serves to convert the starch from the malting process, into sugar.

Lautering is separation of the wort from the grains.

Brewing is a complex process, in which wort is boiled when hops are added. During this step, a number of changes occur in the wort, such as coagulation of proteins, evaporation of the wort and flavor and color changes.

Cooling is the process of filtration and rapid cooling of the wort to a temperature suitable for adding the yeast.

Fermentation is the step in which the yeast metabolizes the substances that can be dissolved in the wort. Formation of ethanol, carbon dioxide and heat is characteristic.

Conditioning is the stage when the immature bear has to be held for a period of time to refine the flavor of the beer. During this process, hydrogen sulphide is released from the beer.

The last two steps are *filtration* and *packaging* of the mature beer.

3. APPEARANCE OF CORROSION IN THE BREWERY

Before determination of corrosion prevention and management methods, it is essential to identify the areas affected by corrosion. On Figure 1, schematic presentation of the processes in the brewery is given, and the critical points are marked. According to this, corrosion could appear in different places, such as the lauter tun, storage tanks, CO_2 recovery units, fermentation tank, etc., as well as in the equipment for auxiliary operations, i.e. CIP (clean-in-place) stations [2, 3].

Author's address: [1]OKTA Crude Oil Refinery AD, Skopje, Macedonia, [2]Faculty of Agricultural Sciences and Food, Skopje, Macedonia

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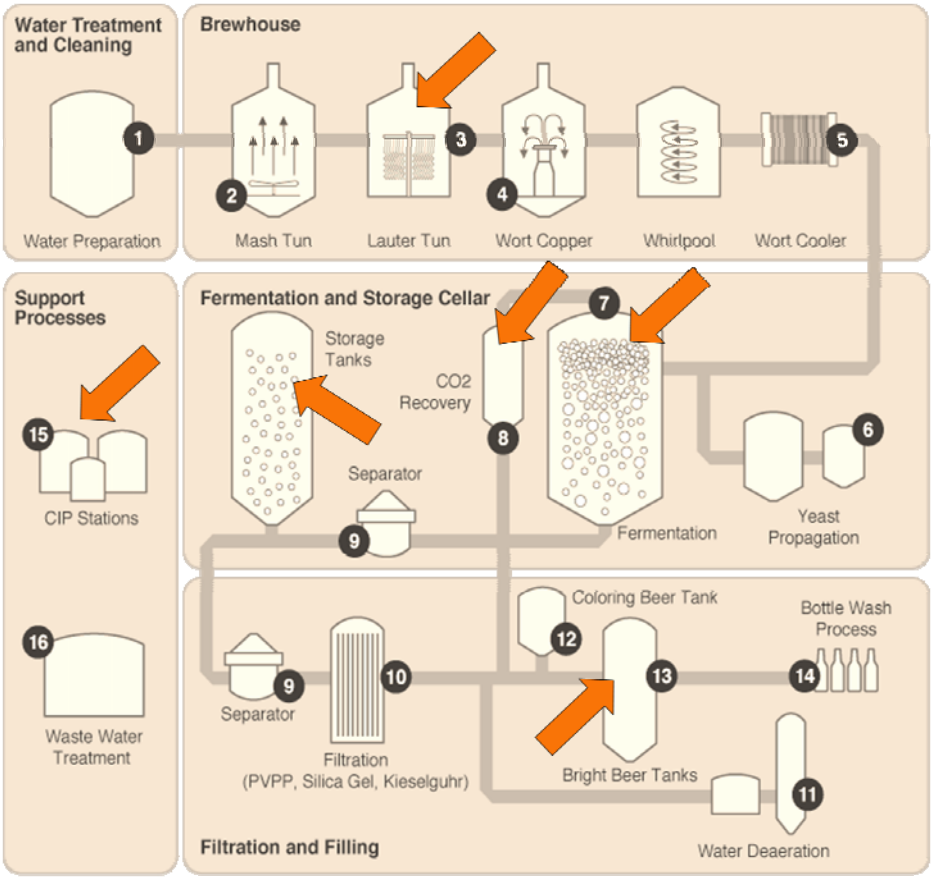


Figure 1 - Diagram of the brewing process with critical corrosion locations

The use of different materials in the lauter tun (e.g. steel for the vessel and brass for the false bottom), combined with the damaging of the internal floor coating, can cause forming of galvanic corrosion cells [2].

The fermentation tanks have more severe environments than the storage tanks. Today, most of these vessels are made from stainless steel, which provides satisfatory results, but materials such as low carbon steels are known to be used, also. The heating copper coils located in the tank, combined with a bare steel surface (on location with damaged coating), can result in aggresive corrosion of the steel in the acidic CO_2-saturated product [1].

Two examples of stainless steel tank corrosion are given on figure 2; appearance of a) pitting, b) cracks [4].

The corrosion in the CO_2 recovery plant often affects the gas side of the stainless steel piping, compressors and valves. Usually, it is caused by processed water, treated with ClO_2 in the brewery. The chlorine dioxide acts as an oxidizing agent and undergoes the following reaction:

$$ClO_2^- + 2H_2O + 4e^- \rightarrow Cl^- + 4OH^- \ (E^0 = 0.76\ V)$$

This spontaneous reaction causes corrosion in the CO_2 recovery plant.

The agents used for cleaning of the equipment and piping are also associated with corrosion. Corrosion only occurs under harmful circumstances, such as rapid thermal changes (which are an underlying cause for tank implosion) and contact of CIP acid with dirty surfaces (which causes pitting corrosion) [5]. Under the described conditions, the disinfectant will oxidize the metal surface, as described by the following reduction half-reaction:

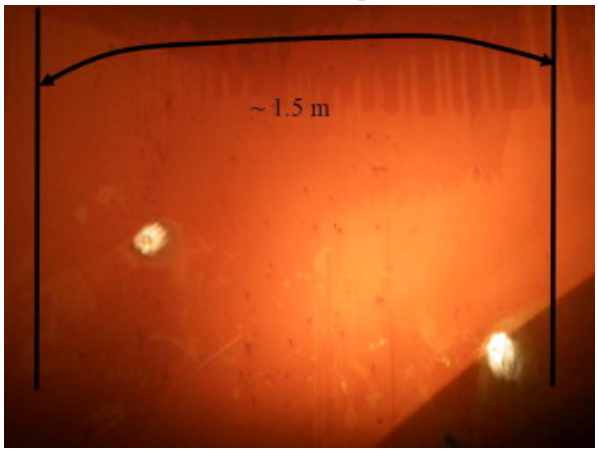
$$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \ (E^0 = 0.89\ V)$$

In this reaction, hypochlorite is shown as the oxidizing agent, but in fact, there are other cleaning agents that could be used instead (e.g. peractetic acid, hydrogen peroxide and chlorine dioxide). The hypochlorite is also an inhibitor of bacterial corrosion that kills the bacteria before they are involved in the corrosive damage. For this reason, this process is not affected by microorganisms.

The oxidation half-reaction of brewery-related metal (e.g. steel) would be:

$$Fe_{(s)} \rightarrow Fe^{2+}{}_{(aq)} + 2e^- \ (E^0 = 0.44\ V)$$

The overall reaction potential is 1.33 V, which means that this reaction occurs spontaneously.



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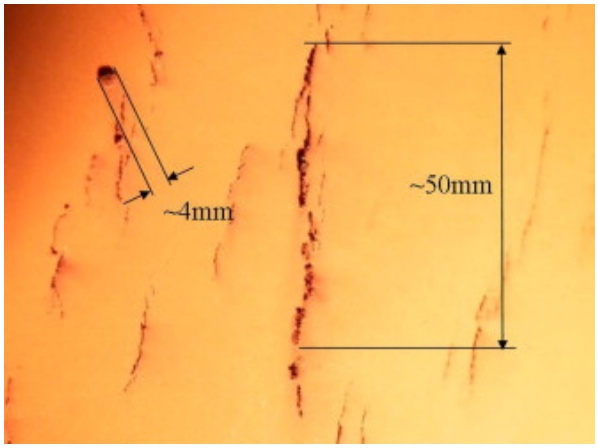

b)

Figure 2 - Examples of corrosion in stainless steel tank

3.1 Common materials in the brewery and their corrosion

Every brewery has various types of equipment, ranging from standard power plant equipment (boilers, condensers, etc.) to specific sophisticated laboratories for handling yeasts, malts and hops essences. This wide range of equipment implies use of different metals and special alloys.

Any metal in direct contact with the beer should not react to produce off-flavors. This is the main reason that stainless steel is commonly used. These steels are acid resistant and do not taint the product. Other metals and alloys used in the brewery are: brass, copper, aluminum and mild steel [6, 7].

3.1.1 Steel

Because iron affects the shelf-life of beer, steel is not a major material for construction of equipment which is in direct contact with the product. Steel can be used as a material for less important auxiliary equipment or combined with linings or coatings for brewery equipment (e.g., epoxy-lined fermentation and storage tank) [6, 8].

3.1.2 Stainless steel

Most of the brewery equipment currently used is fabricated from the 300 series alloys (AISI 304 or 316) [9] and includes kettles, tanks, tubs, plate coolers, and even some pasteurizers [2]. These alloys are much more corrosion resistant and, when passivated, are essentially inert to the beer. However, the one weakness of the stainless steel is chlorine, which is a common ingredient in cleaning solutions [1, 5-7].

Active chlorine present in bleach solutions can cause the protective oxide layer on stainless steel to deteriorate; if there is a scratch on the wall, or a crevice created by a rubber gasket against the steel, then these areas can become electrically different from the surrounding area, creating a galvanic cell, which leads to crevice corrosion [7]. The corrosion develops following the mechanism described in the previous section. This type of corrosion can occur when the bleach water is still in the vessel i.e., not circulating, or, at the water surface, if the keg is only half-full. In the latter case, the crevice is represented by the waterline. Usually, this type of corrosion manifests as pitting or pinholes.

Bio-fouling and beerstone scale (CaC_2O_4) can cause the same corrosion phenomena. The metal surface underneath the deposit becomes depleted of oxygen via biological or chemical means, and corrosion occurs [7, 8]. This is the main reason why the removal of beerstone is important.

3.1.3 Copper

Because of its properties, copper has been the traditional metal in breweries for centuries. However, with the advent and the use of new alkaline cleaners, some corrosion issues have arisen. Copper is relatively inert to both wort and beer; with regular use, a stable oxide layer will form on the vessel wall, which will protect it from further interaction with the product [2, 6].

However, copper can develop a toxic oxide called verdigris. Verdigris includes several chemical compounds – cupric acetate, copper sulfate, cupric chloride, etc., which are soluble in weakly acetic solutions, like beer, and can lead to copper poisoning [8]. Because of this, proper cleaning of the copper vessels is required.

In general, copper is more acid than alkaline resistant. Oxidizers such as bleach and hydrogen peroxide will cause blackening of copper and brass due to formation of black oxides [7]. When these

oxides are removed, a new metal surface is exposed to corrosion. For this reason, alkaline cleaners, such as ammonia and oxidizers, which are very useful for dissolving organic deposits, should be used with caution. Copper is not resistant to oxidizing acids and non-oxidizing acids containing dissolved oxygen. Usually, it is resistant to non-oxidizing acids, such as acetic, hydrochloric and phosphoric acids [2, 7].

3.1.4 Brass

Brass is an alloy of copper and zinc, which also contains a small percent of lead, for improved machinability. The present lead can be dissolved by the wort and although this small amount of lead does not present a health issue, the best solution is to avoid the use of leaded brass altogether [6, 8].

The reason that brass fittings are not commonly used in commercial breweries is that the CIP systems and the chemicals used with stainless steel are too corrosive to brass.

3.1.5 Aluminum

Aluminum has many favorable properties – good formability, machinability and thermal conductivity. The most commonly used alloys are 3003 and 3004, which have very good corrosion resistance [6, 8]. Under normal brewing conditions, aluminum by itself will not corrode and does not affect the product in any way.

However, aluminum will corrode if placed adjacent to another metal (e.g., copper) submerged in wort or beer; aluminum and brass or copper couples should not be used for long term storage of beer [8]. The use of casting cleaners and bleach should be avoided, because they will cause pitting.

4. CORROSION CONTROL IN THE BREWING PROCESS

Beer is corrosive; not only it is acidic, but it also contains live organisms that cause biofouling and biocorrosion [1, 7]. Beer can be corrosive to the tanks and fluid lines used in the brewing process, as well as to the brewing building.

The only way to control corrosion during the brewing process is to control the pH value. This parameter depends on multiple factors, such as yeast strain, water hardness, bacterial infection and the process itself [7].

The pH value of the beer is about 4 when fresh, but when exposed to oxygen, for example, after dispense, this value can drop to 3.5 – 3.3 and even bellow 3 [10-13]. These acidity levels usually do not affect stainless steel, which is not the case with aluminum alloys. These materials' oxide layers are attacked by any pH less than about 4 or over about 9. The pH values of common fluids in brewing industry are given in table 1 [13].

Table 1 - Most common fluids in the brewery

pH	Fluid
1.0	Hydrochloric acid
2.2	Lactic acid
3.3 – 3.7	Wheat beer
4.4 – 4.7	Lager beer
5.5	Unfermented beer
7 – 8	Tap water
8.5	Sodium carbonate
13	Caustic soda

Because of this, the aluminum containers are lined with protective coatings. However, if the coating is damaged, the broken down coating flakes can get into the extractor valves, and more important, the keg itself can be corrosively attacked. This is most expressed on the welded joints and can compromise the vessel's integrity [7].

Acidity is usually expressed in terms of lactic acid, although there is great number of other organic and inorganic acids present. The acidity levels should be maintained at constant values, but slight fluctuations can be expected. This parameter can be affected by the various strains of yeast, as well as improper wort aeration, but it also depends on the character of the product.

Although the highlight of this paper is on preservation and protection of the equipment, the most important concern is the final quality of the product. For this reason, the best solution would be to establish a balance between these two aspects. From the beginning, through the entire process of beer production, the pH value fluctuates, depending on the different phases. Various factors can contribute towards higher or lower pH values [5].

The increase of pH can be caused by cold fermentation coupled with a reduced assimilation of buffering substance by yeast, use of water high in carbonates, as well as by a number of other factors. Lower pH can be expected in all-malt beers, yeast that tends to flocculate early, a slight upward adjustment of pitching temperatures and of the maximum temperature during fermentation, etc [10-13].

The pH value should be maintained in optimal range in every stage of the process; this can be achieved by balancing these factors with opposite effects. The process should be properly executed, to avoid large pH variations, which would also contribute to higher quality of the final product.

5. CORROSION PREVENTION IN THE BREWING INDUSTRY

The corrosion prevention methods are the best way to eliminate corrosion in the breweries. This can be accomplished in several ways:

- Use of special alloys – several alternative corrosion resistant alloys are available. The corrosion and stress corrosion cracking of the stainless steels from the 300 series can be prevented by use of type 444 or 446 ferritic stainless steel [2]. These alloys are also more resistant to biofouling conditions than 304 [7].
- Use of coatings and linings – these materials provide effective protection of the metal surface and serve as a barrier between corrosive environment and metal. The coatings and linings are safe and do not affect the quality of the final product.
- Use of inhibitors in wastewater – this method is a good way for corrosion prevention in the waste treatment facilities, which are especially subjected to aggressive conditions.
- Use of cathodic protection – this technique can be very effective in such equipment as the bottle-line pasteurizer. Cathodic protection works very well in preventing galvanic and biological corrosion. However, one problem when applying this technology is the possible formation of oxygen as a by-product on the cathode [2, 7].

The most common types of corrosion found in the brewing industry are: pitting, crevice and intergranular corrosion, as well as biofouling and biocorrosion, to a lesser extent [1, 5, 7, 9].

Pitting and crevice corrosion can be prevented by control of the alloy's environment. This can be achieved with good welding preparation, choosing appropriate steel grade for corrosive environments, as well as appropriate post-welding treatment [5, 9].

Prevention of intergranular corrosion can be accomplished in several ways: treatment at high temperatures (> 1050^{o}C) and rapid cooling, which enables precipitation of carbides, reduction of carbon content and addition of titanium and niobium, which reduces or stops the diffusion of carbon across grain boundaries [5].

6. CONCLUSION

Beer production process is complex one from aspect of corrosion – many different materials are used and various types of fluids and environments are included.

Corrosion in the brewing industry is important from several major points of view: expenses, health and safety and risk management.

When corrosion occurs in the brewing equipment, financial expenses can include repair and replacement of the equipment, resulting in loss of product or efficiency and contamination of the product.

Beer is a food product, which means that the quality of the product must be in accordance with the international food quality standards. Corrosion in the brewery equipment produces metal ions that dissolve in the liquid product. Furthermore, if there is severe corrosion, there is potential for mechanical failure of the metal, resulting in a safety risk for the employees.

Corrosion presents a major risk to an industry and therefore, companies need to follow industrial risk assessment techniques in order to prevent it from having negative economic, environmental and safety repercussions. This is why it is important to understand corrosion, and the chemistry behind it – in order to prevent its occurrence.

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IZVOD

POJAVA, UPRAVLJANJE I PREVENCIJA KOROZIJE U INDUSTRIJI PIVA

U prehrambenoj industriji, sektor proizvodnje piva je jedan od najteže pogođenih korozijom. U samom procesu se koriste velike količine vode za proizvodnju piva, flaširanje, skladiranje i čišćenje. Samo po sebi, pivo je kiselo i agresivno u odnosu na niskolegirani ugljenični čelik. Osim toga, pivo sadrži žive mikroorganizme koji mogu da izazovu biokoroziju. Sredstva koja se koriste za čišćenje postrojenja isto tako mogu da prouzrokuju probleme sa korozijom. Korozija izaziva velike troškove, u smislu oštećenja opreme. Povrh toga, korozioni produkti rastvoreni u pivu mogu da umanje kvalitet finalnog proizvoda.

Ovaj rad se bavi pojavom korozije u različitim fazama procesa proizvodnje piva, kao i proučavanjem metoda upravljanja i prevencije korozije. Analizirani su različiti tipovi materijala koji se koriste u pivarama, sa aspekta njihove korozione otpornosti. Takođe, razgledani su uslovi procesa koji mogu da izazovu koroziju. Takođe su razgledani upravljanje i prevencija korozije putem kontrolisanja procesnih parametara i selekcije poboljšanih materijala.

***Ključne reči**: industrija proizvodnje piva, korozija, uzroci i rešenja*

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VERA OBRADOVIĆ, DUŠICA B. STOJANOVIĆ
IRENA ŽIVKOVIĆ, PETAR S. USKOKOVIĆ,
RADOSLAV ALEKSIĆ

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Dynamic mechanical properties of aramid fabrics impregnated with multiwalled carbon nanotubes

Carbon nanotubes (CNT) represent allotropes of carbon with a cylindrical nanostructure. In multiwalled carbon nanotubes (MWCNT), graphitic layers make up concentric tubes. The multiwalled nanotubes length in our research is from 3 μm to 30 μm and their outer diameter is from 13 nm to 18 nm. Their purity is greater than 99 wt.%. The carbon nanotubes possess extraordinary physical properties, great electrical and thermal conductivity. The addition of carbon nanotubes as the reinforcement in polymer composites can significantly improve the composite mechanical properties.

In the study, the pristine multiwalled carbon nanotubes (MWCNT) were introduced in order to additionally enhance mechanical properties of materials for ballistic protection.

Keywords: *multiwalled carbon nanotubes, p-aramid fabrics, AMEO silane, mechanical properties*

INTRODUCTION

Carbon nanotubes (CNT) represent cylindrical carbon molecules composed of carbon atoms linked in hexagonal shapes (Figure 1). In multi walled carbon nanotubes (MWCNT), multiple rolled graphitic layers make up concentric tubes [1].

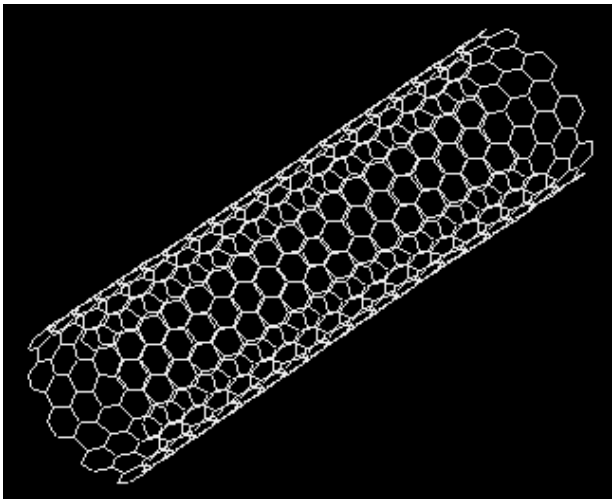

Figure 1- Carbon nanotube structure

The carbon-carbon bond in graphite is one of the strongest in constitution, thus CNTs are great candidates to be the stiffest structure ever synthesized. It is remarkable that the tubes are flexible and do not crack in bending while examining them under a transmission electron microscope (TEM) [2].

Author's address: Faculty of technology and metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia

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Carbon nanotubes expose extraordinary mechanical, electronic and magnetic properties. CNTs are probably the strongest composition with a tensile strength greater than steel, but only with one sixth of the weight of steel [3].

A common goal for adding fillers into polymers is to increase the modulus or stiffness. Various filler parameters are taken into account for their good performance in the composite. They include the size of particles, geometry, orientation, stiffness, aspect ratio (high ratio is eligible) and the strength of filler-matrix interactions [4, 5].

The interactions between the filler and the polymer matrix are important to enhance the filler dispersion and the adhesion of the polymer matrix to the filler surface, which increases the effective filler volume and creates the stress transfer from the matrix to the filler when the material is exposed to mechanical distortion. Novel nano-sized particles are good candidates in reinforcing the polymeric materials especially when they can meet certain reinforce demands at low filler loadings [5].

CNTs are perfect choice as fillers in polymer composites because of their high aspect ratio (length/ diameter ratio, which can be up to 132000000/1), small size, strength, stiffness, low density and high conductivity. When a conducting polymer is used as a matrix, the nanotube fillers greatly increase electrical transfer at low nanotube concentrations [2, 6].

Compatibility with the polymer matrix can be provided by chemical modification of MWCNTs. Carbon MWCNTs exhibit very high hardness and corrosion resistance. Their high adsorption capacity is due to their large surface area. They highly adsorb hydrogen sulfide, sulfur dioxide, disulfides, chlorine,

fluorine, ammonia, etc. Addition of MWCNTs into polymers improves their strength characteristics. MWCNTs have widespread applications, from electronics and space industry to medicine and building industry. They can be used for sensors, lithium ion batteries, fuel cells, medical implants, drug delivery, etc [7].

In the study, the pristine multiwalled carbon nanotubes (MWCNT) were introduced in order to additionally enhance mechanical properties of materials for ballistic protection. The polyurethane *p*-aramid multiaxial fabric forms (Colon fabrics) were coated with MWCNT/poly (vinyl butyral) (PVB) ethanol solution. The surface of one sample of the fabrics was coated with γ-aminopropyltriethoxysilane (AMEO silane)/ethanol solution. The mechanical properties of prepared fabrics were studied by dynamic mechanical analysis (DMA).

MATERIALS

A polymer powder poly (vinyl butyral) (Mowital B60H, Kuraray Specialities Europe) and absolute ethanol (Zorka Pharma, Šabac) were used for preparing the PVB solution (10 wt.%). The multiwalled carbon nanotubes (Cheap Tubes Inc, USA) were introduced into the PVB solution. The nanotubes length was from 3 μm to 30 μm and their outer diameter from 13 nm to 18 nm. Multiaxial aramid fabrics (Martin Ballistic Mat, Ultratex, Serbia) were used with *p*-aramid fiber type Colon (Heracron, Kolon Industries, Inc, Korea) impregnated with polyurethane (Desmopan, Bayer) [8]. The fabric sample dimensions were 15 cm × 15 cm.

EXPERIMENTAL PART

The experiments were carried out with the PVB solution in concentration of 10 wt.% where ethanol was used as the solvent. The MWCNTs were added into the solution with concentration of 0.1, 0.5 and 1.0 wt.%. Each of these solutions was ultrasonicated for 15 minutes in order to provide good dispersion of the carbon nanotubes and the stability of the solution for one month (Figure 3).

There were five samples of composites which consisted of four pieces of fabrics:

1) The first one was produced by impregnation of both sides of the fabric with 10 wt.% PVB solution in ethanol (6 g of PVB was dissolved in 54 g of ethanol, and the same content of this solution was used for the next four composites);

2) The second composite was obtained by impregnation of both sides of the fabric with 0.1 wt. % MWCNT/PVB/ethanol solution (6 mg of MWCNT was added into the PVB/ethanol solution);

3) The third composite was produced by impregnation of both sides of the fabric with 0.5 wt. % MWCNT/PVB/ethanol solution (30 mg of MWCNT was added into the PVB/ethanol solution);

4) The fourth composite was obtained by impregnation of both sides of the fabric with 1.0 wt. % MWCNT/PVB/ethanol solution (60 mg of MWCNT was added into the PVB/ethanol solution);

5) Surface modification of the fifth composite was led by impregnation with 2 wt.% AMEO silane/ ethanol solution (the solution which contained 2 g of AMEO silane dissolved in 98 g of ethanol and stirred for ten minutes on a magnetic stirrer for the hydrolysis of AMEO silane). Then, the composite was produced by impregnation of both sides of the fabric with 1.0 wt. % MWCNT/PVB/ethanol solution.

The samples were coated with the appropriate solutions and left to stand for 24 hours for ethanol evaporation (Figure 4 and Figure 5). They were processed in the compress machine at a temperature of 170 °C and under a pressure of 3 bars for 30 minutes.

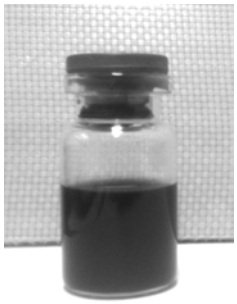

Figure 2 - 1.0 wt.% MWCNT/PVB/ethanol solution after the ultrasonication

Figure 3 - Neat Colon fabric

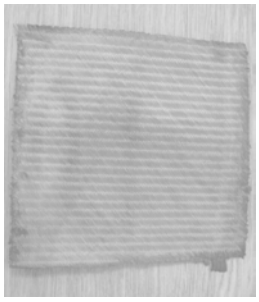

Figure 4- Colon fabric impregnated with 1.0 wt.% MWCNT/PVB/ethanol solution

Dynamic mechanical thermal analysis (DMA, Q800 TA Instruments, USA) for the *p*-aramid fabrics was conducted in a dual cantilever mode at a frequency of 1 Hz. The temperature ranged from 30 °C - 40 °C to 170 °C with a heating rate of 3 °C/min for the evaluation of the storage modulus (E') and damping factor (Tan Delta, tan δ).

RESULTS AND DISCUSSION

The storage modulus and Tan Delta are determined as functions of temperature for all types of the composites.

The plot depicted in Figure 5 shows that the modulus of Colon/PVB samples is decreasing with the addition of unmodified multiwalled carbon nanotubes. The storage modulus value for Colon/PVB and Colon/PVB/0.1 wt.% MWCNT is 2747 MPa at a temperature of 40 °C. It is evident that with the addition of MWCNT there is no increase in the modulus. For the Colon/PVB/0.1 wt.% MWCNT composite the storage modulus is 2031 MPa.

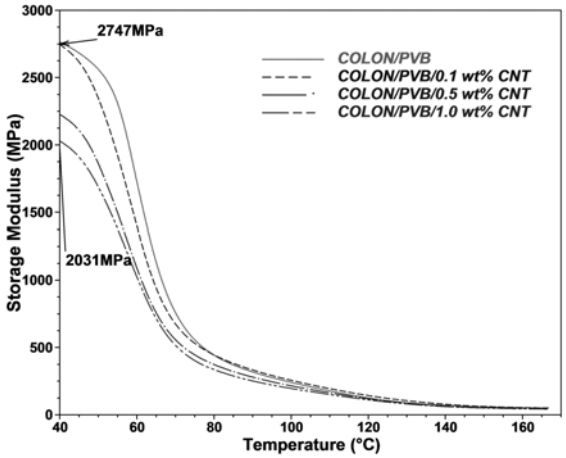

Figure 5- Storage modulus of Colon/PVB fabrics with various contents of MWCNT

The high value of Tan Delta of these fabrics indicates to the steady motion of polymer macromolecules. The first peak shows the glass transition temperature, T_{g1}, of PVB and the second one, T_{g2}, the glass transition of hard segment of polyurethane in the impregnated Colon fabrics. The T_{g1} value of the Colon/PVB sample is 67.09 °C, while this value of Colon/PVB/1.0 wt.% MWCNT is 64.85 °C (Figure 6, Table 1). Thus, there is no increase in thermal stability with the addition of MWCNT.

Tan Delta of these fabrics shows that the strongest bond between PVB and MWCNT is with the highest concentration of MWCNT (1.0 wt.%, figure 7). At the temperature of 64.85 °C the tan δ_1 value of Colon/PVB/1.0 wt.% MWCNT is 0.3132 (at the temperature of about 150 °C tan δ_2 is 0.5249) and is less than the value of Colon/PVB which is 0.3144 (67.09 °C). Tan δ_2 for the same composite is 0.5759 at the temperature ~150 °C, figure 6, table 2).

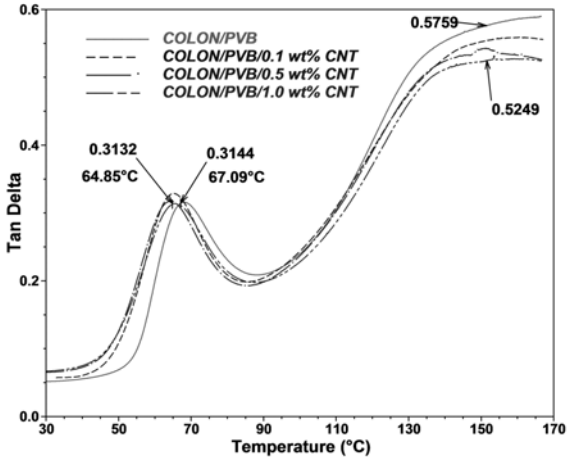

Figure 6- Tan Delta of Colon/PVB fabrics with various contents of MWCNT

Table 1 - DMA results of Colon/PVB and Colon/PVB/ /1.0 wt% CNT composites

Composite	E' (MPa, 40°C)	T_g (°C)
Colon/PVB	2747	67.09
Colon/PVB/ 1.0 wt% MWCNT	2031	64.85

Table 2 - Tan Delta of Colon/PVB and Colon/PVB/ 1.0 wt% CNT composites

Composite	tan δ_1	tan δ_2
Colon/PVB	0.3144	0.5759
Colon/PVB/ 1.0 wt% MWCNT	0.3132	0.5249

Impregnation of Colon fabrics with AMEO silane maximized the storage modulus of the Colon/ PVB/1.0 wt% CNT composite due to stronger bonds between CNT and AMEO modified Colon/PVB surface (Figure 7 and Figure 8). The storage modulus value of the Colon/AMEO/PVB/1.0 wt.% MWCNT composite is 1135 MPa, while it is 737.6 MPa for the Colon/PVB sample at the temperature of ~70 °C, which is close to the glass transition temperature of PVB.

The glass transition temperature of the AMEO modified composite is 71.16 °C, which provides thermal stability of this composite (figure 8, table 3).

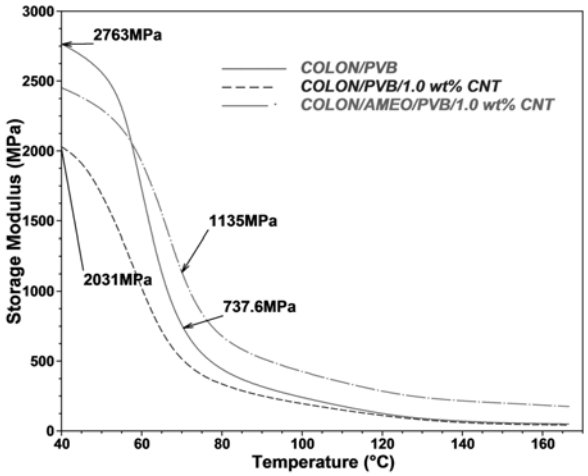

Figure 7 - Storage modulus of Colon/PVB/1.0 wt.% MWCNT fabrics with and without AMEO silane surface modification

Table 3 - DMA results of Colon/PVB and Colon/ AMEO/PVB/1.0 wt% CNT composites

Composite	E' (MPa,	T_g (°C)
Colon/PVB	737.6	67.09
Colon/AMEO/PVB/ 1.0 wt% MWCNT	1135	71.16

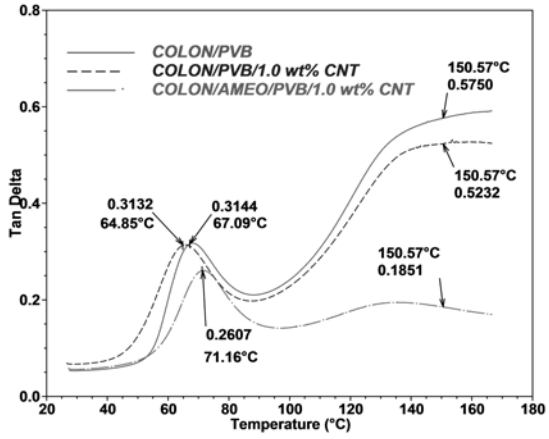

Figure 8- Tan Delta of Colon/PVB/1.0 wt.% MWCNT fabrics with and without AMEO silane surface modification

Tan δ_1 of Colon/AMEO/PVB/1.0 wt.% is decreased to 0.2607, compared to the value of 0.3144 for Colon/PVB composite. With the glass transition temperature of polyurethane (~ 150 °C), the AMEO modified composite has the decreased value of the damping factor - tan δ_2 = 0.1851 (Figure 8, Table 4).

Table 4 - Tan Delta of Colon/PVB and Colon/AMEO/ PVB/1.0 wt% CNT composites

Composite	tan δ_1 (70 °C)	tan δ_2 (150 °C)
Colon/PVB	0.3144	0.5750
Colon/AMEO/PVB/ 1.0 wt% MWCNT	0.2607	0.1851

CONCLUSION

The mechanical properties of prepared composites were studied by dynamic mechanical analysis (DMA). It was determined that the Colon/PVB/1.0 wt.% MWCNT composite had the lower storage modulus value of 2031 MPa compared to the value of the Colon/PVB composite which was equal to 2747 MPa at a temperature of 40 °C. The values of the storage moduli for the Colon/AMEO/PVB/1.0 wt.% MWCNT and Colon/PVB composites were 1135 MPa and 737.6 MPa, respectively. The increase of storage modulus was achieved by impregnation of aramid fabrics with AMEO silane. Thus, the chemical modification of aramid fabrics was accomplished and the covalent bond between polymers and fabrics was created which contributed to reduced motion of polymer macromolecules (PVB, polyurethane), and decreased values for damping factor of Colon/ AMEO/PVB/1.0 wt.% MWCNT. The composite Colon/PVB/1.0 wt.% MWCNT had lower values of damping factor, storage modulus and glass transition temperature compared to the Colon/PVB composite. Also, the AMEO modified composite had higher value of storage modulus above 55 °C and greater glass temperature than both the polymers with 1.0 wt.% MWCNT.

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IZVOD

DINAMIČKO MEHANIČKA SVOJSTVA ARAMIDNIH LAMINA IMPREGNISANIH SA VIŠESLOJNIM UGLJENIČNIM NANOCEVIMA

Ugljenične nanocevi (carbon nanotubes, CNT) predstavljaju alotropsku modifikaciju ugljenika cilindrične nanostrukture. Kod višeslojnih ugljeničnih nanocevi (multiwalled carbon nanotubes, MWCNT), grafitni slojevi obrazuju koncentrične cevi. U našem istraživanju dužina višeslojnih nanocevi iznosi od 3 μm do 30 μm i njihov spoljašnji prečnik je od 13 nm do 18 nm. Njihova čistoća je veća od 99 mas.%. Ugljenične nanocevi imaju izvanredna fizička svojstva, veliku električnu i toplotnu provodljivost. Njihovim dodatkom u vidu ojačanja u polimernim kompozitima se mogu značajno poboljšati mehanička svojstva kompozita.

U ovom radu su čiste višeslojne ugljenične nanocevi bile korišćene sa ciljem da se poboljšaju mehanička svojstva materijala za zaštitu u balistici.

Ključne reči: *višeslojne ugljenične nanocevi, p-aramidne lamine, AMEO silan, mehanička svojstva*

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Originalni naučni rad

JOVAN JOVANOVIĆ, Elektrotehnički fakultet, Beograd,
JOHN SMITH, EE Dept., University of ….

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Ključne reči: *vreme, transformacija, koncentracija*

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2. PODNASLOV (na primer EKSPERIMENTALNI RAD)

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Ostali delovi rukopisa se obrađuju u dve kolone razmaknute za 5mm. Rad kucati sa proredom single i veličinom slova 11 (Times New Roman).

Posle naslova rada i imena autora sledi kratak sadržaj (ne više od 100 reči) na srpskom jeziku pisan italikom. Najviše 6 ključnih reči treba da bude napisano ispod sadržaja. Podnaslove u rukopisu pisati u boldu velikim slovima veličine 11. Na kraju rada dati kratak sadržaj (Abstract) sa ključnim rečima (key words) i naslovom rada na engleskom jeziku.

3. PODNASLOV (na primer REZULTATI)

Jednačine se pišu u jednoj koloni sa numeracijom uz desnu ivicu, kao:

$$J\frac{d\omega(t)}{dt}+F\omega(t)=T_e(t)-T_o(t). \qquad (1)$$

U slučaju potrebe, duže jednačine se mogu pisati preko obe kolone.

4. PODNASLOV (na primer ZAKLJUČAK)

Tabele, slike i slike mogu, po potrebi, da budu na jednoj ili dve kolone. Iznad tabele treba da stoji natpis, npr.:

Tabela 2 - Rezultati eksperimentalnih merenja.

Ispod ilustracije treba da stoji objašnjenje (vidi primer slike 1).

Sliku ubaciti na mesto gde se o njoj govori u tekstu

Slika 1 - Rezultati simulacije

Fotografije bi trebalo da budu jasne i kontrastne crno bele. Odgovarajuća skala sa povećanjem treba da prati svaku mikrofotografiju, poželjno je da to bude u donjem desnom uglu.

LITERATURA

Literatura se u tekstu navodi u uglastim zagradama po redosledu citiranja. Na primer, u [2] je pokazano. U nastavku se daju primeri navođenja literature.

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Časopisi se citiraju na sledeći način:

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ABSTRACT

NASLOV RADA NA ENGLESKOM JEZIKU

Napisati kratak sadržaj rada na engleskom jeziku, odnosno prevesti rezime na srpskom.

Key words: ključne reči na engleskom jeziku

STEVAN STOJADINOVIĆ[1], JELENA BAJAT[2], RASTKO VASILIĆ[3], VESNA MIŠKOVIĆ -STANKOVIĆ[2]

Originalni naučni rad
UDC:620.197.5669.7

Karakterizacija oksidnih slojeva dobijenih plazma elektrolitičkom oksidacijom aluminijuma u natrijum volframatu

U radu su prikazana ispitivanja morfologije i faznog sastava površina oksidnih slojeva dobijenih metodom plazma elektrolitičke oksidacije aluminijuma u 0.1 M vodenom rastvoru natrijum volframatu pri stalnoj gustini struje od 15 mA/cm^2, kao i njihova koroziona stabilnost. Pokazano je da hrapavost dobijenih slojeva raste sa vremenom trajanja procesa, dok mikro tvrdoća uzoraka dostiže maksimalnu vrednost posle 5 minuta od početka procesa i posle tog vremena opada. Osidni slojevi su delimično kristalizovane i uglavnom se sastoje od γ-Al_2O_3, α-Al_2O_3 i WO_3, a sadržaj γ-Al_2O_3 raste sa trajanjem PEO procesa. Dobijeni oksidni slojevi imaju veću impedansu od čistog aluminijuma, pri čemu dužem vremenu PEO procesa ne odgovara i najveća impedansa. Najveću korozionu stabilnost su pokazali oksidni slojevi dobijeni posle 7.5 minuta od početka anodizacije.

Ključne reči: *aluminijum, plazma elektrolitička oksidacija, mikro tvrdoća, SEI, korozija*

1. UVOD

Plazma elektrolitička oksidacija (PEO) je ekološki čista tehnologija koja omogućava dobijanje oksidnih slojeva na aluminijumu, magnezijumu, titanijumu, cirkonijumu, tantalu i drugim lakim metalima, kao i na njihovim legurama [1-5]. Dobijeni oksidni slojevi imaju kontrolisanu morfologiju i sastav, odlično se vezuju za podlogu koja se anodizira, imaju izvanredne električne i termičke osobine, veliku tvrdoću, otpornost na habanje i koroziju, itd. [6-8]. Ove osobine čine oksidne slojeve dobijene PEO procesom pogodne za primenu u vazduhoplovstvu, automobilskoj industriji, tekstilnoj industriji, biomedicinskim uređajima, itd.

PEO je kompleksan proces koji uključuje istovremeno procese formiranja oksidnog sloja, rastvaranja i dielektričkog proboja. Na početku oksidacije na substratu se formira tanak barijerni anodni oksidni sloj. Debljina ovog sloja je ograničena na nekoliko stotina nanometara, zbog dielektričkog proboja usled jakog električnog polja (10^7 V/cm), koji je praćen pojavom mikro pražnjenja preko cele površine oksida i intenzivnim izdvajanjem gasa. Veliki broj kanala za pražnjenje se pojavljuje na defektima u površinama oksida [9] i lokalno velike gustine struje se stvaraju na mestima nečistoća težeči da popune defekte i prekinu lokalna pražnjenja. Mikro pražnjenja dovode do lokalizovanih visokih temperatura i pritiska (10^3 K do 10^4 K i 10^2 MPa do 10^3 MPa) [10,11], omogućavajući formiranje oksidnih slojeva koje se sastoje, ne samo od čistog oksida substrata koji se anodizira, već i od oksida koji sadrži i komponente elektrolita [12].

U ovom radu su prikazani rezultata istraživanja mikro tvrdoće i korozione stabilnosti oksidnih slojeva dobijenih PEO procesom na aluminijumu u vodenom rastvoru natrijum volframata ($Na_2WO_4 \cdot 2H_2O$). Oksidni slojevi na aluminijumu koji sadrže volfram su od interesa zbog njihovih katalitičkih, poluprovodničkih i korozivnih osobina [13,14].

2. EKSPERIMENTALNI DEO

Anodni oksidni slojevi formirani su na aluminijumskim uzorcima dimenzija 30 mm x 10 mm 0.12 mm i 99.7 % čistoće. Pre anodizacije aluminijumski uzorci su čišćeni acetonom u ultrazvučnoj kadi. Anodizacija aluminijuma je vršena u režimu konstantne gustine struje od 15 mA/cm^2 u elektrolitičkoj ćeliji na temperaturi od 20 ^{o}C.

Morfologija i mehaničke osobine oksidnih površina (hrapavost i mikro tvrdoća) su ispitivane pomoću AFM mikroskopa (AFM; Veeco Instruments, model Dimension V). Hrapavost i mikro tvrdoća (odnos primenjene sile indentacije i 2D utisnute površine) su dobijene korišćenjem diNanoScope softvera (verzija 7.0) i prezentirane vrednosti su izračunate kao srednja vrednost za nekoliko različitih uzoraka dobijenih pod istim uslovima anodizacije. Kristaliničnost oksidnih slojeva je analizirana pomoću Phillips PW 1050 X-ray difraktometra.

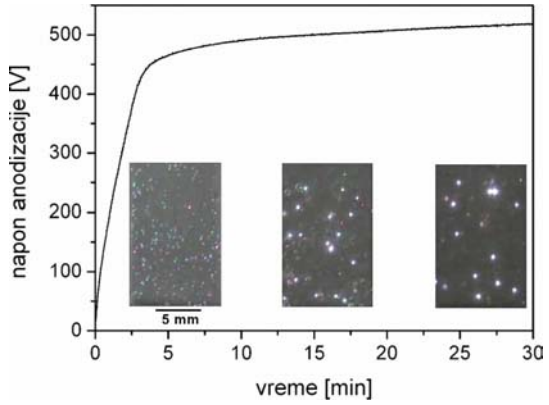
Koroziona stabilnost oksidnih slojeva dobijenih PEO procesom na aluminijumu je određivana polarizacionim merenjima, snimanjem polarizacionih krivih u rastvoru 3 % NaCl, kao i spektroskopijom elektrohemijske impedancije (SEI) u istom rastvoru. Gustine struje korozije, j_{kor}, su procenjene iz preseka anodne Tafelove prave sa potencijalom otvorenog kola (POK). Impedansni dijagrami su dobijeni na potencijalu otvorenog kola korišćenjem Reference 600 potenciostata/galvanostata/ZRA (Gamry Instriments), u opsegu frekvencija od 100 kHz do 0,01 Hz, korišćenjem amplitude naizmeničnog napona od 7 mV.

Adrese autora: [1]Univerzitet u Beogradu, Fizički fakultet, Beograd, [2]Univerzitet u Beogradu, Tehnološko-metalurški fakultet, Beograd, [3]Fakultet zaštite životne sredine, EDUCONS Univerzitet, Sremska Kamenica

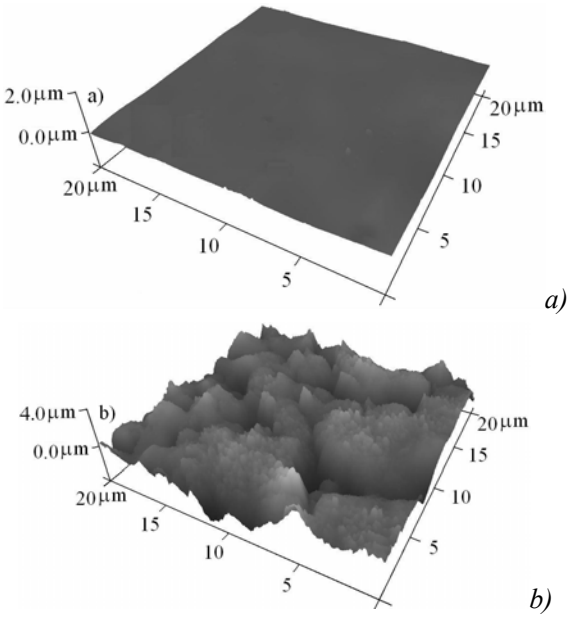
Rad primljen: 18. 03. 2013.

3. REZULTATI I DISKUSIJA

Na slici 1 je dat tipičan oblik krive zavisnosti napona od vremena u toku anodizacije aluminijuma u 0.1 M $Na_2WO_4 \cdot 2H_2O$. Od početka anodizacije napon raste linearno sa vremenom do napona od oko 400 V (prvih 160 s). U ovoj fazi proces je sličan klasičnoj anodizaciji i primetan je relativno uniformni rast kompaktnog barijernog anodnog oksidnog sloja (slika 2a). Dalji proces anodizacije je praćen značajnim odstupanjem napona od linearne zavisnosti, koje počinje na tzv. probojnom naponu. Kako se napon anodizacije približava probojnom naponu, javlja se veliki broj mikro pražnjenja, ravnomerno raspoređenih preko cele površine oksida. Veličina mikro pražnjenja postaje veća, a gustina manja, sa vremenom anodizacije. Posle proboja na površini oksida se javlja veliki broj pukotina, pora i kanala (slika 2b).

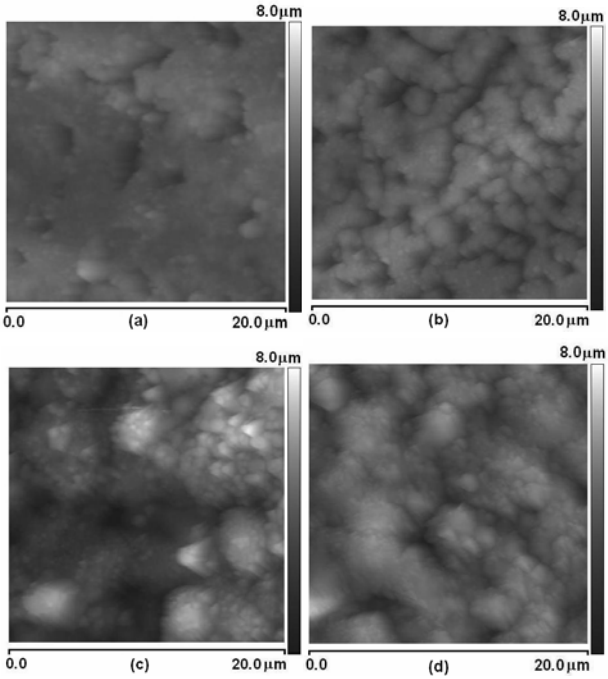


Slika 1 - Zavisnost napona u toku anodizacije aluminijuma u 0.1 M $Na_2WO_4 \cdot 2H_2O$ (j = 15 mA/cm^2 t_{el} = 20 °C)

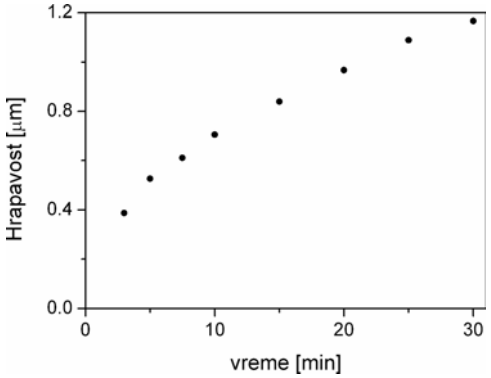


Slika 2 - 3D AFM slike površina oksida: a) pre proboja (vreme anodizacije 100 s); (b) posle proboja (vreme anodizacije 180 s)

Morfologija oksidnih slojeva formiranih na aluminijumu (slika 3) jasno pokazuje da se broj mikro pora smanjuje, a njihova veličina raste tokom PEO procesa. Naime, mikro pražnjenja se generišu dielektričkim probojima kroz nepravilnosti u oksidnom sloju. Njihov broj se smanjuje tokom anodizacije, odnosno sa rastom oksidnih slojeva i samim tim se broj pražnjenja smanjuje. Porast veličine kanala za pražnjenja posledica je smanjenja mesta za proboj kroz koje prolazi veća gustina struje [9]. Takođe, deblji slojevi oksida imaju veću hrapavost (slika 4). U početnoj fazi PEO procesa, kanali za mikro pražnjenja su raspoređeni ravnomerno i površina oksida ima malu hrapavost. Kako se broj kanala za pražnjenje smanjuje sa vremenom PEO procesa, na površini oksida se javljaju neuniformnosti, što dovodi do povećanja hrapavosti.

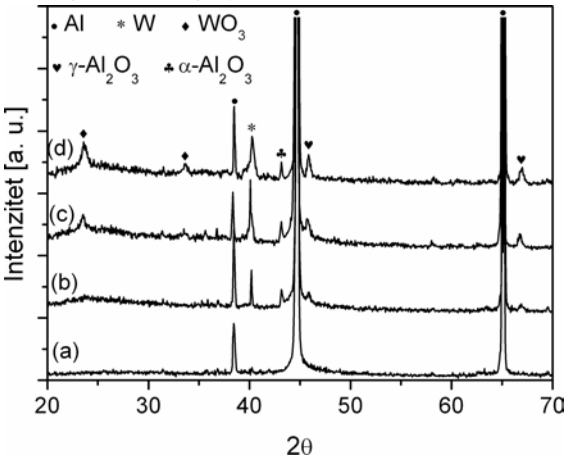


Slika 3 - AFM slike oksidnih površina u različitim etapama PEO procesa: a) 3 min; b) 5 min; c) 15 min; d) 30 min.



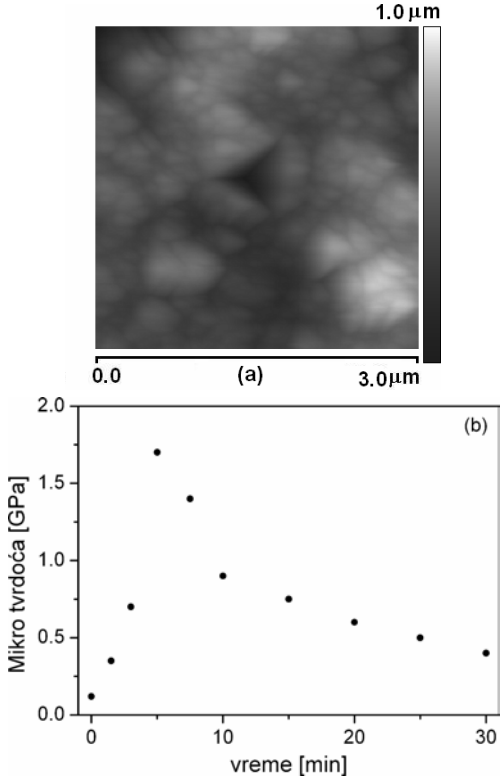
Slika 4 - Uticaj vremena PEO procesa na hrapavost površine oksida

XRD spektri za četiri oksidna sloja formirana PEO procesom u toku različitog vremena prikazani su na slici 5. Oksidni slojevi su delimično kristalizovane i uglavnom se sastoje od γ-Al_2O_3, α-Al_2O_3 i WO_3. Elementarni aluminijum uglavnom potiče od supstrata i zato su difrakcione linije aluminijuma toliko jake. Sadržaj γ-Al_2O_3 raste sa vremenom PEO procesa. U toku PEO procesa istopljena alumina se izbacuje kroz kanale za pražnjenje i njen kontakt sa elektrolitom dovodi do brzog očvršćavanja na granici oksid-elektrolit. Brzo očvršćavanje alumine favorizuje formiranje γ-Al_2O_3 [15].



Slika 5 - XRD spektri oksida u različitim etapama PEO procesa: (a) 3 min; (b) 5 min; (c) 15 min; (c) 30 min.

Morfologija dobijenih površina je ograničavajući faktor za određivanje mikro tvrdoće primenom AFM-a. Da bi izračunali mikro tvrdoću potrebne su velike ravne površine uzoraka. Kao što je već pokazao na AFM slikama (slika 3) površine oksida imaju veliki broj nepravilnosti i veoma veliku hrapavost. Nanoindentacija ovih površina je često praćena pucanjem velikog dela površine bez, ili sa slabo definisanim otiskom dijamanatskog nanoindentera. Zbog ovih ograničenja vrednosti mikro tvrdoće su dobijene kao srednja vrednost nekoliko merenja dobijenih iz različitih uzoraka (pripremljenih pod istim uslovima anodizacije). Slika 6a pokazuje primer oblasti nanoindentacije, dok je uticaj PEO vremena na mikro tvdoću oksidnih slojeva prikazan na slici. 6b. Aluminijumski supstrat ima mikro tvroću oko 0.12 GPa, koja raste do oko 1.7 GPa u prvih pet minuta PEO procesa, a zatim počinje da opada. Ovo može biti posledica promene sastava faza (slika 5) i/ili promene poroznosti oksidnih slojeva (slika 3). U prvom slučaju, manja mikro tvrdoća je povezana sa povećanjem frakcije γ-Al_2O_3 kod uzoraka sa dužim vremenom PEO procesa, dok u drugom slučaju, smanjenje mikrotvrdoće potiče od povećane poroznosti i površinske hrapavosti površina oksida.

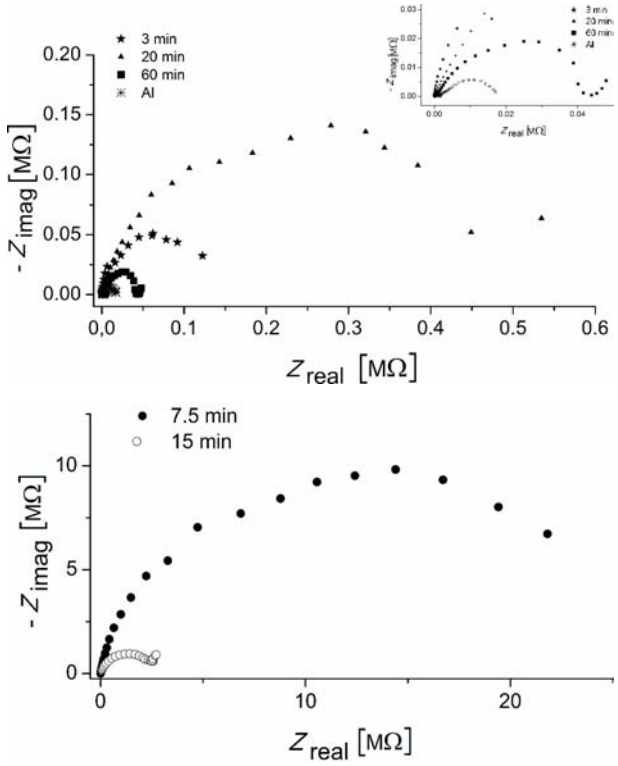


Slika 6 - (a) AFM slika PEO površine nakon procesa nanoindentacije; (b) Uticaj vremena PEO procesa na mikro tvrdoću oksidnih površina.

Koroziona stabilnost oksidnih površina formiranih PEO procesom u toku različitog vremena ispitivana je polarizacionim i SEI merenjima. Na slikama 7a i b prikazani su impedansni dijagrami u kompleksnoj ravni za različite uzorke posle 30 min delovanja korozionog agensa.

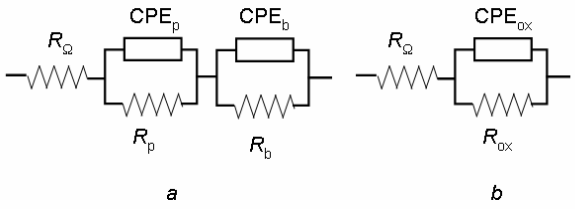
Sa slika 7 se vidi da svi oksidni slojevi imaju veću impedanciju od čistog aluminijuma, pri čemu dužem vremenu PEO procesa ne odgovara i najveća impedancija. Naime, impedancija oksidnih slojeva na aluminijumu dobijenih tokom 3, 7.5, 15 i 20 min je veća u odnosu na impedanciju oksidnog sloja dobijenog dugim PEO procesom od 60 min, kao i čistog aluminijuma. Fitovanje dobijenih eksperimentalnih SEI podataka je vršeno korišćenjem odgovarajućih ekvivalentih električnih kola (slika 8) [16-20] i programa Gamry Instruments Echem Analyst, verzija 5.50.

PEO slojevi na aluminijumu se sastoje od dva oksidna sloja: unutrašnjeg, barijernog i spoljašnjeg, poroznog sloja. Parametri u ekvivalentnim električnim kolima na slici 8a su: otpornost elektrolita, R_Ω, otpornost spoljašnjeg, poroznog sloja, R_p, otpornost unutrašnjeg, barijernog sloja, R_b, i elementi sa konstantnim faznim uglom, CPE_p i CPE_b se odnose na spoljašnji i unutrašnji oksidni sloj.



Slika 7 - Impedansni dijagrami u kompleksnoj ravni za oksidne slojeve formirane PEO procesom tokom različitog vremena, posle 30 min delovanja 3 % NaCl

Ekvivalentno električno kolo na slici 8b pored otpornosti elektrolita, R_Ω, ima još i ukupnu otpornost oksidnog sloja, R_{ox}, i element sa faznim uglom CPE_{ox} koji se odnosi na ukupnu kapacitivnost oksidnog sloja. Rezultati dobijeni fitingom eksperimentalnih krivih su prikazani u tabeli 1.

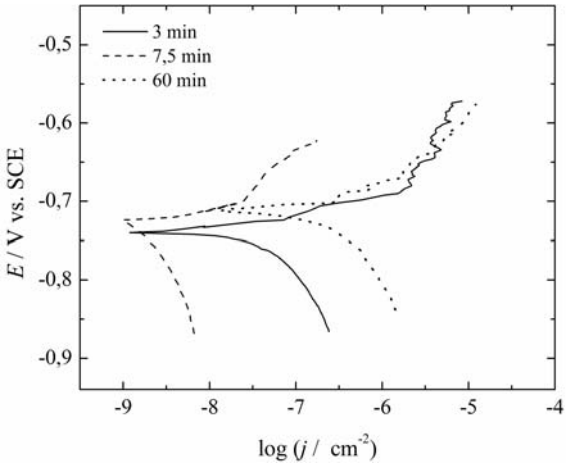


Slika 8 - Ekvivalentna električna kola

Vrednosti impedancije spoljašnjeg, poroznog sloja su znatno manje od impedancije unutrašnjeg, barijernog sloja (tabela 1) i kod nekih uzoraka se one preklapaju, dajući SEI spektre sa jednom vremenskom konstantom, $R_{ox}CPE_{ox}$ (za 3, 7.5 i 15 minuta PEO procesa). Impedansi dijagrami u kompleksnoj ravni za ove oksidne slojeve su fitovani ekvivalentnim električnim kolom prikazanim na slici 8b.

Na osnovu SEI rezultata primećuje se prvo rast kompaktnog barijernog oksidnog sloja u odnosu na čist Al, (tabela 1) sa dužim PEO procesom, koji se daljim produžavanjem PEO procesa, od 15 min pa na dalje, ponovo smanjuje. Manje vrednosti R_{ox} (R_b) i veće vrednosti CPE_{ox}(CPE_b^*) za oksidne slojeve dobijene kraćim PEO procesom ukazuju da vreme od 3 min nije dovoljno dugo da bi se formirao unutrašnji, barijerni sloj, dovoljne debljine i kompaktnosti, dok se dužim vremenima PEO procesa (20 i 60 min) dobijaju oksidni slojevi manje korozione stabilnosti, usled velike poroznosti (slike 2 i 3), kroz koje elektrolit brzo prodire i smanjuje korozionu stabilnost. Najveće vrednosti otpornosti i najmanje vrednosti kapacitivnosti, ukazujući na najveću korozionu stabilnost, su pokazali oksidni slojevi dobijeni tokom 7.5 i 15 minuta, pri čemu su oni dobijeni tokom 7.5 PEO procesa imali za red veličine veću vrednost R_{ox} od onih dobijenih tokom 15 min.

Koroziona stabilnost oksidnih slojeva je ispitivana i polarizacionim merenjima i neke od dobijenih E–log j zavisnosti su prikazane na slici 9. Gustine struje korozije, j_{kor}, su određene iz preseka anodne Tafelove prave sa potencijalom otvorenog kola (POK). Vrednosti gustina struja korozije za ispitivane oksidne slojeve prikazane su u tabeli 1. Podaci u tabeli 1 su srednje vrednosti 3-5 merenja.



Slika 9 - Polarizacione krive u 3% rastvoru NaCl za oksidne slojeve formirane PEO procesom tokom različitog vremena

Bolja koroziona postojanost oksidnih slojeva dobijenih tokom srednjih vremena od 7.5 i 15 min je potvrđena i polarizacionim merenjima, tj. manje vrednosti j_{kor} su na ovim oksidima u odnosu na one koji su dobijeni ili kratkim ili znatno dužim vremenima. Najmanja struja korozije odgovara PEO procesu od 7.5 min, i ona je za jedan do dva reda veličine manja od j_{kor} ostalih oksida. Ovi rezultati su u skladu sa SEI merenjima.

Na osnovu svih prikazanih merenja može se zaključiti da su morfologija i poroznost presudne u određivanju korozione stabilnosti oksidnih prevlaka na aluminijumu.

Tabela 1 - Vrednosti SEI parametara i gustine struje korozije, j_{kor}, za oksidne slojeve formirane PEO procesom u toku različitog vremena, posle 30 min delovanja 3 % NaCl

PEO vreme/min	R_p / Ω cm^2	CPE$_p$		R_{ox} (R_b^*) · 10^{-4} / Ω cm^2	CPE$_{ox}$ (CPE$_b^*$)		j_{corr} / μA cm^{-2}
		$Y_o \cdot 10^7$/ s^n Ω^{-1} cm^{-2}	n		$Y_o \cdot 10^9$/ s^n Ω^{-1} cm^{-2}	n	
Al	4130	4.30	0.72	1.2	12.7	0.76	0.44
3				12.5*	11*	0.95	0.28
7.5				2580	9.51	0.93	0.0020
15				250	5.51	0.82	0.040
20	942	5.76	0.74	29.3*	6.86*	0.80	0.35
60	500	2.60	0.74	5.83*	136*	0.75	0.45

ZAKLJUČAK

Na osnovu eksperimentalnih rezultata ovog rada, može se zaključiti da morfologija i fazni sastav oksidnih slojeva na aluminijumu dobijenih metodom plazma elektrolitičke oksidacije u natrijum volframatu direktno zavise od vremena trajanja procesa. Oksidni slojevi su delimično kristalizovani i uglavnom se sastoje od γ-Al_2O_3, α-Al_2O_3 i WO_3, dok sadržaj γ-Al_2O_3 raste sa trajanjem PEO procesa. Mikro tvrdoća oksidnih slojeva dostiže maksimalnu vrednost posle 5 minuta od početka procesa i posle tog vremena opada kao posledica povećanja hrapavosti slojeva sa trajanjem procesa. Koroziona stabilnost takođe zavisi od vremena trajanja procesa i najbolja je za oksidne slojeve dobijene posle 7.5 minuta Na osnovu prikazanih rezultata, jasno je da su morfologija i poroznost dobijenih oksidnih slojeva presudne za korozionu stabilnost.

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ABSTRACT

CHARACTERIZATION OF OXIDE COATINGS FORMED BY PLASMA ELECTROLYTIC OXIDATION OF ALUMINUM IN SODIUM TUNGSTATE

This paper presents our recent research on morphology and phase composition of oxide coatings formed by plasma electrolytic oxidation of aluminum in 0.1 M sodium tungstate at constant current density of 15 mA/cm^2 and corrosion stability of such coatings. Roughness of obtained oxide coatings increases with prolonged process time, while their microhardness reaches maximal value after about 5 minutes from the onset of the process and then decreases. Oxide coatings are partly crystallized and mainly consist of γ-Al_2O_3, α-Al_2O_3 i WO_3, with γ-Al_2O_3 content increasing with prolonged PEO time. All obtained oxide coatings have higher impedance than pure aluminum and no relationship between PEO time and impedance is found. The evolution of impedance spectra shows that samples obtained after 7.5 minutes of PEO time have most efficient corrosion protection of aluminum substrate.

Key words: *aluminum, plasma electrolytic oxidation, microhardness, SEI, corrosion*

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Scientific paper

DIANA KIRIN[1], BOYAN BOYANOV[2], NIKOLINA ILIEVA[1]

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UDC:504.45.7.054

Biodiversity and heavy metal pollutions in freshwater ecosistems in border areas from Tunja river

The purpose of the carried out examinations is to investigate heavy metal pollutions and the biological variety of the freshwater ecosystems of the Tunja River, Bulgaria, and to make an ecological evaluation of their condition. The Tunja River is related to the Aegean water collecting region. Basic abiotic (temperature, pH, conductivity μS/sm, COD, BOD_5, ionic groups – PO_4 mg/l, $N\text{-}NO_3$ mg/l, $N\text{-}NO_2$ mg/l and heavy metals – Pb, Zn, Cd and Cu, structure of the river bed, dominant tree vegetation, etc.) and biotic characteristics (total number of specimens, prevalence, mean intensity, etc.) were determined. The bioindicative macrozoobenthos was characterized for assessment of the ecological status of the examined freshwater ecosystem. Helminths communities of Squalius orpheus and heavy metal contaminations in fish tissues, organs and chub parasite Acanthocephalus anquillae were determined. The present studies are connected with applying of the new approach for integrated environmental assessment of the freshwater ecosystem based on the living communities and fish parasite communities.

Key words: *bioindication, heavy metals, macrozoobenthos, chub parasite communities, Tunja River*

INTRODUCTION

Riparian habitats are characterized by a wide variety of abiotic parameters of the restricted area, which is a prerequisite for high species diversity of the elements of flora and fauna. Middle and lower part of the river Tunja have created conditions for the development of largest longoza forests. These unique ecosystems are constantly subjected to negative anthropogenic, climatic and hydrological impacts. This makes it necessary to seek, a reasonable compromise between human activity and sustainability of natural systems. The lack of flooding and low Tunja in recent years have triggered a process leading to change and increase floristic diversity. The trend of kserofitization is expected to change the appearance of dense habitats and the disappearance of a number of characteristic species. Studies of the biodiversity and the state of freshwater ecosystem of the Tunja River are comparatively small [17; 22-25; 31; 33-34; 37].

The major negative anthropogenic impact on the Tunja River ecosystem associated with the changes of the studied freshwater communities are farm activities (using of fertilizers, pesticides; wastewater from livestock, etc.; 50% of the region are agricultural lands), constructions, tourism, etc. [5,6,32]. Tunja River is included in the National monitoring program (Water Body Type BGTR12 – Medium sized rivers) [28].

Author's address: [1]Agricultural University – Plovdiv, Department of Ecology and protection of Environment, 12 Mendeleev Str., Plovdiv, Bulgaria, [2]Paisii Hilendarski'University of Plovdiv, Department of Chemical Technology, 24 Tsar Assen Street, Plovdiv, Bulgaria

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These researches would allow making recommendations for preservation of the biodiversity, to plan possibilities for preservation of the natural water resources and negative aspects of transborder impact, etc.

MATERIALS AND METHODS

The Tunja River (Fig. 1) is one of the biggest rivers in central part of South Bulgaria (East Aegean Water Basin). The river springs from the central part of Stara Planina.

Mountain, Peak Yurushka Gramada, eastern of the Botev Peak. The Tunja River (350 km in Bulgaria from total 390 km) is the biggest tributary of Maritsa River, influent to Maritsa River on the territory of Turkey, before town of Odrin. The river has a watershed area of 7884 km^2, its main tributaries being Mochuritsa, Popovska and Sinapovska river.

The basic abiotic and biotic characteristics of the freshwater ecosystem biotopes were determined (temperature, pH, conductivity μS/sm, COD, BOD_5, ionic groups – PO_4 mg/l, $N\text{-}NO_3$ mg/l, $N\text{-}NO_2$ mg/l and heavy metals – Pb, Zn, Cd and Cu, structure of the river bed, dominant tree vegetation, etc.). Samples of water and sediments were collected according to the Guidance on sampling of rivers and watercourses - ISO 5667-6:1990, introduced as a Bulgarian standard in 2002. Heavy metal concentration of the water and sediment samples, fish tissues, organs and parasites were carried out according to standard techniques. The samples were analyzed for content of Cd, Cu, Pb and Zn by ICP Spectrometry [2].

Figure 1 - Tunja River

During the three seasons (spring, summer and autumn) of 2011-2012, 18 samples of water and sediments, 19 taxa and 103 specimens of macrozoobenthos in the region between village of Konevec and town of Elhovo from the Tunja River (last part of the river, before the border area with Turkey), were examined. Samples of macrozoobenthos were collected by the EN 27828:1994/ISO 7828:1985; EN ISO 9391:1995/ISO 9391:1993; EN ISO 5667-1:2006/AC:2007; EN ISO 5667-3:2003/AC:2007, etc. Method for presentation on biological data (EN ISO 8689-2:2000) are enjambment.

Methods have been developed at European level projects AQEM and STAR (AQEM consortium, 2004). All samples were fixed in 4% formaldehyde. They are laboratory sorted by systematic groups and then are kept in 70% ethyl alcohol. Analyses of the biological diversity of bioindicative groups of organisms (bioindicative macroinvertebrate fauna - macrozoobenthos) were determined according to quantitative data. The criteria and methods have been applied [4,13,14, 26,29,30,36]. Modified Irish Biotic Index (MIBI), Ecological Quality Ratios Index for Ecological Quality Assessment (EQR), Index based on presence of Ephemeroptera, Plecoptera, Trichoptera Index (EPT), Rhithron Feeding Type Index (RETI) and Saprobic index of Pantle and Buck (SPB) were used for biomonitoring analysis. For an ecological evaluation of the situation of the analyzed freshwater ecosystems, principal biotic indexes have been fixed: Tn/spe – total number of taxa; Tn/sps – total number of specimens, HB (index of Brillouin, diversity), Dmg (index of Margalef, diversity); H' (index of Shannon, diversity), etc [13,18-21,30,37].

The model fish species chosen for this study are from Cyprinidae (chub, *Squalius orpheus* Kottelat & Economidis, 2006). The fish specimens were caught by nets in the river with the Official permission from the Ministry of Agriculture and Food, Republic of Bulgaria. Fish samples (33 specimens) were collected in the period between May and September, 2012. The scientific and common names of the fish hosts were used according to the FishBase database [12]. The analysis of the dominant structure of the found fish parasite taxa were presented to the level of the component communities. The ecological terms prevalence, mean intensity are used, based on the terminology of Bush et al. [3]. Analyses of helminth community structure were carried out during the three seasons and in both levels: infracommunity and component community [3]. The infracommunity data were used to calculate the total number of species, mean number of helminths, the Brillouns diversity index (HB), etc. [16,20].

RESULTS AND DISCUSSION

I. General characterization of the studied biotopes. Physicochemical monitoring.

Studies have been performed of freshwater ecosystems from the Tunja River between the village

of Konevec (Biotop 1, after town of Yambol and near to Gorna Topchiya Reserve) and the town of Elhovo (Biotop 2, after town of Elhovo and before Balabana Reserve). Biotope 1 is 264.4 km from the springs of the river and 75.9 km from the border area with R. Turkey. The length of the area is 200-250 m Watercourse is slow and easy. In places woody debris are formed. The bottom substrate of the river is silt and mud. Biotope 2 distances of 251.8 km from the springs of the river and 70.5 km from the border. The length of the section is 300 m. Flow is slow and easy. Rare places in the riverbed sand sediments are formed by vegetation, as well as wood and concrete waste parts. The substrate of the river bed is sand, mud and silt. The section under research in the biotopes is 14-16 m wide and about 0.5-1.5 m deeps. The banks are stable, overgrown with vegetation and deeply shaded on the right bank of solid wood finish. The waterside wood vegetation is represented mainly by *Populus alba*, *Salix alba*, *Ulmus minor*, *Fraxinus oxicarpa*, *Fraxinus excelsior*, *Quercus peduncoliflora, Quercus robur, Acer campestre, Tamarix tetrandra*. Left bank is found in places overgrown with tall natural and semi-natural grassland. Macrophytes have secondary coverage and are from the taxa *Typha* sp., *Potamogeton* sp. and *Phragmites austriacus*, mainly on the left bank. *Typha* sp. and *Potamogeton* sp. are bioindicators for β-mezosaprobic ecological status.

The water of the river in this region of study (Biotope 1, 2) is alkali with acidity from 8.58 pH to 8.87 pH, measured by temperature of the water from 18.5 ^{o}C – 31.4 ^{o}C during the three seasons of the study. Values of the COD and BOD_5 are for second and third category of surface flowing waters, respectively. The waters of the Tunja River in the examined region are distinguished by a low content of ionic groups, compared to Limit Admissible Concentration (LAC) for second category of surface flowing waters (in accordance with the BG State Standards – Regulation 7) with the exception of PO_4, $N\text{-}NO_2$ and $N\text{-}NO_3$. In the two biotopes their content was compared for IIIrd and above IIIrd category of waters (2.3-2.9 mg/l; 0.05-0.06 mg/l, and 21.4-25.3 mg/l, respectively). Conductivity for all samples was compared for the first category of surface following waters (Table 1). There was not any increased content of heavy metals detected in water samples of Tunja River (Pb, Cd, Cu, Zn) for the two biotopes of the period of this research (in accordance with the BG State Standards – Regulation 7 of the Ministry of Environment and Waters of Bulgaria for LAC for second category of surface flowing waters).

Table 1 - Basic abiotic indices of the studied freshwater ecosystem from the Tunja River

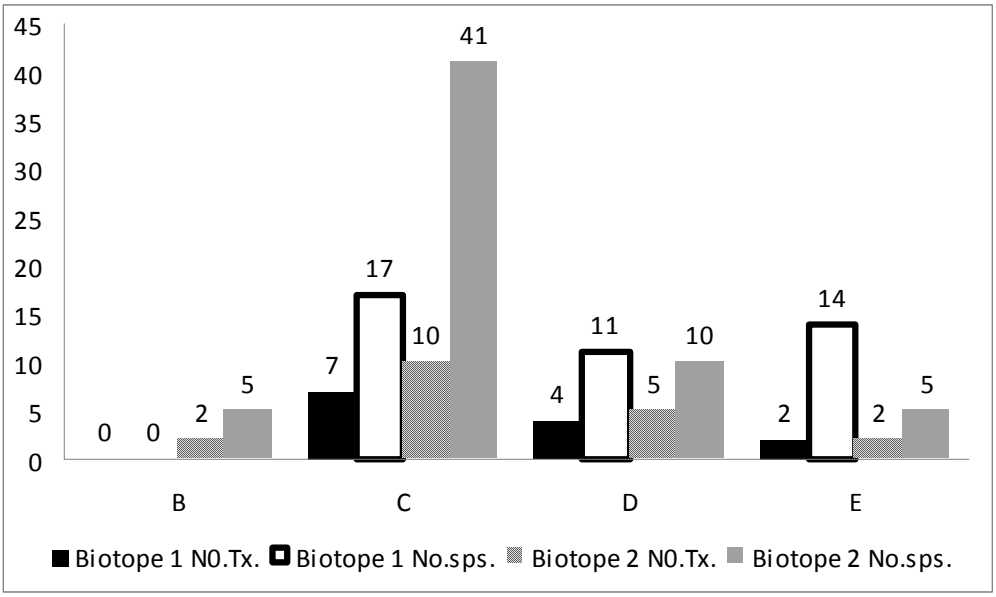
Abiotic indices	Min-Max	Mean±SD	SE mean	C.V.	Category
Temperature (^{o}C)	18.5 - 31.4	24.95±9.122	6.45	36.56	
Acidity (pH)	8.58 - 8.87	8.725±0.205	0.145	2.35	III
Conductivity μS/cm	378 - 384	381±4.243	3.0	1.114	I
COD mg/l	43 - 45	44±1.414	1.0	3.214	II
BOD_5 mg/l	17 - 21	19±2.828	2.0	14.886	III
PO_4 mg/l	2.3-2.9	2.6±0.424	0.3	16.318	>III
$N\text{-}NO_3$ mg/l	21.4-25.3	23.35±2.758	1.95	11.810	>III
$N\text{-}NO_2$ mg/l	0.05-0.06	0.055±0.007	0.003	12.856	III

II. Biodiversity of the macrozoobenthos and bioindication.

The biomonitoring study of the hydrobiontic macroinvertebrate fauna (macrozoobenthos) in the research region during the three seasons of the research period show the presence of 19 bioindicating taxa and 103 specimens from 13 orders.

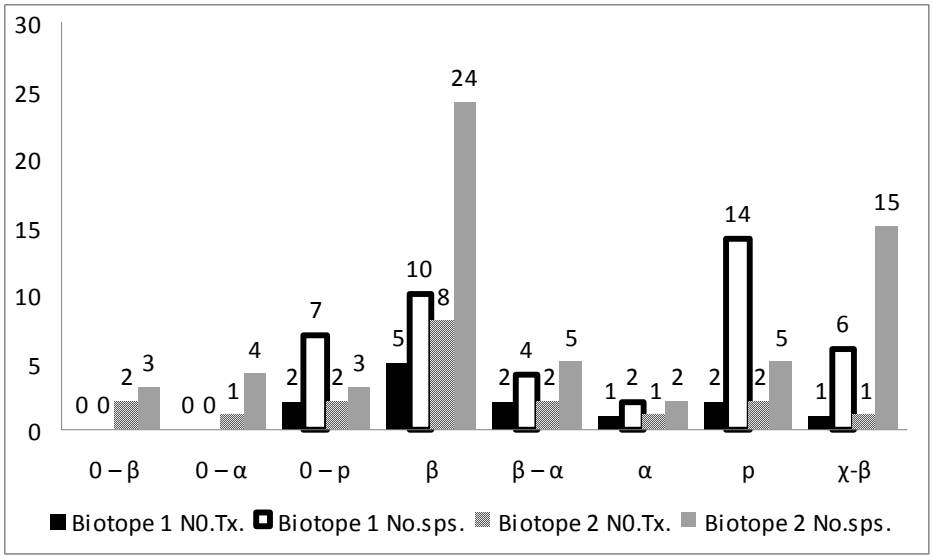
With higher number of taxa and specimens is distinguished Biotope2 (13 taxa and 49 specimens; 19 taxa and 79 specimens, respectively). In Biotope 1, *Chironomus plumosus* L. showed the highest number of specimens (9), followed by *Baetis vernus* Curt. and *Gammarus pulex* (L.) (on 6 specimens, respectively), *Nematoda* sp. and *Tubifex tubifex* Müller, 1774 (on 5 specimens, respectively). In Biotope 2 with the highest number of specimens were fixed *G. pulex* (15 specimens), followed by *Ch. plumosus* (4 specimens). The determined bioindicating taxa were from four taxa of sensitivity (B, C, D, E) (Fig. 2). The dominant were these from group C (relative tolerant forms) – on 7 taxa and 17 specimens in Biotope 1; 10 taxa and 41 specimens in Biotope 2, followed by group D (tolerant forms) – on 4 taxa and 11 specimens; 5 taxa and 10 specimens, respectively for the two biotopes. On the third position is group E (more tolerant forms). It was presented with two taxa and on 14 and 5 specimens, respectively in biotopes 1, 2. More

weakly were presented groups B (less sensitive forms) – only in Biotope 1 with 2 taxa and 5 specimens. The most sensitive group (A) was not presented. Totally for the two biotopes for sensitive group C was fixed 10 species and 58 specimens, followed by group D – 5 taxa and 21 specimens; group E – 2 taxa and 19 specimens; group B – 2 taxa and 5 specimens. Only *Dytiscus* sp. bioindicating 0-α-mesosaprobity (presented only in Biotope 1) and only *G. pulex* bioindicating χ-β-mesosaprobity (presented in the two biotopes, but with higher number of specimens in Biotope 2) (Fig. 3). Two species of determined macrozoobenthos bioindicating p-saprobity (*T. tubifex* and *Ch. plumosus*). They are with higher number of specimens in Biotope 1. *Asellus aquaticus* (L.) bioindicating α-mesosaprobity (on 2 specimens in the two biotopes). Two taxa showed 0-p saprobity (Nematoda sp. and *Tipula* sp.) and another two showed α-β-mesosaprobity (*Tabanus* sp.; *Culex* sp.). *Hyphydrus* sp. and *Stenophylax* sp. bioindicating o-β-mesosaprobity. With the highest number were taxa bioindicating o-β-mesosaprobity – 7 taxa (*Radix peregra* Drap., *B. vernus*, *Leptophlebia* sp., *Aechna* sp., *Notonecta* sp., *Haemopsis sanguisuga* L., *Chaoborus flavicans* Meigen).



Note: No.taxa – Number of taxa; No.sps. – Number of specimens.

Figure 2 - Number of bioindicative taxa (specimens) and sensitive groups



Note: No.taxa – Number of taxa; No.sps. – Number of specimens.

Figure 3 - Number of bioindicative taxa (specimens) and saprobic groups

Totally, with the highest number of taxa and specimens were presented β-mesosaprobity macrozoobenthos (8 taxa and 34 specimens), followed by χ-β-mesosaprobity (2 taxa and 21 specimens), by p-saprobity (2 taxa and 19 specimens) and 0-p-saprobity (2 taxa, 10 specimens). All other saprobity groups were presented with less number of specimens than 10.

III. Helminth communities of Squalius orpheus Kottelat & Economidis, 2006 and bioindication.

As a result of the helminthological study of 33 specimens *Squalius orpheus* Kottelat & Economidis, 2006 from the Tunja River, a total of 8 species of helminths was recovered. This are the species: *Ichthyocotylurus pileatus* (Rud., 1802) (metacercaria); *Clinostomum complanatum* (Rud., 1819) (metacercaria); *Caryophyllaeides fennica* (Schneider, 1902); *Caryophyllaeus brachycollis* Janiszewska, 1951; *Bothriocephalus achielognatii* Jamaguti, 1934; *Ligula intestinalis* (L., 1758) (plerocercoid); *Acanthocephalus anguillae* (Müller, 1780); *Rhabdocona denudata* (Dujardin, 1945). All helminth species were reported for the first time in the helminths communities in Sq. *orpheus* from the Tunja River. Fish were catched between two biotopes and before town of Elhovo. Highest mean intensity (MA) showed *I. pileatus* (MA=7.00), followed by mean intensity of *C. brachycollis* (MA=5.00). Dominant structute of the determinated helminth communities were definited according criterias of Bush et al. According these criterias, only *Acanthocephalus anguillae* (P%=51.50) are a core species for the helminth communities of the chub. *C. brachycollis* (P%=15.15) are component species of this communities. All the rest species of helminthes were accidental species for the helminth communities of *Sq. orpheus* from the Tunja River.

IV. Heavy metal (Cu, Pb, Zn and Cd) contaminations in fish and fish parasites.

The contamination of Cu, Pb, Zn and Cd in tissues and organs of *Sq. orpheus* and chub acanthocephalans *Ac. anguillae* were analyzed (Table 2). Bioconcentration factor (BCF= [Chost(parasite)tissues] / [Csediments] and bioaccumulation factor (BAF= [Cparasite] / [host tissues]) were calculated [35]. The bioconcentration factor allowed to establish the accumulation order and to examine fish used as biomonitors of trace of metal pollutants in freshwater ecosystems.

Table 2 - Heavy metal contamination in Sq. orpheus and fish parasites Ac. anguillae

Heavy metals mg/kg	**Cu**	**Pb**	**Zn**	**Cd**
Ac. anguillae	**7.3**	**152.93**	**71.16**	**<0,01**
BCF	0.52	2.82	1.09	-
Skin	4.8(4.2-5.2)	16.12(13,0-18,2)	40.27	0,4(<0,1-0,4)
BAF	1.52	9.49	1.77	
Bone	2.93(2,25-4,2)	16.03(12,5-20,1)	18.29(12.5-28.3)	0,5(0,2-0,9)
BAF	2.49	9.54	3.9	
Muscle	2.38(2,2-4,2)	4.65(1,4-5,2)	5.84(2.5-14.92)	<0,01
BAF	3.07	32.89	12.18	
Fet	6.22(6,2-6,5)	13.38(0,4-12,8)	42.2(25.39-63.14)	<0,01
BAF	1.17	11.43	1.7	
Sediments	13.95	54.12	65.28	2.05

The contamination of lead in tissues of *Ac. anguillae* is 2.82 more than it's in sediments from the river and 1.09 more for zinc. Bioaccumulation factors are higher in *Ac. anguillae* for Cu, Pb and Zn than in examined fish tissues and organs. In all cases they are the highest in the muscles of the tested fishes against the contaminations in the acanthocephalans (BAF_{Cu}= 3.7; BAF_{Pb}=32.98; BAF_{Zn}=12.18). Parasite bioindication is essential by determination of the ecological status of ecosystems.

Studies of authors in recent years have focused mainly on tracking changes in different groups physicochemical indicators of freshwater ecosystem of the Tunja River [22-24]. Publications describing the results of hydrobiological monitoring based on bioindicating matcrozoobenthos date back about 30 years ago [17,31,37].

In this study, an integrated new approach is applied for an ecological evaluation of the situation of the examined ecosystem. Established in *Sq. orpheus* helminth communities are poor of species diversity,

but they are presented with a higher total number of helminths. The results for helminth communities of *Sq. orpheus* showed improvement in saprobity in research area and the presence of species dominating in helmith communities (prevalence and mean intensity), indicating α–mezosaprobity (*A. anguillae*, *P. laevis*) and β–α-mezosaprobity (*I. pileatus*, followed by that of *C . brachycollis*). They are closely linked and dependent on the biology and ecology of specific, identified in the survey helminth species and the role of intermediate host as bioindicators of natural ecosystems studied (Table 3).

Table 3 - Spearman correlation coefficient (r_s) and levels of significance determined for relatioships between the content of heavy metals in the bottom sediments, Sq. orpheus and A. anguillae

x-y	Heavy metals	r_s	p
Sediment-skin	Cu	0.402	<0.05
	Pb	0.775**	<0.01
	Zn	0.745**	<0.01
Sediment-bone	Cu	0.415*	<0.05
	Pb	0.759**	<0.01
	Zn	0.748**	<0.01
Sediment-muscle	Cu	0.057^{ns}	>0.05
	Pb	0.882***	<0.001
	Zn	0.715**	<0.01
Sediment-fet	Cu	0.421*	<0.05
	Pb	0.738**	<0.01
	Zn	0.732	<0.01
Sediment- *A. anguillae*	Cu	0.982***	<0.001
	Pb	0.999***	<0.001
	Zn	0.996***	<0.001

Note: *significant correlation p<0.5;
**highly significant correlation p<0.01;
***very significant correlation p<0.001;
^{ns} non-sygnificant correlation p>0.05.

Determined indices of diversity, evennes and dominance significantly showed better environmental conditions in Biotope 2 (after town of Elhovo) compared with these in the Biotope 1. Especially convincingly this was confirmed by the indices of the helminth communities of the chub caught before town of Elhovo (before Biotope 2).

The waters of the Tunja River in the region under research for the three seasons were distinguished as a whole by a low content of ionic groups and heavy metals for second category of surface flowing waters. According these examinations values of saprobity showed β-mezosaprobity in lower part of the Tunja River (Biotope 1, after town of Elhovo) and α-mezosaprobity in Biotope 1 (after town of Yambol and village of Konevec) as well as before town of Elhovo, according to the data of fish parasite communities. Studied ecosystem is with biotic index 3 and EQR 0.6 in Biotope 2 and is distinguished with biotic index 2 and EQR 0.4 in Biotope 1. Anthropogenic impacts are from farm activity near the region of these biotopes. The river ecosystem as a whole has good condition during the spring period of the study and bad, during the summer and autumn (Table 4).

Table 4 - Basic biotic indicators for ecological appraisal

Basic biotic indicators	Macrozoobenthos communities		Helminth communities *Sq. Orpheus*
	Biotope 1	Biotope 2	
Total N0. of taxa	14	20	8
Total N0. of specimens	49	79	111
EPT	2	4	-
RETI	0.25	0.45	-
Dmg	3.34	4.35	1.49
H'	2.35	2.59	1.95
HB	2.0	2.25	1.40
Saprobity	α	β	α
BI (EQR)	2(0.4)	3(0.6)	-

Note: Tn/tx – Total number of taxa; Tn/sps – Total number of specimens; EPT–Ephemeroptera/Plecopera/Trichotera Index; RETI–Rhithron Feeding Type Index; Dmg - index of Margalef, diversity; H' – index of Shannon, diversity; HB - index of Brillouin, diversity; BI(EQR)-Biotic index (Ecological Quality Ratios for Ecological Quality Assessment).

The present studies were made with applying the new approach for integrated environmental assessment in two biotopes of the river, giving rise to changes in the definition of ecological status and trophic structure of river ecosystem with free living communities and fish parasite communities.

Acknowledgement

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IZVOD

BIODIVERZITET I ZAGAĐENJA TEŠKIM METALIMA U SLATKOVODNOM EKOSISTEMU U POGRANIČNIM ZONAMA REKE TUNJA

Cilj ispitivanja je da se ispita sadržaj teških metala i zagađenja na biološku raznovrsnost slatkovodnih ekosistema reke Tunja, Bugarska, i da se da ekološka procena njihovog stanja. Reka Tunja sakuplja vode Egejskog regiona. Izvršeno je određivanje osnovnih abiotičkih (temperatura, pH, provodljivost i µs/sm, HPK, BPK5, jonske grupe – PO_4 mg/l, N-NO_3 mg / l, N-NO_2 mg / l, i teški metali - Pb, Zn, Cd i Cu, struktura rečnog korita, dominantno drvo vegetacija, itd) i biotičkih karakteristika (ukupan broj uzoraka, učestalost, intenzitet, itd. Bioindikativna makrozobentoza je karakteristična za procenu ekološkog statusa ispitivanog slatkovodnog sistema. Određivani su mikroorganizmi Helminths of Squalius orpheus, paraziti Acanthocephalus anquillae i teški metali u tkivima i organima riba. Sadanje studije su povezani sa primenom novog pristupa za intregisanu ocenu životne sredine slatkovodnih ekosistema na osnovu životnih zajednica i zajednica parazita riba.

Ključne reči: *bioindikacija, teški metali, makrozoobentosa, parazitske zajednice, reka Tunja*

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VESNA DIMOVA

Scientific paper
UDC :545

A quantum chemical investigation of tautomerion forms of 4-phenyl-5-(4-hydroxyphenyl)-1,2,4-triazoline-3-thione

4-phenyl-5-(4-hydroxyphenyl)-1,2,4-triazoline-3-thione (TT) was obtained by the oxidative cyclization of the appropriate 4-hydroxybenzoyl phenylthiosemicarbazide. From the obtained spectral analysis it is possible to consider that the 1,2,4-triazoline-3-thiones may exist in thion-thiol tautomeric forms. The molecular conformations and electronic properties of TT containing various reaction centers were investigated by the AM1 semiempirical method. The total energies, heat of formation, dipole moments, geometric parameters, ionization potential, full atomic charges, E_{HOMO} and E_{LUMO} (energies of frontier molecular orbital) and their electron densities were calculated. Ionization constants and protonation site in TT molecule were obtained experimentally. The proton affinities for the different atoms (nitrogen, oxygen and sulfur) of the investigated triazole molecule were calculated using AM1 method, and possible protonation sites were discussed. The quantum chemical investigations of tautomerion froms of TT were in accordance with our previously experimental investigation for protonation/deprotonation process of TT: PA of TT calculated for S atom form C=S group was higher than the other atoms, meaning that the electrophilic attack of the proton on this atom is easier than the other; the most acidic hydrogen atoms were N-H/S-H (first deprotonation process) and OH (second deprotonation process).

Key words: *1,2,4-Triazoln-3-thion, AM1, Total Energies, Heats of Formation*

1. INTRODUCTION

Keeping in mind the importance of triazole derivatives for living bodies, [1-4] we carry on working on triazole derivatives as one of the most biologically active classes of compounds, possessing a wide spectrum of activities. The 1,2,4-triazole nucleus is associated with diverse pharmacological activities such as antibacterial, antifungal, hypoglycemic, antihypertensive and analgesic properties. It is also know that some of aminomethyl triazole derivatives possess corrosion - inhibition activity and they can be used as additives in greasy oils pr in photopolymerizing paints for improving adhesion. During the last ten years, some new 1,2,4-triazole derivatives were synthesized and investigated [5-11].

This paper reports semi empirical quantum chemical investigation of chosen triazole derivative, previously synthesized and investigated (experimenttally determined acid-base constants - important from various points of view) [9,10]. Triazole compounds are five member ring containing three nitrogen atoms, which exist mainly with different structural formulas. The parent 1,2,4-triazole (1H form) is in tautomeric equilibrium with the 1,2,4-triazole (4H form). The interconversion of the two tautomeric forms occurs rapidly and their separation is difficult. However, the 1,2,4-triazole tautomer (i) is preferred over the 1,3,4-triazole tautomer (ii) (the less symmetrical 1H form is favoured over the symmetrical 4H form) (Fig. 1).

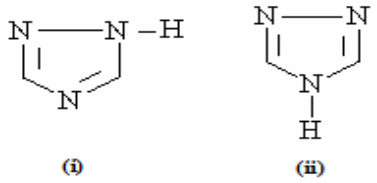

Figure 1 - Tautometric 1,2,4-triazole: 1H-1,2,4-triazole (i) and 4H-1,2,4-triazole (ii)

Mercapto derivatives of 4,5-disubstituted-1,2,4-triazoles are especially interesting as complexing agents due to presence of four potential donor atoms: three nitrogen, one sulfur and one oxygen. Consequently many metal derivatives of ligands of this type have been prepared, and they have also been used as analytical reagents [12]. Mercapto triazoles have been proposed to exist as thion-thiol tautomers, both in solute and in solid state.

In continuation of our interest for 4,5-disubstituted-1,2,4-triazole derivatives, 4-phenyl-5-(4-hydroxyphenyl)-2,4-dihydro-3H-1,2,4-triazoline-3-thione (TT) obtained by oxidative cyclization of the appropriate 4-hydroxybenzoyl phenylthiosemicarbazide, [5] was chosen for quantum-chemical study (Fig. 2). It is important that the tautomeric interconversion must be taken into consideration to investigate the physical and chemical properties of

Author's address: University Ss. Cyril and Methodius, Faculty of Technology and Metallurgy, Rudjer Boskovic 16, Skopje, Republic of Macedonia

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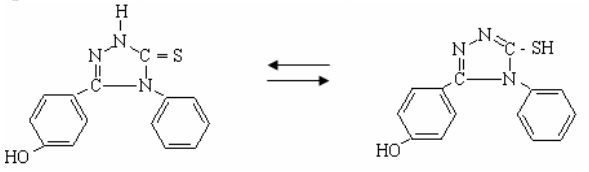
the compounds which exist in a tautomeric equilibrium (thion - thiol forms).



1a *1b*

Figure 2 - Thion (1a) and thiol (1b) tautomers of 4-phenyl-5-(4-hydroxyphenyl)-2,4-dihydro-3H-1,2, 4-triazoline-3-thione (TT)

The molecular conformations and electronic properties of chosen TT molecule containing various reaction centers were investigated by AM1 semi-empirical method. The total energies, heats of formation, dipole moments, rotational barriers, geometric parameters, ionization potential, full atomic charges, E_{HOMO} and E_{LUMO} (energies of frontier molecular orbitals) and their electron densities were calculated and discussed. Ionization constants and protonation site in TT molecule were obtained experimentally [9].

The proton affinities for the different atoms (nitrogen, oxygen and sulfur) of the investigated triazole molecule were calculated using AM1 and possible protonation sites were discussed. The obtained correlation between experimentally obtained acid dissociation constants and semi empirical computed data were discussed.

2. EXPERIMENTAL

2.1 Synthesis of TT

A mixture of appropriate thiosemicarbazide and NaOH solution was refluxed for 4 hours. On cooling, it was solidified (sodium salt of TT). This was dissolved in cold ice water and acidified with hydrochloric acid to pH 5-6. The solid which appeared was filtered, washed with water (neutral pH), dried and recrystalized from ethanol [5].

2.2 Identification and characterization of TT

IR [λ_{max}/cm^{-1}]: 1500 (C=N); 1330 (C=S); ^{1}H NMR [DMSO-d$_6$, ppm]: 6.68 and 7.09 (4H, ABq), 7.17-7.56 (m,5H$_{arom.}$), 10.0 (bs,1H,OH), 14.00 (bs,1H, NH); ^{13}C NMR [DMSO-d$_6$, ppm]: 115.3, 128.8, 129.3, 129.8, (CH); 116.3, 134.8, 150.7, 159.2, 168.2 (qC); UV[EtOH, λ/nm]: 255; 267; 285; Anal. calcd/found for $C_{14}H_{11}N_3OS$ (MW 269.318): C, 62.43/62.92%; H 4.08/4.44%; N 15.60/15.20%; Melting point: 250^{o}C; Yield 95% [5].

2.3 Quantum chemical investigation

Theoretical calculations were carrying out at the restricted Hartree-Fock level (RHF) using AM1 semi empirical SCF-MO method in the HYPERCHEM program, implemented on an Intel Pentium pro 200 MHz computer. All the structures were optimized to a gradient norm of < 0.1.

3. RESULTS AND DISCUSSION

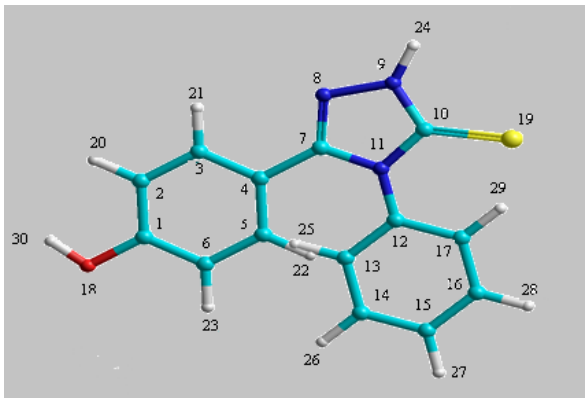


Figure 3 - Molecular structure of TT showing atomic numeration

3.1 Absorption spectra

As in the case of other heterocyclic thione, [13-16] it is possible to consider that the 1,2,4-triazoline-3-thiones may exist in thion-thiol tautomeric forms.

The UV spectra of TT in neutral media (water) was characterized by the presence of absorption maxima at about 255 nm, 267 nm and 285 nm, characteristic of electron transition in the 1,2,4-triazoline-3-thione ring [13]. Those results showed that the thione structure dominates: maximum at 255 and 285 nm, indicated that compound exist predominantly in the thion form in ethanolic solution[10] and maximum at 285 nm indicated the presence of a chromophoric C=S group.

In addition to the UV data, the IR and NMR data of compound support the thion form in solid state and in nonpolar solvent; IR spectra in KBr disk showed no absorption bands at about 2600-2550 cm^{-1} which is indicative of the thiol form; the IR absorption due to C=S functions in TT appeared at about 1330 cm^{-1}. The ^{1}H NMR spectra of TT in DMSO-d$_6$ exhibited the NH signals between 13.55 and 14.10 ppm (supporting the thion structure). The signals associated with other functional groups appeared in the expected regions.

Since, experimental determination of the protonation center of the triazole molecule was made, [9] the theoretical calculation of protonation parameters and the conformational analysis of TT system also appear important. The chosen molecule contains one hetero- and two aromatic rings, and interaction between them affect on the proton affinity and other properties.

On the other hand, the effect of tautomeric change on electronic properties can be evaluated by the theoretical investigation of the molecule. According

the literature data, semiempirical methods have been used widely for the quantum - chemical investigation of various heterocyclic compounds.

So, in this study, AM1 semiempirical method was used for detailed quantum-chemical investigation of 4-phenyl-5-(4-hydroxyphenyl)-2,4-dihydro-3H-1,2,4-triazoline-3-thione (TT). Molecular structure of TT showing atomic numeration is presented in Figure 3.

3.2 Geometry features of TT

The study of the geometry and preferred conformation of TT is important because of the possible usefulness of such information as an aid to the understanding of mode of action of TT as acid as and base and co-coordinative species.

Two isomeric forms, namely thion and thiol forms, of the TT are possible (Fig. 2; 1a and 1b). The optimized geometrical parameters of 1a and 1b forms of the studied TT, such as bond length and angles are presented in Table 1.

It is reasonable for the flexible TT molecule to exist in various conformations due to rotatiotn of the 4-hydroxy substituted phenyl and unsubstituted phenyl rings around C4 – C7 and N11 – C12 single covalent bonds (Fig. 3).

In order to investigate the effect of internal rotation on the energy of the molecule, the potential function of internal rotation around C4 – C7 ($\varphi_1$and N11 – C12 (φ_2) single bonds were calculated. For these reasons, the φ angle was varied in the range 0 – 180^0 by a step of 30^0 and calculations were preformed with AM1 geometry optimization, for both possible tautomeric forms (1a and 1b).

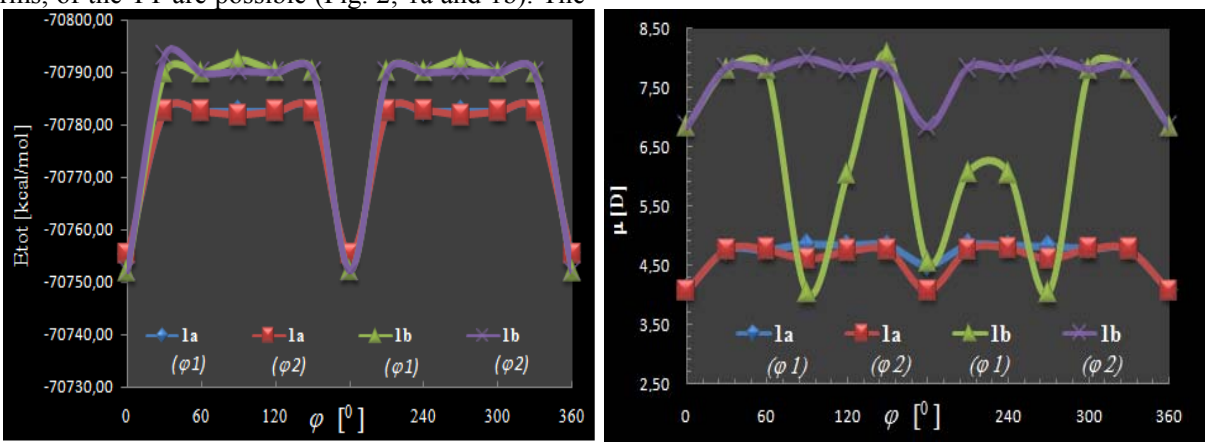


Figure 4 - Calculated E_{tot} and dipole moments varying the φ angle in the range 0 – 180^0 by a step of 30^0

Table 1 - Selected geometrical parameters of the 1a and 1b tautomers

Length [Å]			Angle [deg]			Torsion angle [deg]		
	1a	1b		1a	1b		1a	1b
H30-O18	0.9689	0.9687	H30-O18-C1	108.028	108.015	H30-O18-C1-C6	1.345	1.251
O18-C1	1.3731	1.3744	O18-C1-C6	122.739	122.722	H30-O18-C1-C2	178.723	178.741
C4-C7	1.4611	1.4567	O18-C1-C2	116.522	116.524	C5-C4-C7-C8	30.727	-29.882
C7-N8	1.3546	1.3751	C3-C4-C7	121.426	121.598	C3-C4-C7-C12	32.091	-31.508
N8-N9	1.3420	1.3089	C5-C4-C7	118.860	118.714	C4-C7-N11-C12	5.221	-2.696
N9-C10	1.4124	1.3744	C4-C7-N8	124.675	125.838	C12-N11-C10-S19	4.954	2.164
C10-N11	1.4189	1.4087	C4-C7-N11	126.084	126.582	S19-C10-N9-H24	1.286	-
N11-C7	1.4267	1.4152	C7-N8-N9	106.639	109.855	C7-N8-N9-H24	178.834	-
C10-S19	1.5779	1.6882	N8-N9-C10	113.750	109.720	C7-N11-C10-S19	179.897	-179.764
N9-H24[a]	0.9952	-	N9-C10-N11	102.609	107.89	N9-C10-S19-H24	-	-1.559
S19-H24[b]	-	1.4154	N11-C7-N8	109.237	107.576	N11-C10-S19-H24	-	178.238
N11-C12	1.4157	1.4154	N8-N9-H24[a]	120.866	-			
			C10-N9-H24[a]	125.360	-			
			N9-C10-S19	127.211	127.693			
			N11-C1-S19	130.179	124.416			
			C12-N11-C10	124.048	125.511			
			C7-N11-C12	127.985	129.497			
			C10-S19-H24[b]	-	98.429			

[a]For thion form; [b]For thiol form

The results for E_{tot} and μ obtained by those calculations for thion and thiol form are presented in Figure 4. According to the results, in the conformation 1a when φ_1=330^0 and φ_2=240^0 and in 1b when φ_1=φ_2=90^0, the conjugation between the parent (triazole) and 4- and 5-substituted rings is minimum and the length of C4 – C7 (1a: 1.4611; 1b: 1.4567) and N11 – C12 (1a: 1.4157; 1b: 1.4154) is maximum. Bond length characteristic for 1,2,4-triazoline-3-thione/thiole moiety are: C7-N8, N8-N9, N9-C10, C10-S19 and N9-H24 (for 1a)/S19-H24 (for 1b), data presented in Table 1.

According the results obtained for those distances N-N distance in 1a is around 1.3420 Å which is little shorter form corresponding one in 1,2,4-triazole (1.350 Å), substitute 5-thione-1,24-triazole18 and from normal N-N bond (1.470 Å). Kipping in mind that N-N bond in 1b is between two sp^2 hybridized nitrogen atoms; more bond shortening is expected (1.3089 Å).

The C-N bonds in 1a can by divide in two sets according to the bond type observed: first set: C7-N8 and N9-C10 and second set: C7-N11 and C10-N11.

First type (C7-N8) double covalent bond in triazole ring has values of 1.3546 Å and 1.3751 Å for 1a and 1b, respectively. Those values are larger than typical C=N (1.322-1.352) and corresponding length in similar compounds (1.330 and 1.310 Å) [17].

The single N9-C10 covalent bond in **1a** is around 0.06 Å larger then C7-N8, value which is between typical single C-N bond (~1.48 Å) and double C=N bond (~1.34 Å). This probable can be explained by possibly of existence of two tautomeric forms. Values of same bond in 1b is 1.3744 Å (larger than typical C=N bond), difference that may be significant and which suggest a large double bond character in the second bond formed between two sp^2 hybridized atoms, but in same time influence of thion tautomeric form.

Second type, C7-N11 and C10-N11 bonds is in accordance with their character of single C-N bond in complex 4,5-disubstitute triazole molecule, with values of 1.4267/1.4189 Å for 1a and 1.4152/1.4087 Å for 1b, respectively, but with an evident larger values for bond distance compared with similar compounds (1.3742) [17]. Another explanation for larger C-N bond values of second type in 1a, probably is different type of hybridized N (sp^3) and C (sp^2) atoms, suggesting that the electron density is more localized among C8-N9-N10-C11-S19. Same discussion can be made for C-N bonds for thiole form, although this bond is between same type of hybridized N and C (sp^3) atoms, distance values are shorter in 1b that in 1a.

C=S bond length of 1.5779 Å in 1a are in good agreement with theoretically calculated values for C=S bond for 3,4-disubstituted-5-thione-1,2,4-triazole (1.574 Å).[17] The bond length of C10-S19 (1.6882 Å) in 1b is shorter than the normal single covalent C-S bond (1.82) and same bond in some dithia-cycloalcanes (1.801~1.825 Å), bat it is still longer than the double C=S bond (1.56 Å), suggesting that it has substantial double bond character, as it is expected for compounds which may exist as tautomers (conspicuous absence of SH vibration band at 2500 cm^{-1} in the experimental (i) and theoretical (ii) IR spectrum (Fig. 5) and appearance of triazole NH signals in experimental ^{1}H NMR spectra) [5,9].

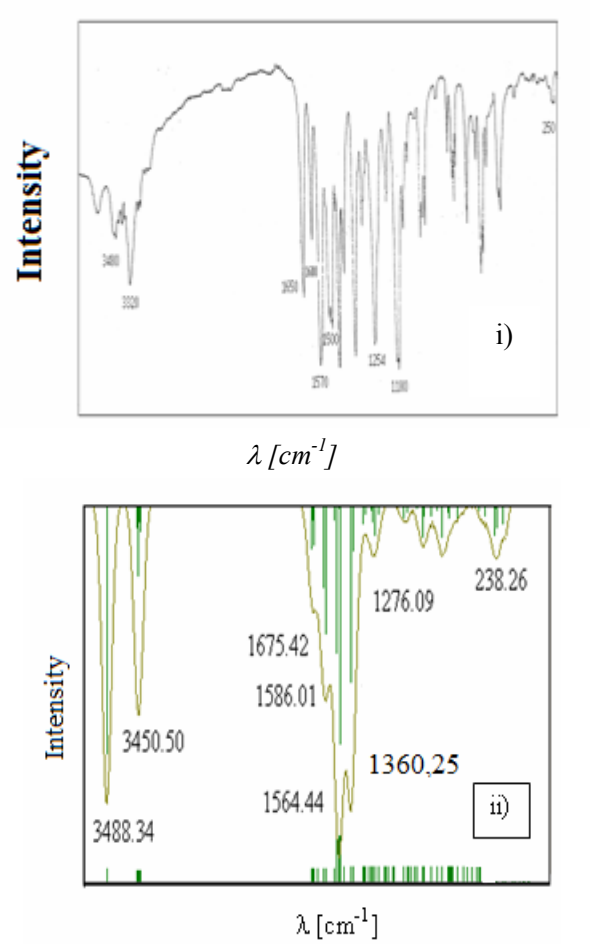


Figure 5 - Comparison between experimental (i) and theoretical (ii) IR spectra of TT

An attempt was made for comparison between experimentally obtained IR spectra and theoretically obtained (Fig. 5). As it can be seen form Figure 5, the position of characteristic bands of theoretically obtained IR spectra (ii) for TT are similar as in experimentally obtained IR spectra (i). Appearance of the bands located at 1586 cm^{-1}, 1276 cm^{-1} and 1360 cm^{-1} in theoretically obtained IR, indicated the formation of C=N N-N=C and C=S bands, res-

pectively in the preferred 1a form. Also the stretching frequency of substituted OH group and CH bands appears at 3488 and 3450 cm^{-1}.

In order to investigate the electronic properties, to find out the reaction centers and to determine the reactivity, TT has been studied using AM1 route.

Total energies (E_{tot}), the heats of formation (ΔH_f^0), E_{HOMO} and E_{LUMO} energies of frontier molecular orbitals, ionization potential (IP = - E_{HOMO}) and dipole moments of 1a and 1b forms of TT have been calculated and given in Table 2. In fact, the stability of heterocyclic systems, such as TT, depends on the conjugation between the: heterocyclic ring, (in this case 1,2,4-triazole), aromatic rings and thion (C=S)/thiol (C-SH) group in position 3 in TT and the interaction between them. The calculated nucleophilicity values are collected in Tab. 2 and indicated biggest nucleophility of 1a form (μ=-8.9431). The results support the greates basicity of 1a compared to the 1b form.

Table 2 - Total energies, heats of formation, semi empirical calculated relative stabilities, E_{HOMO} and E_{LUMO} energies of frontier molecular orbitals, nucleophilicities and dipol moments for 1a and 1b tautomers

	E_{tot} [kcalmol^{-1}]	ΔH_f^0 [kcalmol^{-1}]	RS[a]	E_{HOMO}	E_{LUMO}	μ[b]	μ[D]
1a	-70782.5	102.963	7.416	-8.4341	-0.4990	-8.9431	4.740
1b	-70792.3	95.547		-8.3751	-0.3740	-8.7491	3.998

[a] RS – semi empirical calculated relative stabilities, RS = ΔH_f^0(tautomer 1a)- ΔH_f^0 (tautomer 1b);
[b] μ – nucleophilicities; μ = E_{HOMO} - E_{LUMO}

The IP of 1a form (8.4341) was higher that of 1b form (8.3751) (Tab. 2), but those values are relatively lower than literature reported IP for 1,2,4-triazole. According the literature, the experimental IP of 1,2,4-triazole molecule was 10.00 eV and calculated IP using AM1 and PM3 methods, 10.27 and 10.396 eV, respectively [18].

Table 3 - Atomic charges of the 1a and 1b tautomers

Atomic charge					
Atom	**1a**	**1b**	**Atom**	**1a**	**1b**
C1	0.101	0.093	C16	-0.128	-0.127
C2	-0.163	-0.163	C17	-0.107	-0.103
C3	-0.067	-0.078	O18	**-0.245**	**-0.248**
C4	-0.071	-0.054	S19	**-0.198**	0.220
C5	-0.048	-0.048	H20	0.157	0.154
C6	-0.222	-0.221	H21	0.157	0.143
C7	0.038	-0.018	H22	0.149	0.157
N8	-0.065	-0.075	H23	0.141	0.139
N9	**-0.242**	-0.096	H24	**0.300**	0.053
C10	0.066	-0.236	H25	0.147	0.152
N11	0.195	-0.114	H26	0.141	0.142
C12	0.047	0.024	H27	0.139	0.140
C13	-0.104	0.113	H28	0.141	0.143
C14	-0.126	-0.128	H29	0.149	0.152
C15	-0,112	-0.112	H30	**0.223**	**0.221**

In order to investigate the basicity of TT, prediction of possible protonation centers in molecule witch containing various proton – acceptors atoms, is very significant. The atomic charges for tautomeric forms 1a and 1b are listed in Table 3.

In accordance with the negative charge distribution on N, O and S atoms in TT, some important differences observed are that in tautomer 1a, O18, N9 and S19 were atoms with the largest electron density in the molecule (-0.245; -0.242 and -0.198). In 1b tautomer, O18 was the most negative charged atom (-0.248). In accordance with the negative charge distribution on atoms in the TT, the O18, N9 and S19 were predicted to be the main sites of the molecule for the electrophlic attack of hydrogen. In fact, the determination of the exact protonation place according the negative atomic charge distribution was difficult because the negative atomic charges are relatively similar for previously mentioned atoms.

The most acidic hydrogen atoms were one bonded to: N9 (H24; 0.300) and to O18 (H atom from OH group; 0.223) in 1a, or H30 in tautomer 1b (0.221), but the electron deficiency was much lower in the second one. It would therefore see easier to pull the proton bonded to N9 in first step and subsequently in second step deprotonation process of H30 atom will take a place. The molecular electrostatic potential (MESP) and total charge density of the TT molecule were calculated and presented in Figure 6.

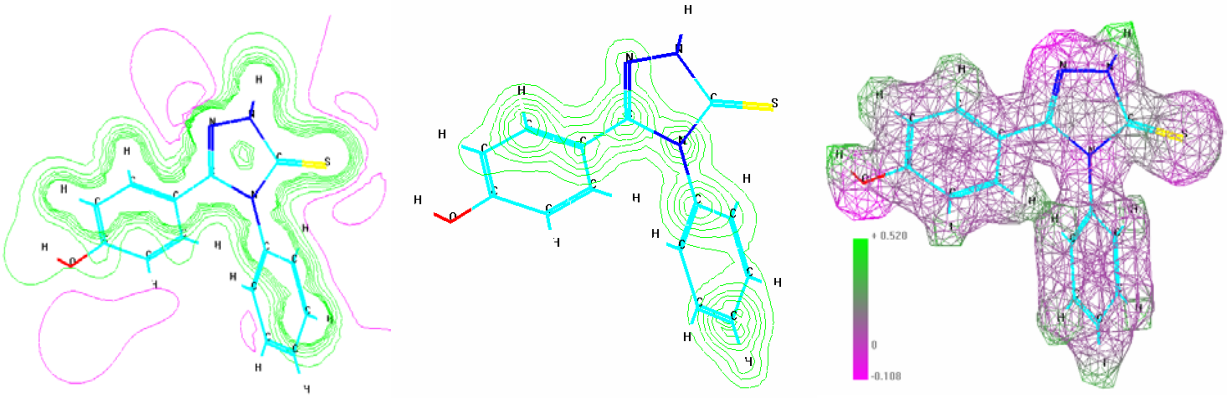


Figure 6 - Electrostatic potential and total charge density (2D contours and 3D mapped isosurface)

Next step for detemination of the exact protonation center of TT system, was calculating the proton affinities for different atoms in the molecule. The possible protonation pathways (mono cations: 2, 3, 4, 5 and 6) and deprotonation pathways (mono anions: 7 and 8) for TT are described in Figure 7.

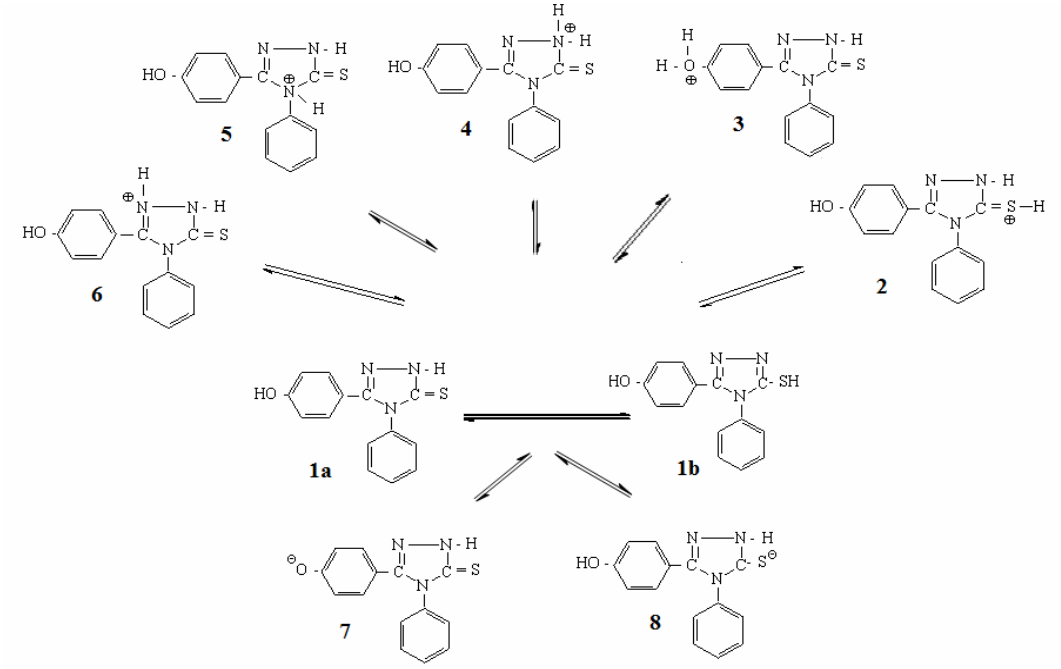


Figure 7 - Possible tautomerisation and protonation patterns for TT molecule

Hence, the stable conformations for the mono-cations formed by the protonation of different atoms in TT, such as: O18, S18, N14, N15 and N17 were determined witht full geometry optimization and the heats of formation (ΔH_f^0), calculated using AM1 method (Table 4).

The proton affinity values for the different atoms were calculated using the equation (1):

$$PA = 367.2 + \Delta H_f^0 (TT) + \Delta H_f^0 (TTH^+) \qquad (1)$$

where, PA is proton affinity, ΔH_f^0 (TT) is the heat of formation for the TT molecule, ΔH_f^0 (TTH^+) is the heat of formation for the cation and 367.2 is the heat of formation for the proton.

Comparing the result showen in Tab. 4 it can be conclude that the PA of TT calculated for S19 is higher than the others. In other words, the electrophilic attack of the proton on the S19 atom is easier than the other atoms. Hence, despite the fact that the stability of thiol form is higher than that thion form (E_{tot}, Tab.2), the proces of proton acception is higher in 1a form, which together with experimentaly obtained data from spectroscopic measurments are indication for dominance of thion form of TT [9].

Table 4 - Total energies, heats of formation, E_{HOMO} and E_{LUMO} energies of frontier molecular orbitals and dipol moments for protonation forms for TT

		1a	PA	1b	PA
S19	E_{tot} (kcal/mol)	-70949.5	**224.041**	-70935.5	199.932
	ΔH_f^0 (kcal/mol)	246.122		262.815	
	μ [D]	5.554		10.64	
O18	E_{tot} (kcal/mol)	-70892.9	199.837	-70904.2	170.717
	ΔH_f^0 (kcal/mol)	301.525		292.030	
	μ[D]	21.440		18.97	
N8	E_{tot} (kcal/mol)	-70896.2	168.862	-70906.5	170.670
	ΔH_f^0 (kcal/mol)	301.302		292.077	
	μ [D]	6.47		1.767	
N9	E_{tot} (kcal/mol)	-70922.2	168.638	-70908.1	171.999
	ΔH_f^0 (kcal/mol)	270326		290.748	
	μ [D]	5.424		5.588	
N11	E_{tot} (kcal/mol)	-70902.7	197.721	-70919.4	186.415
	ΔH_f^0 (kcal/mol)	272.442		276.332	
	μ [D]	2.086		6.537	

An attempt was made for calculation of semi empirical computed acid dissociation constants, using AM1 method.

The acidity of base as is 1,2,4-triazol-3-thione for reaction (2):

$$TT + H_30^+ \rightleftharpoons TTH^+ + H_2O \qquad (2)$$

in aqueous phase can be calculated according to equation (3), where ΔG is the standard free energy:

$$\delta\Delta G(_{TTH}+) = [\Delta G(_{TT}) + \Delta G(_{H3O}+)] - [\Delta G(_{TTH}+) + \Delta G(H_2O)] \qquad (3)$$

The self computed thermodinamic data were used in predicting the pKa values using Eq. (4) in which the $\delta\Delta G(_{TTH}+)$ is the standard free energy charge for reaction (2) (Table 5):

$$pKa(_{TTH}+) = \delta\Delta G(_{TTH}+)/2.303RT \qquad (4)$$

where R is the gas constant ($R=1.987x10^{-3}$ kcalmol^{-1}K^{-1}) and T is the absolute temperature in Kelvin ($T = 298^0$ K).

Table 5 - Aqueous phase calculated termodinamic parametrs of neutral (1a) and S – protonated (2) TT molecule (ε = 78.4)

	ΔH_f [kcalmol^{-1}]	ΔS [calmol^{-1}]	ΔG_f^a [kcalmol^{-1}]	δΔG	$pKa_{(exp.)}$ [b]	$pKa_{(calc.)}$ [c]
1a (neutral)	-148.57	0.208	-210.55	-14.14	-4.4243[e] -4.7209[f]	-10.3681
2 (S – protonated)	-18.64	0.210	-83.91			
H_3O^+ [d]	44.33	46.12	30.58			
H_2O [d]	-68.49	45.09	-81.93			

[a] $\Delta G_f = \Delta H_f - T\Delta S$; [b] taken from reference [9]; [c] calculated using Eq. (4); [d] taken from reference [19]; [e] pKa using HAFM – Hammett acidity function method; [f] pKa using EAFM – "Excess acidity" function method

This quantum chemical investigations of tautomerion froms of 4-phenyl-5-(4-hydroxyphenyl)-1,2,4-triazoline-3-thion were in accordance with our previously experimental investigation for protonation place of TT [9,10]. Experimentaly obtained values for protonation *pKa* (-4.4243 and -4.7209) are characteristic for protonation of S atom form thiourea fragment of 1,2,4-triazoline-3-thione moiety of TT and deprotonation pK values of 7.2385 and 9.9124 correspond to first dissociation of H24 and then dissociation of H30.

As can be seen form Tab. 5, there was a difference between $pKa_{(exp.)}$ and those calculated using AM1 quantun – chemical method (around 6 pKa units), which is considerable difference. This probably can be explained that a large and complex molecule such as is TT, was object of investigation. As an additional fact probably was a possibility for existence of two tautomeric forms of investigated compounds.

4. CONCLUSION

Quantum chemical investigations, in most cases can be used in structure elucidation of organic molecules and this kind of calculation should be performed as a prediction of possible synthesis and the stability of the predictive product.

When the object of investigation was a large and complex molecule, such is TT, there was overlapping of theoretical and experimental results in some areas of investigation, such as prediction of protonation place and dominance of one of tautomeric form. But there was disagreement in final calculation of *pKa* value, which probably was result of structure of investigated molecule and a possibility for existence of two tautomeric forms.

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IZVOD

KVANTNO-HEMIJSKA ISPITIVANJA TAUTOMERNIH FORMI 4-FENIL-5-(4-HIDROKSIFENIL) -1,2,4-TRIAZOLIN-3-TIONA

4-Fenil-5-(4-hidroksifenil) -1,2,4-triazoline-3-tion (TT) dobijen je oksidativnom ciklizacijom odgovarajućeg 4-hidroksibenzoilfeniltiosemicarbazida. Spektralne analize ukazuju na postojanje tion-tiolnih tautomernih formi, 1,2,4-triazolin-3-tiona. Molekularne konformacije i elektronska svojstva TT ispitivane su AM1 semiempirijskom metodom. Ukupna energija, toplota formiranja, dipolni momenat, energija jonizacije, atomske polneze E_{HOMO} i E_{LUMO} i elektronske gustine, su izračunate. Jonizacione konstante i protonaciona mesta u TT, dobijena su eksperimentalno. Protonski afiniteti (PA) za različite atome (azot, kiseonik i sumpor) izračunati su AM1 metodom. Kvantno-hemijska ispitivanja tautomernih formi TT u skladu su sa eksperimentalnim istraživanjima: PA za S atoma iz C = S grupe je veći od ostalih atoma, što ukazuje na lakši elektrofilni napad na ovaj atom.

Ključne reči: *1,2,4-triazolin-3-tion, AM1, ukupna energija, toplota formiranja*

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VINETA SREBRENKOSKA[1],
EMILIJA FIDANCEVSKA[2]

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Environmental issues in materials science and engineering

The industrial engineering consumes of materials and is dependent on a continuous supply of them. Increasing population and living standards cause the consumption rate to grow - something it cannot do forever. Finding ways to use materials more efficiently is a prerequisite for a sustainable future. Recent global attention to the issues and challenges of sustainable development is forcing industries to conduct self-assessments to identify where they stand within the framework for sustainability, and more importantly, to identify opportunities, strategies and technologies that support achieving this goal. Design for environmental sustainability is the long-term view: that of adaptation to a lifestyle that meets present needs without compromising the needs of future generations.

The composite material is a group of materials which they have not yet gained the same amount of utilisation as metallic materials. Since the composites consist of a mixture of several types of materials on macro level they cannot be regarded as homogenous as the steel materials. Both these circumstances complicate the possibilities to form a well-organised system for waste handling. The increased use of composites in industry will create continuously more waste to be handled in the future. Also for this type of materials several regulations put pressure on producers to consider the waste treatment. Examples are prohibition against landfill, producer responsibility for specific groups of products and eventually taxes on waste incineration. All these regulations are aiming for material recycling, due to decreased environmental impact. A common opinion is that recycling composite materials will be especially difficult or not even possible. The main alternative used today for handling composite waste is landfill but also waste incineration is an alternative. To respond to environmental awareness in society and to regulations, companies require new methods for waste disposal.

Key words: *environmental effects, eco-design, composites, waste.*

1. INTRODUCTION

Environmental and societal impacts of production are becoming significant engineering issues. In this regard, the material life cycle is an important consideration. This cycle consists of extraction, synthesis/ processing, product design/manufacture, application, and disposal stages. Materials, energy, and environmental interactions/exchanges are important factors in the efficient operation of the materials cycle. The earth is a closed system in that its materials resources are finite. Environmental issues involve ecological damage, pollution, and waste disposal. Recycling of used products and the utilization of green design obviate some of these environmental problems.

Composites are materials that comprise strong load carrying material (known as reinforcement) imbedded in weaker material (known as matrix). Reinforcement provides strength and rigidity, helping to support structural load. The matrix, or binder (organic or inorganic) maintains the position and orientation of the reinforcement. Significantly, constituents of the composites retain their individual, physical and chemical properties and together they produce a combination of qualities which individual constituents would be incapable of producing alone [1]. Composites can be grouped into categories based on the nature of the matrix each type possesses. Methods of fabrication also vary according to physical and chemical properties of the matrices and reinforcing fibers [2].

Polymer Matrix Composites (PMCs)

The most common advanced compositesare polymer matrix composites. These composites consist of a polymer thermoplastic or thermosetting reinforced by fiber (natural carbon or boron). These materials can be fashioned into avariety of shapes and sizes. They provide great strength and stiffness along with resistance tocorrosion. The reason for these being mostcommonis their low cost, high strength and simplemanufacturing principles.

Metal Matrix Composites (MMCs)

Metal matrix composites, as the name implies, have a metal matrix. Examples of matricesin such composites include aluminum, magnesium and titanium. The typical fiber includes carbon and silicon carbide. Metals are mainly reinforced to suit the needs of design. For example,the elastic stiffness and strength of metalscan be increased, while large coefficient ofthermal expansion, and thermal and electricalconductivities of metals can be reduced by theaddition of fibers such as silicon carbide.

Author's address: [1]Faculty of Technology, Goce Delčev University, "Krste Misirkov" b.b. P.O. Box 201, 2000 Štip, Republic of Macedonia, [2]Faculty of Technology and Metallurgy, Sts. Cyril & Methodius University, MK-1000 Skopje, Republic of Macedonia

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Ceramic Matrix Composites (CMCs)

Ceramic matrix composites have ceramic matrix such as alumina, calcium, aluminosilicate reinforced by silicon carbide. The advantages of CMC include high strength, hardness,high service temperature limits for ceramics, chemical inertness and low density.

Naturally resistant to high temperature, ceramic materials have a tendency to becomebrittle and to fracture. Composites successfully made with ceramic matrices are reinforced with siliconcarbide fibers. These composites offer the same high temperature tolerance of super alloys but with out such a high density. The brittle nature of ceramics makes composite fabrication difficult. Usually most production procedures involve starting materials in powder form.

There are four classes of ceramics matrices: glass (easy to fabricate because of low softening temperatures, include borosilicate and aluminosilicates), conventional ceramics (silicon carbide, silicon nitride, aluminum oxide and zirconium oxide are fully crystalline), cement and concreted carbon components.

Carbon-carbon composites (CCMs)

CCMs use carbon fibers in a carbon matrix. Carbon-carbon composites are used in veryhigh temperature environments of up to 6000^{o}F, and are twenty times stronger and thirty times lighter than graphite fibers.

In production industry the environmental questions are in the focus of attention. Several new strategies for incorporating these issues into design have been developed under designation eco-design or design for environment. The purpose of these strategies are to:

- minimise energy consumption,
- minimise use of material,
- exclude hazardous materials and substances,
- facilitate recycling.

Over the last decades, knowledge of complexity and extent of the environmental problems has increased. From being concentrated on local problems the focus has changed to global problems and resulted in a new viewpoint, sustainable development.The aim of this concept is to reach balance between resource use and environmental impact, so that the environment is able to withstand the burden within the ecological cycle. At the same time the resource distribution should be fair.

2. ENVIRONMENTAL CONTEXT

The extensive effect on the environment is connected to human activities and unrestrained exploitation of natural resources, which is illustrated in Figure 1.

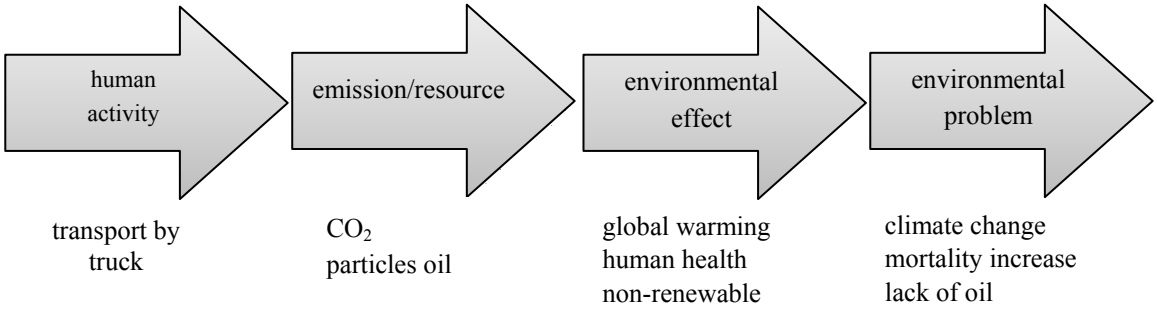

Figure 1 - The chain of events resulting in environmental problems

Examples of such activities can be found through the whole life cycle of a product from raw material extraction, product manufacturing, use of the product to the waste disposal. Examples of emissions generated in transportation by trucks are carbon dioxide, CO_2, and particles, resulting in global warming and deteriorating human health. Increasing use of resources as oil decreases non-renewable sources. The effects mentioned cause climate change and increased mortality. The increasing use of oil also may lead to shortage, due to insufficient supply.This exploitation has resulted in a high standard of living in the industrialised countries. With this high standard follows a high consumption of products leading to increased consumption of resources and energy[3].

Materials play a crucial role in technology-economy-environment scheme (Fig.1).A material that is utilized in some end product and then discarded passes throughseveral stages or phases.These stages sometimes are termed the “total materials cycle“ or just “materials cycle” and representsthe life circuit of a material. Raw materials are extracted from their natural earthly habitats bymining, drilling, harvesting, etc. These raw materials are then purified, refined,

and converted into bulk forms such as metals, cements, petroleum, rubber, fibers, etc. Further synthesis and processing results in products that are what may be termed‘‘engineered materials’’and examples include metal alloys, ceramic powders, glass,plastics, composites, semiconductors, elastomers. Next, these engineered materialsare further shaped, treated, and assembled into products, devices, and appliancesthat are ready for the consumer - this constitutes the "product design, manufacture,assembly“ stage. The consumer purchases these products and uses them (the “applications” stage) until they wear out or become obsolete. At this time the product constituents may either be recycled/reused or disposed of as waste, normally being either incinerated or dumped as solid waste in municipal land-fills - as such, they return to the earth and complete the materials cycle [4].

Thus, this materials cycle (Figure 2) is really a system that involves interaction sand exchanges among materials, energy, and the environment.

One approach that is being implemented by industry to improve the environmental performance of products is termed *life cycle analysis/assessment.* With this approach to product design, consideration is given to the environmental assessment of the product, from material extraction to product manufacture to product use, and, finally, to recycling and disposal. Some times this approach isalso labeled as “green design“. One important phase of this approach is to quantifythe various inputs (e.g., materials and energy) and outputs (e.g., wastes) for eachphase of the life cycle. In addition, an assessment is conducted relative to the impact on both global and local environments in terms of the effects on the ecology, human health, and resource reserves [5].

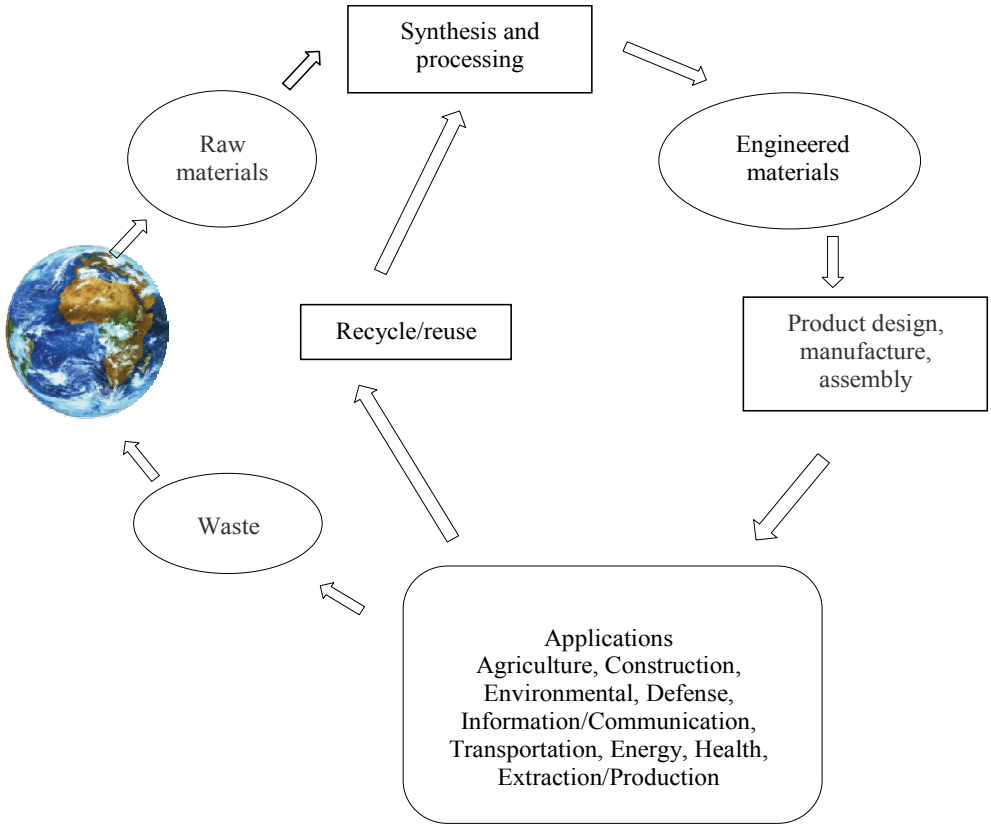

Figure 2 - Schematic representation of the total materials cycle

3. SELECTING MATERIALS FOR ECO-DESIGN

For selection of materials in environmentally responsible design we must first ask: which phase of the life cycle of the product under consideration makes the largest impact on the environment? If material production consumes more energy than the other phases of life, it becomes the first target. The energy required to shape a material is usually much less than that to create it in the first place. Certainly it is important to save energy in production. But high priority often attaches to the local impact of emissions and toxic waste during manufacture and this depends crucially on local circumstances. Clean manufacture is the answer here. The eco-impact of the use phase of energy - using products depends on mechanical, thermal and electrical efficiencies; it is minimized by maximizing these [6].

The environmental consequences of the final phase of product life have many aspects or requirements which are summarized in the following guidelines:

- Toxicity - it means that avoiding toxic materials such as heavy metals and organometallic compounds is good because they in landfill, cause long term contamination of soil and groundwater.
- Potential of recycling - it means examination the using of materials that cannot be recycled, since recycling can save both material and energy and to minimize recycling of materials for which this is possible.
- Controlled combustion - when recycling is impractical the best way is to recover energy by controlled combustion.
- Biodegradability - it means the using of materials that are biodegradable or photo - degradable, although these are ineffectual in landfill because the anaerobic conditions within them inhibit rather than promote degradation.

Rational selection of materials to meet environmental objectives starts by identifying the phase of product life that causes greatest concern: the material production, the product manufacture, the product use or the product disposal. Dealing with all of these requires data not only for the obvious eco-attributes (energy, CO_2 and other emissions, toxicity, ability to be recycled, and the like) but also data for mechanical, thermal, electrical and chemical properties. Thus, if material production is the phase of concern, selection is based on minimizing the embodied energy or the associated emissions (CO_2 production, for example). But if it is the use phase that is of concern, selection is based on other constraints on stiffness, strength, cost, etc.

4. METHODS OF END OF LIFE TREATMENT: STATE OF THE ART

The methods are divided into the following groups: 1. reuse; 2. mechanical material recycling; 3. energy recovery; 4. material recycling and energy or chemical recovery.

Important stages in the materials cycle where materials science and engineeringplays a significant role are recycling and disposal. The issues of recyclability and disposability are important when new materials are being designed and synthesized. Further more, during the materials selection process, the ultimate disposition of the materials employed should be an important criterion. From an environmental perspective, the ideal material should be either totally recyclable or completely biodegradable. Recyclable means that a material, after having completed its life cycle in one component, could be reprocessed, could reenter the materials cycle, and could be reused in another component - a process that could be repeated an indefinite number of times. By completely biodegradable, we mean that, by interactions with the environment (natural chemicals, microorganisms, oxygen, heat, sunlight, etc.), the material deteriorates and returns to virtually the same state in which it existed prior to the initial processing. Engineering materialsexhibit varying degrees of recyclability and biodegradability.

Preparing for the future end of life treatment is important for product manufacturers, due to the increased environmental demands (based on legislation) and common awareness. This is especially important for products containing composite materials since these materials commonly are thought not to be recyclable because they are multiphase in nature. The two or more phases/materials that constitute the composite are normally intermixed on a very fine scale and consequently, complete phase/material separation is virtually impossible, and recycling procedures that require material separation are impractical [7].

The model presented in Figure 3 starts with the composite waste.

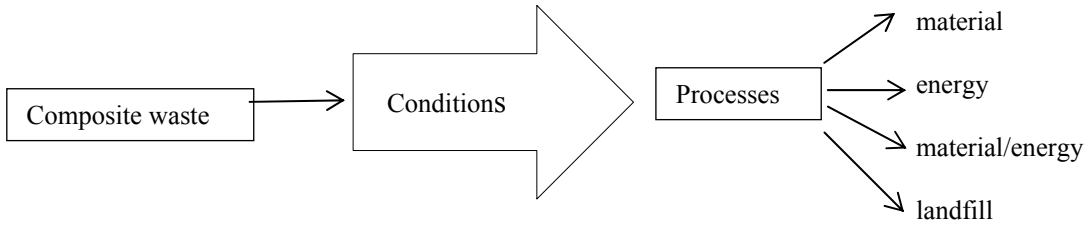

Figure 3 - A model for treatment of composite waste

Dependent on the disposal options chosen a number of processes are used to obtain material, energy, material/energy or to decide on landfill. These processes are identified by their process properties. The treatment conditions are set by the required processes through their process properties, which are coupled to information about the waste, the waste properties.

For example, process properties, which we need to know in order to accomplish a cutting process, are capacity, size of end of life product, cutting edge material/hardness etc. These properties need to be

correlated to the waste properties including information on type of material, size and metallic inserts etc. [8].

5. CONCLUSION

Because of increasing environmental demands, especially on dealing with products end of life phase, product manufacturers and designers must consider the future disposal of their products. For conventional materials like steel and aluminium well-functioning recycling methods exists. This is not the case for structures of composites, which are used more extensively. The composites consist of a mixture of several types of materials on macro level and they cannot be regarded as homogenous as the steel materials. These circumstances complicate the possibilities to form a well-organized system for waste handling. Several techniques do exist but they are not yet commercially available. The current disposal methods of composites are landfill and incineration. Many investigations have pointed out recycling of composite materials as the best alternative considering environmental effects. Since recycling composites is a complicated process, especially recycling polymer composite it is important to acquire comprehensive information about the constituents of these materials.

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ИЗВОД

ПИТАЊА ЗАШТИТЕ ЖИВОТНЕ СРЕДИНЕ У МАТЕРИЈАЛИМА НАУКА И ИНЖЕЊЕРСТВО

Индустријски инжењеринг троши материјале и зависи од сталног снабдевања. Повећање броја становника и животног стандарда проузрокује да потрошња расте - нешто што се не може заувек уради. Проналажење начина да се користе материјали ефикасније је предуслов за одрживу будућност. Недавна глобална пажња о питањима и изазовима одрживог развоја присиљава индустрије да спроведе самопроцене и да идентификују где они стоје у оквиру одрживости, и што је још важније, да се идентификују могућности, стратегије и технологије које подржавају постизање овог циља. Дизајн за одрживост животне средине је дугорочан и окренут на поглед адаптације на живот који задовољава садашње потребе без угрожавања потреба будућих генерација.

Композитни материјал је група материјала који још нису стекли исту количину коришћења као метални материјали. Пошто се композити састоје од мешавине неколико врста материјала на макро нивоу, они се не могу сматрати хомогеним као челични материјали. Обе ове околности компликују могућности да формирају добро организован систем за отпадом. Повећано коришћење композита у индустрији ће створити континуирано више отпада који ће се руковати у будућности.

Такође, за ову врсту материјала, неколико прописа врше притисак на произвођаче да размотре третман отпада. Примери су забрана бацања на депоније, одговорности произвођача за специфичне групе производа и напослетку порези на спаљивање отпада. Сви ови прописи имају за циљ материјалну рециклажу, због смањеног утицаја на животну средину. Заједничко мишљење је да ће рециклажа композитних материјала бити посебно тешка или чак и не могућа. Главна алтернатива данас за руковање отпадом композитних материјала је депонија, али и спаљивање отпада је алтернатива. Да би се одговорило на еколошке свести у друштву и прописима, компаније захтевају нове методе за одлагање отпада.

***Кључне речи**: еколошки ефекти, еко-дизајн, композити, отпада.*

Рад примљен: 10.12.2012.

Оригинални научни рад

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Tables and graphs should essentially contribute to better understanding and interpretation of the results of work. Photos, drawings and other illustrations should be clear and of good quality with author's signature at the back. Places for tables and illustrations should be clearly marked in the manuscript.

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JOURNAL MATERIALS PROTECTION

SNEŽANA AKSENTIJEVIC[1], JELENA KIURSKI[2], ZAGORKA AĆIMOVIĆ PAVLOVIĆ[3]

Originalni naučni rad
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Olovo u otpadnim vodama metaloprerađivačke industrije Zapadne Srbije

Regioni u Republici Srbiji u kojima je razvijena metalska, metaloprerađivačka industrija su lokaliteteti gde se detektuje prisustvo teških metala u zemljištu, vodi, a posebno u sedimentu koji se ponaša kao sedište i potencijalni izvor metala u akvatičnoj sredini. U frekvenciji vremena koncentracija metala se povećava iznad dozvoljenih granica, a preko lanca ishrane može imati negativan uticaj i na čoveka.

Cilj rad se odredi koncentracija teškog metala olova u vodi i sedimentu u Zapadnoj Srbiji, Sevojnu, gde posluju dva velika proizvođača poluproizvoda od bakra i aluminijuma. Programski paket MAT LAB korišćen je za definisanje distribucije olova između čvrste i tečne faze u funkciji rastojanja od mesta izlivanja industrijskih otpadnih voda.

***Ključne reči**: teški metali, olovo, voda, sediment*

UVOD

Sadržaj teških metala u prirodnim vodama je uglavnom nizak zbog male zastupljenosti u litosferi i pedosferi (osim gvožđa). Usled intezivnog industrijskog razvoja, koji nije pratila istovremena primena adekvatnih mera zaštite okoline, prisutno je zagađivanje voda teškim metalima. Ukoliko teški metali dospeju u vodu, akumuliraju se u ekosistemima i vodenim organizmima (bakterijama, algama, beskičmenjacima i ribama), a preko lanca ishrane dospevaju i u kopnene biljke, životinje i čoveka [1].

Različiti prirodni i antropogeni izvori olova su doveli do povećanja njegovih koncentracija u biosferi i vodenim sistemima.

Olovo se kao sastojak velikog broja minerala pojavljuje u prirodnim vodama u koncentracijama od 1 μg/l i manjim. Otpadne vode iz rudnika olova, iz industrije prerade olova, proizvodnje pigmenata, olovnog benzina i drugih izvora, unose olovo i njegova jedinjenja u prirodne vode. Jedinjenja Pb^{2+} su najčešće prisutna u prirodnim vodama (kod pH < 7). Sa smanjenjem pH vrednosti povećava se rastvorljivost olova u vodi. Prirodni sadržaj olova u rekama i jezerima je 1 – 10 μg/l [2].

Raspodela i migracija olova u prirodnim vodama uslovljena je intezivnim taloženjem i kompleksiranjem sa organskim i neorganskim ligandima. U procesu hidrolize fosfata i sulfida olova pri pH > 6 obrazuje se $Pb(OH)^+$, pri pH > 10 rastvoreni $Pb(OH)_2$. Pb^{2+} i $Pb(OH)^+$ u vodi se nalaze u jednakim koncentracijama, a pri pH 8 dominiraju joni $Pb(OH)^+$, koji se po svojim sorpcionim osobinama znatno razlikuju od Pb^{2+} [3].

Adrese autora: [1]Visoka poslovno – tehnička škola strukovnih studija, Trg S. Save 34, Uzice, [2]Fakultet tehničkih nauka, Trg D. Obradovica 6, Novi Sad, [3]Tehnološko – metalurški fakultet, Karnegijeva 4, Beograd

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Često na nivo i hemijske osobine olova u vodi utiču grupe povezane za olovo [4].

Jedan od najznačajnijih procesa u sistemu sediment/voda koji utiče na sudbinu i ponašanje jedinjenja u okolini je proces sorpcije. Sa njom se vrši udaljavanje određenih jedinjenja iz vode (ali ne iz vodenog sredine) njihovim vezivanjem za suspendovane čestice i sediment. Sorbat se transportuje zajedno sa sedimentom i mogu biti depozit u rekama i ostati u neodređenom vremenskom periodu. Koncentracija metala u rastvorenoj fazi je kontrolisana sorpcijom na čvrstoj fazi koja se može odvijati veoma brzo.Neki metali se mogu jače vezati za čestice sedimenta, pa se one teže desorbuju. Elementi kao što su Pb i Cu su čvrsto vezani za čestice sedimenta, dok su Ni, Cd i Zn vezani u manjoj meri [5].

Intezitet sorpcije olova sa sedimentima zavisi od karakteristika njegovog granulometrijskog sastava i sadržaja organske materije. U odsustvu rastvorenih kompleksoobrazujućih oblika, olovo se u potpunosti sorbuje i taloži pri pH > 6. U kiseloj sredini huminske kiseline sorbuju olovo intezivnije nego glinovite čestice. Obrnut proces zapaža se pri pH ≥ 6.5 kada se obrazuju rastvoreni huminski kompleksi olova.

Izuzetno jako se vezuje u redukcionim uslovima precipitacijom sa sulfidnim mineralima, kompleksira se sa nerastvorenim organskom materijama i veoma je efikasno imobilisan precipitacijom sa gvožđe oksidnim mineralima pri oksidacionim uslovima [6].

Transportom sedimenta u zavisnosti od fizičko-hemijskih karakteristika sedimenta može doći do resuspenzije sedimenta i desorpcije metala u vodu, pri čemu se ispoljavaju šteteni efekti na živi svet i ljude kroz lanac ishrane, putem vode ili direknog kontakta [7].

MATERIJALI I METODE

Istraživanja koncentracije nivoa teških metala u vodi i sedimentu vršena su u industrijskoj zoni Sevojna gde se nalaze dva velika proizvođača polu-

proizvoda od bakra i aluminijuma i njihovih legura u periodu proleće - jesen 2009. godine.

Preradom bakra i njegovih legura dobijaju se: limovi, trake, ploče, žice, profili. Preradom aluminijuma i njegovih legura postupkom livenja, valjanja i presovanja dobijaju se: trake, limovi, bojeni aluminijum, folije.

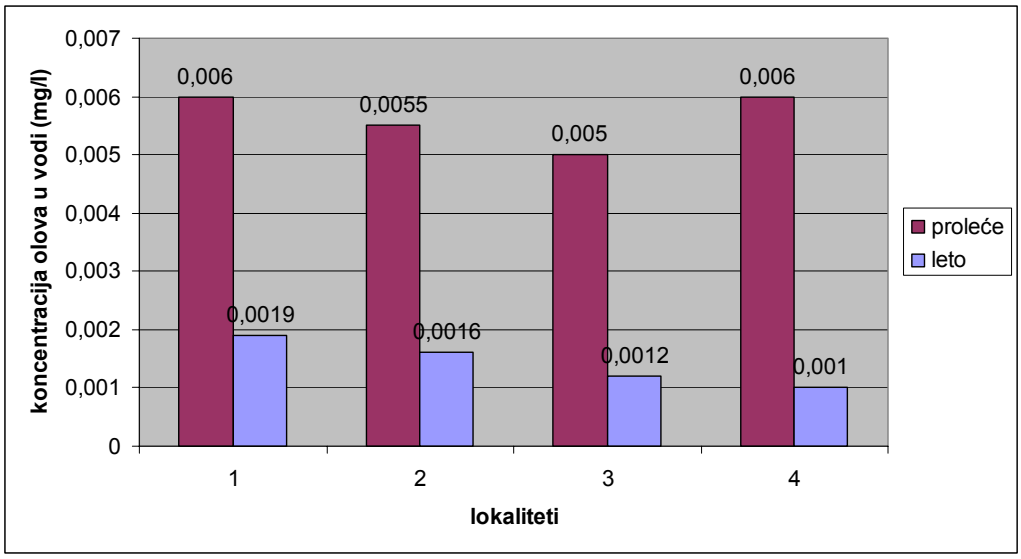
Rukovanje, skladištenje i priprema uzoraka vode izvršena je u skladu sa standardnom metodom EPA 200.7 u plastične posude od 1 litra, prethodno očišćene sa 10% rastvorm azotne kiseline. Pre samog uzimanja uzoraka posude su 2-3 puta isprane vodom koja se analizira.

Površinski sediment uzorkovan je u plastične posude od 1l i analizane ukupne koncentracije ispitivanih teških metala u sedimentu vršena je metodom EPA 3050 B.

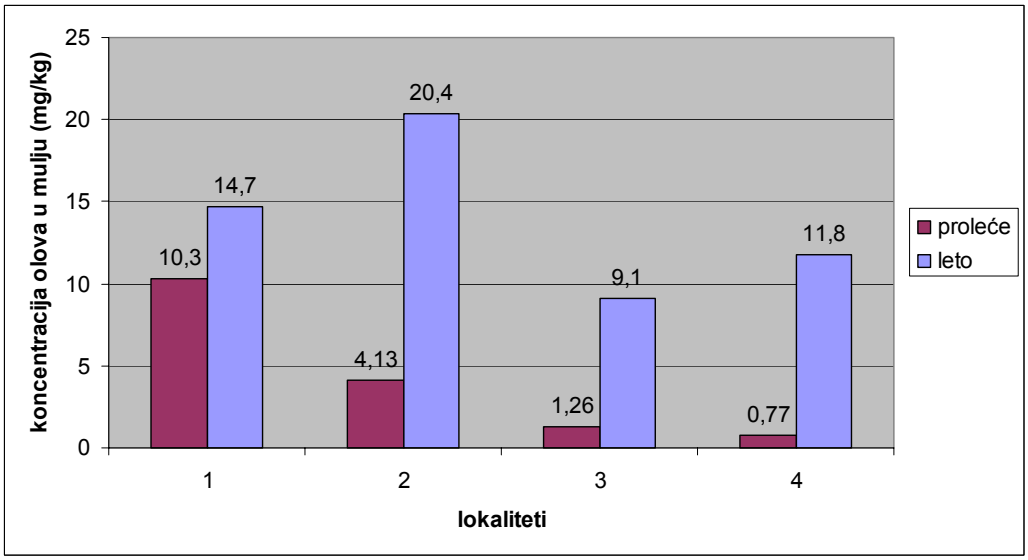
REZULTATI

Prema zakonskoj regulativi Republike Srbije - Pravilniku o opasnim materijama u vodi („Sl. Glasnik SRS“, br. 31/82) [8] i Pravilniku o dozvoljenim količinama opasnih i štetnih materija u zemljištu i vodi za navodnjavanje i metodama njihovog ispitivanja („Sl. Glasnik SRS“, br. 23/94) [9] maksimalno dozvoljene koncentracija za olovo u vodi je 0,05 mg/l (I/II klase); 0,1 mg/l (III/IV klase). U vodi za navodnjavanje do 0,1 mg/l, a u zemljištu do 100 mg/kg.

Sadržaj olova u vodi na svim lokalitetima veći je u proleće nego u leto i kretao se od 0,0016 mg/l do 0,001mg/l, slika 1. Sadržaj olova nije prešao MDK (Sl.glasnik SRS 31/82).



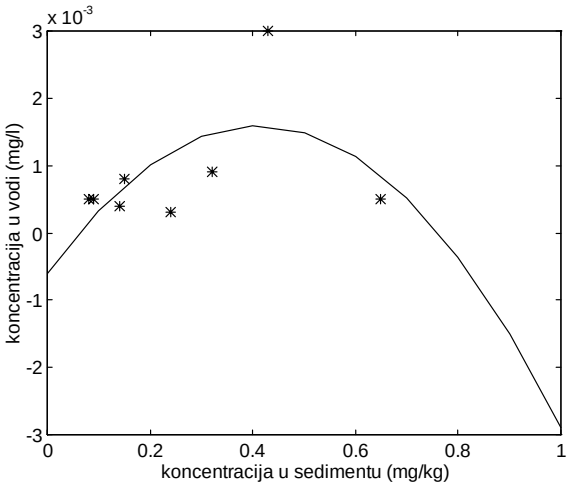
Slika 1 - Promena koncentracije olova u vodi-proleće/leto 2009. godine



Slika 2 - Promena koncentracije olova u sedimentu - proleće/leto 2009.godine

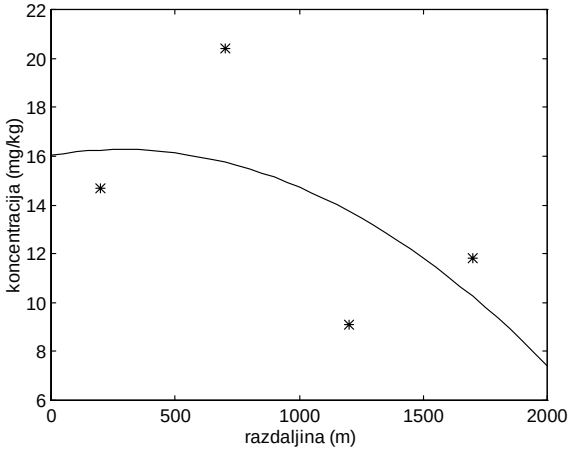
Sadržaj olova u ispitivanim uzorcima veći je u leto i varirao je od 0,77 mg/kg do 20,4 mg/kg, slika 2. Ni na jednom mernom mestu sadržaj nije prešao MDK (Sl. Glasnik RS, br. 23/94).

Korišćenjem programskog paketa MATLAB – metoda najmanjeg kvadarata dobijene su polinomske zavisnosti. Distribucija metala u vodi i sedimentu sa rastojanjem date su na slikama od 3 – 6.



Slika 3 - Distribucija olova u vodi sa rastojanjem - proleće

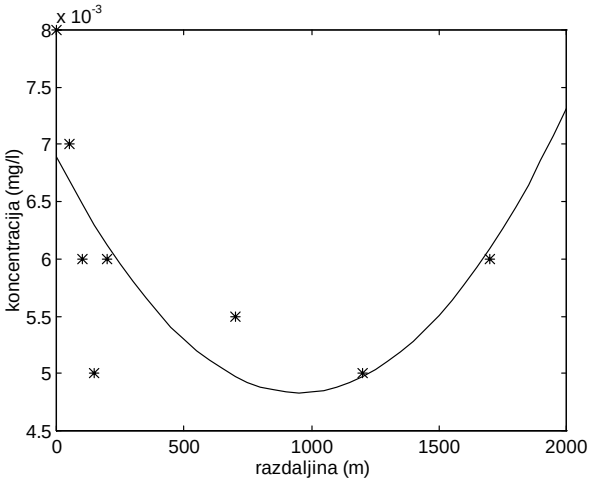
$y = 1.0000 \times 10^{-10} x^2 - 8.1000 \times 10^{-7} x + 2.0730 \times 10^{-3}$



Slika 4 - Distribucija olova u sedimentu sa rastojanjem-proleće

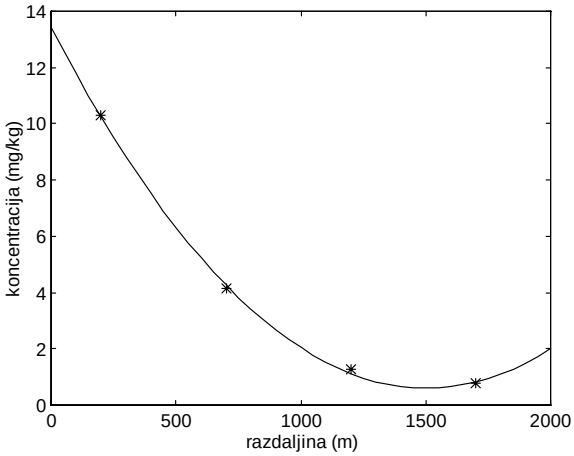
$y = -3.0000 \times 10^{-6} x^2 + 1.7000x 10^{-3} x + 16.0300$

Distribucija ispitivanih metala u vodi i sedimentu po rastojanju od mesta direktnog izlivanja otpadnih voda iz metaloprerađivačkog sistema, pokazuje da se koncentracije smanjuje u peridu proleća, a raste u toku leta.



Slika 5 - Distribucija olova u vodi sa rastojanjem – leto

$y = 2.2648 \times 10^{-9} x^2 - 4.3208 \times 10^{-6} x + 6.8917 \times 10^{-3}$



Slika 6 - Distribucija olova u sedimentu sa rastojanjem-leto

$y = 5.6800 \times 10^{-6} x^2 - 1.7084 \times 10^{-2} x + 13.4440$

Na mernom mestu na kome dolazi do porasta koncentracije, sa desne obale reke Đetinje se nalazi saobraćajnica. Vodostaj reke je niži leti nego u proleće. Uzrok povećane koncentracije olova u vodi u toku leta je automobilski saobraćaj kao i naftni derivati, a u tom delu rečnog toka postoji pristupačno mesto za prilaz automobila.

ZAKLJUČAK

Svaki teški metal odlikije se specifičnim ekološkim osobinama. Karakteriše ih široka disperzija i transport na velike udaljenosti, bioakumulacija, ulazak u lanac ishrane, izazivanje fizioloških poremećaja u živim organizmima.

Olovo je visokotoksičan teški metal koji se vremenom nagomilava u organizmu ljudi i životinja.

Otrovan je u svim svojim jedinjenjima. U ljudski organizam prodire kroz respiratorni sistem, gastrointestinalni trakt i kožu. Transportuje se krvlju i depnuje u kostima.

Na osnovu dobijenih rezultata sadržaja metala u vodi i sedimentu, može se zaključiti da su metali dominatno prisutni u sedimentu. Poređenjem sadržaja, generalno koncentracije metala uzorkovanih voda i sedimenata u proleće veće su nego u leto i za većinu metala ne prelaze MDK.

Razlog ove razlike u koncentraciji metala između dva perioda ispitivanja je proces intezivnog sagorevanja fosilnih goriva u zimskim mesecima, čiji produkti se talože na površini snega, a otapanjem snega stižu do površinskih voda. Vodostaj u proleće je bio znatno viši sa vrlo turbulentnim tokom vode. Moguće je da su zahvaćeni i drugi izvori zagađenja sa okolnih poljoprivrednih zemljišta (korišćenje pesticida, veštačkih đubriva, odlaganjem komunalnog, industrijskog i drugog otpada).

Protok vode u letnjem periodu bio je znatno niži nego u proleće. Kvalitet malog vodotoka (Dragića potoka) je znatno lošiji i u velikoj meri pod direktnim uticajem industrijskih otpadnih voda, a ima mali potencijal za samoprečišćavanje. Detektovan je pogoršan kvalitet sedimenta.

Ponašanje teških metala u svakom ekosistemu je veoma kompleksno i zato se moraju posebno analizirati za svaki deo odvojeno u cilju shvatanja delovanja i složenih odnosa koji vladaju u ekosistemu.

Dobijeni rezultati dalje se mogu koristiti za procenu, zaštitu i povećanje kvaliteta vode i sedimenta u ispitivanom području.

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ABSTRACT

LEAD IN WASTEWATER METAL PROCESSING INDUSTRY WESTERN SERBIAN

In The Republic of Serbia which has been developed metallurgy, metal industry of the site where they detect the presence of heavy metals in soil, water, and especially in the sediment, which acts as a seat and a potential source of metals in the aquatic environment. The frequency of time metal concentrations increase above the allowable limits, and through the food chain may have a negative impact on humans.

This paper aims to determine the concentration of heavy metals such as lead in water and sediments in western Serbia, Sevojno, which operate two large producers of semi-finished copper and aluminum. MAT LAB software package was used to define the distribution of lead between the solid and liquid phases in function of the distance from the spill of industrial waste water.

***Key words**: heavy metals, lead, water, sediment*

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Scientific paper

RADOJKA JONOVIĆ[1], LJILJANA AVRAMOVIĆ[1]
MILE BUGARIN[1], RADMILA MARKOVIĆ[1]
ZORAN STEVANOVIC[1], MARKO JONOVIĆ[2]

Originalni naučni rad
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Proces luženja bakra iz rudarskog otpada sa otpadnim vodama

Rudarstvo je, kao glavna industrijska grana u Boru, tokom proteklih sto godina, imalo ogroman uticaj na životnu okolinu samog grada, ali i šireg regiona. Kao posledica rudarenja nastaju kisele rudničke otpadne voda koje se generišu iz kopovskih raskrivki i flotacijskih jalovišta. Ove kisele rudničke vode slivaju se ka akumulaciji „Robule" i Borskoj reci, koja pripada slivu reke Timok, i zajedno sa čvrstim otpadom predstavljaju opasnost po životnu okolinu regiona, dok raskrivka i jalovište predstavljaju "rudnik na otvorenom" u kome se nalazi oko 148.000 t bakra. Tema ovog rada je mogućnost integralnog tretmana otpadnih rudničkih voda i vanbilansnih delova ležišta. Urađena je detaljna fizičko-hemijska karakterizacija rudničkih otpadnih voda iz akumulacije „Robule", karakterizacija raskrivke deponovane na „Oštreljskom" planiru kao i karakterizacija flotacijskog jalovišta. Izvršena su ispitivanja procesa luženja bakra iz uzorka raskrivke sa kiselim otpadnim vodama i postignut stepen izluženja od 67 % bakra, kao i luženja bakra iz uzoraka jalovine sa stepenom izluženja bakra od 76 %.

Ključne riječi: *bakar, luženje, rudarski otpad,otpadne vode*

UVOD

Najčešće primenjivan postupak u svetu za valorizaciju bakra iz vanbilansnih rudničkih materijala je hidrometalurški postupak. Postupak se sastoji od sledećih faza: usitnjavanje, luženje, solventna ekstrakcija i elektrolitičko izdvajanje bakra. Hidrometalurški postupak je primenjen u zemljama (SAD, Čile, Australija, i Peru) koje imaju lako dostupne vanbilansne depozite sa niskim sadržajem bakra i sa više oksidnih oblika [1, 2].

Količina odložene kopovske raskrivke na „Oštreljskom" planiru procenjuje se na $56x10^6$t, sa srednjim sadržajem ukupnog bakra od 0.21%, i 27 $x10^6$t jalovine odložene na napuštenom borskom flotacijskom jalovištu. Prisutna količina bakra u navedenim vanbilansnim sirovinama od oko $148x10^3$t bakra. Ova količina bakra ne može da se valorizuje klasičnim pirometalurškim postupcima već zahteva istraživanja u cilju primene hidrometalurških postupaka. Bakar prisutan u vanbilansnim sirovinama predstavlja značajan ekonomski resurs ukoliko se valorizuje na adekvatan način uz prihvatljivu i održivu tehnologiju. U suprotnom, predstavlja veliki generator zagađenih rudničkih voda koje se direktno ulivaju u sliv Borske reke, pri čemu se znatno utiče i na kvalitet vode nizvodno do Timoka, i dalje sve do Dunava.

U radu je data fizičko-hemijska karakterizacija rudničkih otpadnih voda iz akumulacije „Robule", raskrivke deponovane na Oštreljskom planiru kao i flotacijskog jalovišta. Formirani su tehnološki uzorci za laboratorijska istraživanja procesa luženja bakra. Ispitani su parametri perkolacionog i agitacionog luženja bakra. Raskrivka sa „Oštreljskog planira" tretirana je postupkom perkolacionog luženja simuliranjem uslova koji vladaju na terenu. Ispitani su parametri koji utiču na povećanje bakra u lužnim rastvorima. Flotacijska jalovina tretirana je postupkom agitacionog luženja. Definisani su parametri perkolacionog i agitacionog luženja kopovske raskrivke i flotacijske jalovine sa rudničkim otpadnim vodama iz akumulacije „Robule".

EKSPERIMENTALNA ISTRAŽIVANJA I DISKUSIJA REZULTATA

Za fizičko-hemijsku karakterizaciju uzorkovano je flotacijsko jalovište u Boru sa 2 profila i ukupno 4 mesta (oko 50 kg jalovine), dok je sa „Oštreljskog" planira formiran tehnološki uzorak u ukupnoj količini od 250 kg. Granulometrijski sastav kompozitnog uzorka flotacijske jalovine flotacijskog jalovišta u Boru prikazan je u tabeli 1.

U tabeli 2 prikazan je granulometrijski sastav tehnološkog uzorka sa „Oštreljskog" planira nakon drobljenja uzorka do krupnoće 100% - 12.5 mm.

Adrese autora: [1]Institut za rudarstvo i metalurgiju Bor, Zeleni bulevar 35, 19210 Bor, [2]TMF, Univerzitet u Beogradu, Karnegijeva 4

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Tabela 1 - Granulometrijski sastav kompozitnog uzorka - polje 1 napušteno Borsko jalovište

Otvor sita, mm	+0.295	+0.208	+0.147	+0.104	+0.074	-0.074 + 0
Masa uzorka, %	1.3	4.6	7.9	10.1	8.2	67.9

Tabela 2 - Granulometrijski sastav izdrobljenog tehnološkog uzorka

Otvor sita, mm	-12.5+10	+8.0	+5.0	+3.3	+1.1	-1.1 + 0
Masa uzorka, %	18.5	19.1	24.5	12.3	19.4	6.2

U tabeli 3 prikazan je sadržaj ukupnog i oksidnog bakra i gvožđa u kompozitnom uzorku flotacijske jalovine sa borskog flotacijskog jalovišta kao i u formiranom tehnološkom uzorku sa „Oštreljskog“ planira.

Tabela 3 - Sadržaj ukupnog i oksidnog bakra i gvožđa u uzorcima

Uzorci	Cu-uk	Cu-ox	Fe
Tehnološki uzorak - Oštreljski planir,%	0.23	0.12	7.21
Napušteno Borsko flotacijsko jalovište, % (površinski sloj dubine do 1 m)	0.034	0.0029	6.85
Napušteno Borsko flotacijsko jalovište, % (slojevi od 3 do 20 m dubine)	0.43	0.18	16.56

Veoma nizak sadržaj ukupnog, a pre svega oksidnog bakra u površinskom sloju borskog flotacijskog jalovišta (debljina površinskog sloja od 2 do 3 m) pokazuje kakav je efekat kiselih kiša na rastvaranje prisutnih komponenata u jalovini, pri čemu generisane kisele rudničke vode sa sobom nose jone rastvorenih teških metala. To prouzrokuje kontaminaciju površinskih i podzemnih vodotokova. Laboratorijska ispitivanja procesa luženja vršena su na uzorcima iz dubljih slojeva borskog flotacijskog jalovišta u kome je prosečni sardžaj ukupnog bakra 0.44%, pri čemu je učešće oksidnog bakra do 60%.

Rudnička voda iz akumulacije „Robule“ ima sledeći hemijski sastav:

Cu-69,10 mg/dm^3; Pb <0.05 mg/dm^3; Zn-26.30 mg/dm^3; Cd-0.12 mg/dm^3;

Ni-0.34 mg/dm^3; Cr<0.02 mg/dm^3; Se<0.020 mg/dm^3; As<0.010 mg/dm^3;

Fe-739.00 mg/dm^3; susp. mater.-12.0 mg/dm^3; SO_4^{2-} -8243,10 mg/dm^3;

Sadržaj metala je iznad zakonom propisanih maksimalno dozvoljenih vrednosti, a izmerena pH vrednost od 3.5 ukazuje na kiseli karakter otpadne vode iz akumulacije „Robule“.

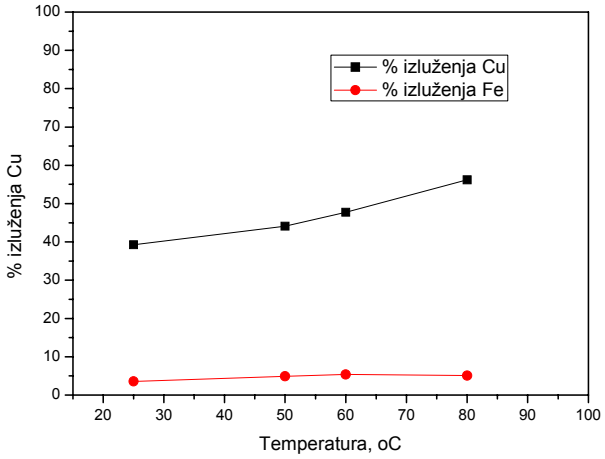
Formirani kompozitni uzorak sa „Oštreljskog“ planira tretiran je postupkom perkolacionog luženja. Kao lužni rastvor korišćena je otpadna rudnička voda iz akumulacije “Robule” nakon korekcije pH vrednosti sa sumpornom kiselinom. Eksperimenti luženja izvedeni su na opremi laboratorijskog tipa koja se sastoji od dve kolone za perkolaciono luženje izrađene od pleksiglasa dimenzija: DxL= 90 x 900mm, DxL=150x900mm, i prateće opreme. Nakon eksperimentalnog istraživanja definisani su optimalni parametri luženja na uzorku od 8 kg:

- Lužni rastvor, “Robule” voda, pH 1,5
- Č: T=1:1,5
- Vreme luženja: 5 dana (I ciklus) + 5 dana (II ciklus)
- Vreme prirodne oksidacije: 5 dana (između ciklusa)
- Protok: 300 ml/h

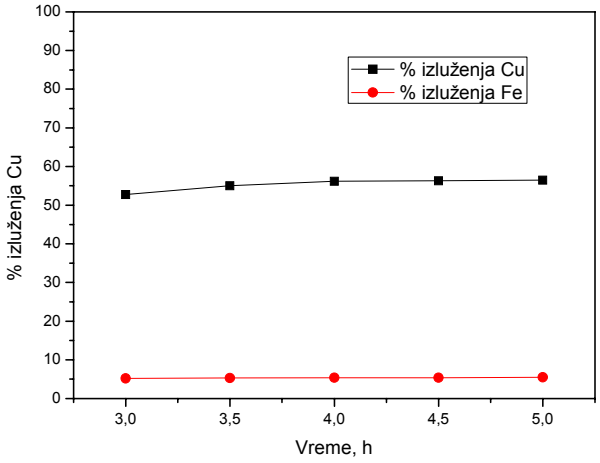
Nakon procesa luženja postignut je stepen izluženja bakra od 67 % Cu, a sadržaj bakra u rastvoru od 4,16 g/l predstavlja polazni rastvor za SX-EW proces (solventna ekstrakcija-elektrolitičko izdvajanje bakra).

Urađen je TCLP test (Toxicity Characteristic Leaching Procedure) uzorka Oštreljskog planira dobijenog nakon perkolacionog luženja. Rezultati testa ukazuju na mogućnost bezbednog odlaganja čvrstog ostatka nakon luženja po životnu okolinu.

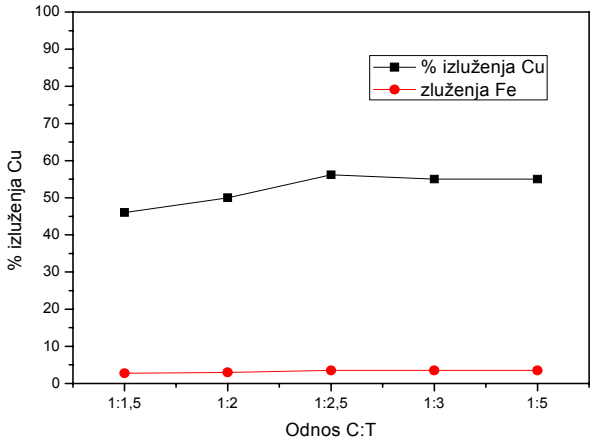
Uzorci sa flotacijskog jalovišta su tretirani postupkom agitacionog luženja. Opiti su izvedeni u staklenom laboratorijskom reaktoru sa mehaničkim mešanjem. Rezultati luženja uzoraka sa starog flotacijskog jalovišta, prikazani su na slikama 1,2 i 3.



Slika 1 - Zavisnost stepena izluženja bakra od temperature



Slika 2 - Zavisnost stepena izluženja bakra od vremena luženja



Slika 3 - Zavisnost stepena izluženja bakra od odnosa Č:T

Postignut je stepen izluženja bakra od 61% pri temperaturi od 90°C, vremenu 3 h i odnosu Č:T=1:2,5. U prisustvu oksidansa, ferisulfata, postignut je veći stepen izluženja bakra od 76 %. Rastvori posle luženja sa sadržajem bakra do 1.5 g/dm^3 pogodni su za SX-EW proces.

ZAKLJUČAK

Nakon procesa luženja jalovine i raskrivke dobijen je obogaćeni bakronosni rastvor povoljnih kvalitativno-kvantitativnih karakteristika za proces SX-EW. Dalja istraživanja vršiće se u pravcu definisanja uslova SX-EW i dobijanja bakra komercijalnog kvaliteta. Na taj način bi se prikupljanjem rudničkih voda, njihovoj recirkulaciji u procesu kontrolisanog luženja rudarskog otpada pored ekonomskog postigao i ekološki efekat.

Zahvalnost

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ABSTRACT

COPPER LEACHING PROCESS FROM THE OVERBURDEN MATERIALS WITH WASTE WATER

Mining, as a major industry in Bor, over the past hundred years, had an enormous impact on the environment of the city itself, but also for the region. Arise as a result of mining acid mine waste water that is generated from flotation tailings and overburden. These acidic mine waters flowing toward the accumulation of "Robule" and the Bor river, which belongs to the Timok River, and along with solid waste pose a threat to the environment of the region, while the overburden and tailings are "open mine" which is about 148,000 t copper. The theme of this work is the possibility of an integrated waste treatment of mine waters and off parts of the deposit. Underwent detailed physical and chemical characterization of mining waste water from reservoirs "Robule," characterization of overburden deposited in "Oštrelj" plans and characterization of flotation tailings. The studies of leaching of copper from overburden samples with acidic waste water and reached the level of 67% leaching of copper and copper leaching from overburden samples with levels of copper leaching by 76%

Key words: *copper, leacning, overburden materiaals, waste water*

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Scientific paper

ŽELJKO STOJANOVIĆ
SANJA STANISAVLJEV
SNEŽANA RADOSAVLJEVIĆ

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Primena postupka vanadiranja u funkciji produženja radnog veka delova

U radu je dat pregled literaturnih podataka o istraživanju uticaja sloja vanadijum karbida, formiranog termo-reaktivnom difuzijom na površini alatnih čelika i kalupa za livenje i kovanje. U zapadnoj naučno-stručnoj literaturi (USA i Japan) postoji dosta informacija o vanadiranim slojevima dobijenim na alatnim čelicima i kalupima, dok je u našim naučno-stručnim krugovima, i pored superiornih osobina koje sloj pruža u procesu eksploatacije, postupak ostao gotovo nepoznat. Kako je postupak vanadiranja još uvek uglavnom nepoznat našoj široj naučno-stručnoj javnosti, u radu su sistematizovana znanja i opisane osnovne zakonitosti, prednosti i nedostaci postupka vanadiranja, sa osvrtom na karakteristične primere njegove primene na sadašnjem nivou znanja. S obzirom da ekstremno tvrdi sloj formiran postupkom vanadiranja poseduje odlične osobine, od kojih treba izdvojiti: veoma visoku otpornost prema mehanizmu abrazije i athezije, dobre tribo-hemijske osobine i vrlo nizak koeficijent trenja, autori smatraju da će podaci u ovom radu poslužiti kao korisna referenca za proširenje primene ovog postupka i u našim proizvodnim pogonima, kao uobičajenog postupka obrade.

Ključne reči: *vanadiranje, abrazija, athezija, tribo-korozija, alatni čelici, kalupi*

1. UVOD

Životni vek mašinskih elemenata i alata je bitan faktor u proizvodnji, posebno u veliko serijskoj i sofisticiranoj proizvodnji. Tokom godina činjeni su značajni napori za povećanje otpornosti na habanje i radnog veka korišćenjem različitih tehnoloških postupaka. Pokušaji su činjeni u pravcu primene kvalitetnijih materijala i adekvatne termičke obrade, i u smeru primene različitih postupaka modifikacije i presvlačenja površina u cilju povećanja trajnosti. Površinski slojevi se razlikuju od tretiranog osnovnog materijala u pogledu hemijskog sastava, mikrostrukture, kristalne rešetke i ostalih fizičkih i hemijskih karakteristika koje rezultiraju različitim svojstvima u eksploataciji.

Već izvesno vreme, uporedo sa PVD postupcima, primenjuju se postupci difuzionog oblaganja. Ovi postupci imaju svoje poreklo u *Toyota Diffusion Process* i nekoliko patenata, i imaju neke tehničke i ekonomske prednosti nad PVD postupcima, ali i neka ograničenja u primeni [1]. Prednosti postupka difuzionog oblaganja su te da oni stvaraju slojeve veće dubine i veće tvrdoće, kao i superiorne tribološke karakteristike, posebno abraziju i tribokoroziju. Mana ili ograničavajući faktor ovih postupaka je primena na delovima sa bliskim tolerancijama dimenzija. Kako se postupci vrše na visokim temperaturama, izazivajući promene u mikrostrukturi osnovnog metala, posledica je promena dimenzija i stvaranje sloja na površini mašinskog elementa. Na taj način, promene dimenzija su veće nego kod primene PVD postupka.

Adresa autora: Partizanska 34/e, 23208 Elemir
Rad primljen: 20. 01. 2013

Osnovna razlika između difuzionog formiranja karbidnog sloja i postupka presvlačenja je u tome, da je kod difuzionog formiranja karbidnih slojeva supstrat najvažniji faktor koji utiče na formiranje karbidnog sloja.

Termalna **d**ifuzija (TD) ili **t**ermo**r**eaktivni **d**ifuzioni (TRD) postupak oblaganja razvijen je od strane *Toyota Motor Corporations Central R & D Laboratories* u Japanu, posebno da reši problem habanja. [2] TD postupak proizvodi gladak, tanak i neporozan sloj ekstremno tvrdog vanadijum karbida na površini čelika. Glavna prednost TD postupka je ta, da je za razliku od drugih konvencionalnih presvlaka koje su samo deponovane na površinu, TD obloga metalurški difuziono vezana na čeličnom supstratu.

Ovo difuziono vezivanje (prijanjanje) pruža neuporedivu otpornost prema ljuštenju i atheziji TD obloge. [2] Nije bitno koliko tvrd ili gladak sloj može biti, ako ne ostaje na alatu, to nije od pomoći. To je ključ uspeha TD obloge u odnosu na ostale tvrde obloge.

Cilj ovog rada je suštinski doprinos interpretaciji i boljem razumevanju postupka vanadiranja, kao i afirmacija postupka, sa ciljem proširenja njegove primene u industriji radi proizvodnje fabrikata visokog kvaliteta.

2. OPŠTE O TERMOREAKTIVNOM FORMIRANJU KARBIDNIH SLOJEVA

Difuziono formiran karbidni sloj na površini čelika ima rastuću primenu u industriji. Ovo je usled činjenice, da su troškovi investicija u potrebnu opremu relativno niski, i visoke otpornosti na abraziju

i tribokoroziju. [1] Postupak se najčešće sprovodi u sonom kupatilu odgovarajućeg sastava, uz dodatak jednog od karbidoobrazujućih elemenata (V, Cr, Nb, W, Ti). Karbidoobrazujući element (npr. vanadijum, V) reaguje na površini čelika sa ugljenikom (C), koji je na visokim temperaturama procesa atomski rastvoren u austenitu, formirajući veoma stabilan V_8C_7 karbid, ili neki drugi karbid (NbC, Cr_7C_3, WC, TiC). Karbidni sloj raste na površini u procesu difuzije ugljenika iz površinskog sloja čelika prema karbidnom sloju, i kroz njega na novoformiranu površinu gde reaguje sa karbidoobrazujućim elementom. Istovremeno, mala količina karbidoobrazujućeg elementa difuzuje kroz formirani karbidni sloj u površinski sloj čelika. Pored visoke temperature, stopa formiranja karbidnog sloja u velikoj meri je pod uticajem hemijskog sastava čelika.

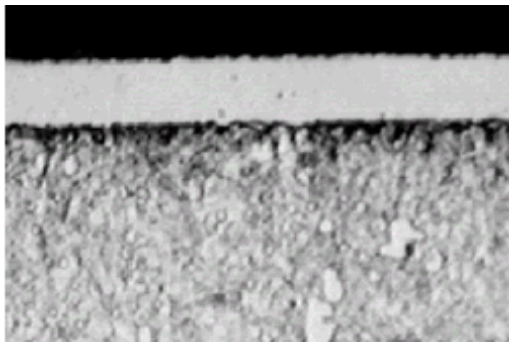
TD postupak je veoma sličan konvencionalnim postupcima toplotnog tretiranja. Aktuelni postupci termodifuzije uključuju potpuno uranjanje delova u rastopljeno sono kupatilo, uglavnom na temperaturama između 950 i 1050 °C. [2] Soli TD postupka su specijalno formulisane i imaju sirup kao konzistenciju, za razliku od konvencionalnih soli za termičku obradu. Ova visokotemperaturna reakcija stvara ekstremno visoku čvrstoću vezivanja. TD oblaganje, metodom u sonom kupatilu, znači da se reakcija obloge javlja gde god so dođe u kontakt sa čelikom. To znači da je oblaganje složenijih dimenzija lako moguće usled potpunog potapanja delova u sonom kupatilu. Takođe, visoka gustina soli pomaže razmeštaju težine alata putem tzv. Arhimedovog principa, što na visokim temperaturama smanjuje distorziju alata pod njihovom sopstvenom težinom [2].

Debljina TD obloge može biti precizno kontrolisana preko prilagođavanja vremena obrade, temperature kupatila i vrste čelika. Delovi, takođe, mogu biti ponovo obloženi. Ponovno oblaganje zavisi od primene, a nakon otprilike 4 ili 5 ponovnih oblaganja potreban je nov alat.

3. PRIMENA NA RAZLIČITIM MATERIJALIMA

Formirani slojevi su bez pora, kao što je prikazano na slici 1, koja prikazuje sloj vanadijum karbida formiran na alatnom čeliku. Iako su različite granične linije jasno uočljive između sloja i osnovnog materijala, visoka temperatura postupka ubrzava međusobnu difuziju atoma između sloja i osnovnog materijala, obezbeđujući tako veliku snagu vezivanja, tako da se sloj neće ljuštiti u teškim eksploatacionim uslovima, kao što je hladno kovanje [3].

Ovaj postupak obezbeđuje sloj koji se sastoji samo od karbida, bez vezivne faze, a to slabo smanjuje žilavost supstrata. [3] Shodno tome, čelici obloženi karbidom pokazuju površinu karakterističnih osobina svojstvenih karbidima, kao što je visoka tvrdoća, odlična otpornost prema habanju, otpornost prema oksidaciji i koroziji, kao i unutrašnju jačinu svojstvenu osnovnom materijalu.



Slika 1 - Vanadirana površina alatnog čelika [3]

Vanadijum karbid, V_8C_7 ima kubnu rešetku visoke tvrdoće (3200-3800 HV) sa veoma dobrim tribološkim svojstvima. [1] Otpornost prema habanju je veoma visoka zato što je sloj vanadijum karbida tvrđi od većine tvrdih mineralnih materijala. Otpornost prema tribokorozivnoj atheziji je veoma visoka, pošto je sloj veoma stabilan i hemijski otporan na agresivna sredstva (NaOH, HCL...). Visoka tvrdoća karbidnog sloja ukazuje na to da je sloj krt i samim tim je smanjena otpornost prema zamoru površine.

Jak metalurški spoj između karbidnog sloja i osnovnog materijala (čeličnog supstrata) daje dobru athezivnost površinskog sloja za osnovni materijal. Čak se mogu dobiti i znatno veće debljine tvrdih površinskih slojeva, od 5 do 20 μm, u poređenju sa debljinom PVD slojeva, od 1 do 3 μm.

Yang i saradnici [4] istraživali su mikrostrukturu i osobine površinskog sloja $Cr_{12}MoV$ čelika, tretiranog postupkom vanadiranja u sonom kupatilu. Rezultati istraživanja su pokazali da je, nakon tretiranja vanadiranjem u sonom kupatilu na temperaturi od 950 °C u trajanju od 5 h zatim kaljenja u ulju, i starenja na temperaturi od 180 °C u trajanju od 2 h, $Cr_{12}MoV$ čelik dobio površinski sloj čija je debljina oko 11,4 μm. Sloj se uglavnom sastojao od vanadijum karbida a njegova debljina i mikrostruktura su jednolike i kompaktne. U isto vreme, dobijeni sloj pokazao je izuzetno visoku površinsku tvrdoću od 2586 HV. Otpornost prema habanju čelika $Cr_{12}MoV$ drastično je poboljšana. Pored toga, rezultati istraživanja su pokazali da nije primećen efekat vanadiranja na hrapavost površine $Cr_{12}MoV$ čelika.

Wang [5] je ispitivao ponašanje habanja Cr_{12} MoV, 65 Nb i GCr15 čelika obloženih sa vanadijum karbidom i kaljenih bez tog sloja. Ispitivanja na habanje vršena su korišćenjem aparature pinondisc pod uslovima suvog klizanja. Mikrostruktura sloja je

određena korišćenjem optičke mikroskopije i rendgenske difrakcije (XRD). Površinske i podpovršinske promene koje su se desile tokom habanja posmatrane su skenirajućom elektronskom mikrspijom (SEM). Otpornost na habanje obloženog Cr_{12} MoV čelika poređena je sa otpornošću na habanje obloženog 65 Nb čelika. Vanadirani Cr_{12}MoV i 65 Nb čelici pokazali su od 9 do 30 puta nižu stopu habanja od neobloženih čelika. Stopa habanja vanadiranih Cr_{12}MoV, 65 Nb i GCr15 čelika povećana je sa povećanjem opterećenja. Potvrđeno je da habanje vanadijum karbida zavisi od karakteristika sloja i snage vezivanja osnovnog materijala i sloja. Visoka otpornost na habanje vanadiranih čelika pripisuje se visokoj tvrdoći sloja vanadijum karbida.

Horvath i Perry [6] vanadirali su komplet ugljeničnih čelika (0,15 do 1,45 % C) hemijskom depozicijom iz parne faze sa ciljem proizvodnje sloja vanadijum karbida. Karbid je bio veoma blizu stalnog sastava ($VC_{0,84}$-$VC_{0,89}$ i mikrotvrdoće 2630 $HV_{0,025}$), nezavisno od sadržaja ugljenika u čeliku. Mikrostruktura karbida je bila sitnozrnasta bez očigledne preferencijalne orijentacije. Međusloj cementita formiran je ispod karbida na čelicima koji su sadržali više od 1,4 % C.

Na primer, na 800 °C tvrdoća sloja vanadijum karbida opada na vrednost od oko 900 HV, koja je još uvek iznad tvrdoće ostalih tretiranih površina. [9] Kako se sloj vanadijum karbida hladi na sobnoj temperaturi, tvrdoća se vraća na vrednost blizu prvobitne tvrdoće od 3200 HV. [9] Njegova sposobnost da održi svoju tvrdoću pod visokim temperaturama dozvoljava mu da dobro obavlja opracije livenja.

Postupak je, takođe, efikasan u operacijama livenja, pošto je tvrdoća vanadijum karbida veća od tvrdoće abraziva, kao što je Al_2O_3, koji se nalazi u glavama za honovanje i brusnim papirima koji se koriste za poliranje jezgara i valjčića (igala). Ovo omogućava da se lako ukloni aluminijum koji se mehanički zalepi za valjčić, bez značajnih oštećenja ili promena dimenzije valjčića. Vreme poliranja i rezultantno habanje valjčića znatno su smanjeni. [7] Drugi razlog njegove efikasnosti u operacijama livenja je taj što vanadijum karbid hemijski ne reaguje sa aluminijumom. On štiti kalupe od agresivne prirode aluminijuma i sprečava hemijske interakcije između legure za livenje i kalupa. Zbog toga su korozija i spajanje smanjeni. [7] U Japanu, postupak se pokazao posebno efikasnim kod konvencionalnih čeličnih kalupa, kao što je H13, alatni čelik obično korišćen za izradu jezgara i jezgrenih valjčića. Štete prouzrokovane livenjem u kalupima značajno su smanjene.

Aghaie-Khafri i Fazlalipour [8] izvršili su ter-moreaktivno difuziono oblaganje vanadijum karbidom DIN 1.2367 čelika za kalupe, u mešavini praha koja se sastojala od ferovanadijuma, amonijum hlorida, glinice i naftalina, na temperaturama od 950, 1050 i 1150 °C u trajanju od 1 do 5 h. Karbidni slojevi su karakterisani mikrostrukturnom analizom, rendgenskom difrakcijom (XRD), analizom mikrotvrdoće i hemijskom analizom. U zavisnosti od vremena i temperature procesa debljina sloja vanadijum karbida formiranog na osnovnom materijalu se kretala u rasponu od 2,3 do 23,2 μm. Tvrdoća slojeva vanadijum karbida bila je oko 2487 HV. Ispitivanje suvog habanja netretiranog i tretiranog DIN 1.2367 čelika za kalupe vršena je na aparaturi pinondisc (valjčić po disku) pri kliznoj brzini od 0,13 m/s. Rezultati su pokazali superiorne karakteristike pri habanju obloženih uzoraka. Takođe je proučavana kinetika vanadijum karbidne obloge ostvarene *pack*-metodom i aktivaciona energija za termoreaktivni difuzioni proces je procenjena na 173,2 kj/mol.

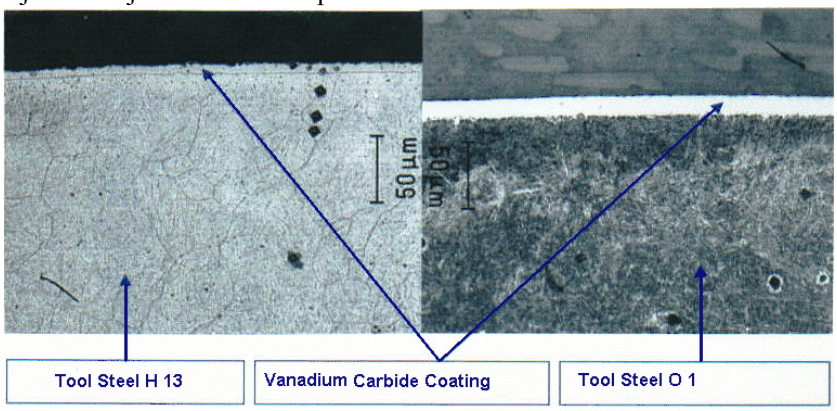
Liu je sa saradnicima [9] vanadirao čelik za rad u hladnom stanju, Cr_{12}MoV. Proučavali su strukturu obloge i snagu vezivanja. Osim toga, vršeno je poređenje eksperimenata otpornosti prema habanju između obloge i osnovnog materijala, a na osnovu rezultata eksperimenta uočeno je opadanje otpornosti vanadiranog sloja prema mehanizmu habanja. Rezultati su pokazali da je obloga vanadijum karbida gusta, sa finozrnastom strukturom i visokom snagom vezivanja. Ove pojave pomažu poboljšanju otpornosti obloge prema habanju. Poređenje performansi habanja obloge i osnovnog materijala pokazalo je da vanadirani površinski sloj može značajno poboljšati otpornost osnovnog materijala prema habanju. Koeficijent trenja je smanjen sa 0,48 na 0,33 a gubitak mase pri habanju je smanjen za 95 %.

Fazluddin i saradnici [10] oblagali su vanadijum karbidom ugljenični čelik EN9 i meki čelik. Uzorci su bili uronjeni u otopljeno sono kupatilo koje je sadržalo odgovarajuće karbido obrazujuće komponente na temperaturama u rasponu od 850 °C do 1100 °C. Uzorci su tretirani sa različitim vremenskim trajanjem u cilju dobijanja obloga različitih debljina. Korozivno ponašanje obloga vanadijum karbida ocenjivano je pomoću ubrzanih elektrohemijskih testova. Rezultati su pokazali da je otpornost karbidne obloge prema koroziji superiornija od netretiranih osnovnih legura.

AISI (American Iron and Steel Institute) 1040 čelici su srednje ugljenični čelici i jeftini materijali koji se široko koriste u proizvodnji jednostavnijih konstrukcija i mašinskih elemenata. Glavna ograničenja ovih materijala su njihova niska tvrdoća i loše karakteristike trenja i habanja. Iz tog razloga, činjeni su mnogi pokušaji poboljšanja njihove tvrdoće i triboloških svojstava.

U cilju poboljšanja mehaničkih osobina AISI 1040 čelika, Calik i saradnici [11] izveli su postupak vanadiranja u kupatilu sa rastopljenim boraksom (55 % Fe-V + 45 % boraksa) na temperaturi od 937 [°C] u trajanju od 4 h pod atmosferskim pritiskom. Ispitni uzorci su sa mešavinom zagrejani u elektrootpornoj peći. Nakon procesa, uzorci su uklonjeni iz peći, ohlađeni na vazduhu, odrezani sa jedne strane, metalografski pripremljeni brušenjem sa brusnim papirom veličine zrna od 1200 i polirani korišćenjem aluminijumske paste prečnika zrna 3 μm. Pre ispitivanja, polirani uzorci su nagriženi sa 4 % Nitalom. Morfologija i debljina sloja vanadijum karbida su posmatrani korišćenjem optičkog mikroskopa. Prisustvo karbida na površini vanadijum karbidne obloge utvrđen je korišćenjem difraktometra, a tvrdoća obloge vanadijum karbida određena je korišćenjem Vickersovog aparata sa opterećenjem od 100 g. Efektivna debljina difuzionog sloja uzoraka vanadijum karbidne obloge bila je oko 5 μm, dok je mikrotvrdoća obloge vanadijum karbida bila oko 1650 HV.

Slika 2 pokazuje deponovani sloj vanadijum karbida na alatnom čeliku za rad u toplom stanjuAISI H13 i na alatnom čeliku za rad u hladnom stanju AISI O1.



Slika 2 - Deponovani (nanešeni) sloj vanadijum karbida na alatnom čeliku za rad u toplom stanju-AISI H13 i na alatnom čeliku za rad u hladnom stanju AISI O1. [12]

4. INDUSTRIJSKA PRIMENA

Tvrd i tanak površinski sloj često se primenjuje na čeliku za rad u hladnom stanju od kojeg je formiran kalup. Obloge su obično ekstremno tvrde keramike sa debljinom od samo nekoliko mikrona, ali su posebno efikasne u poboljšavanju performansi kalupa u otporu prema habanju, pucanju i atheziji. Samo nekoliko tipova obloga se efektivno koriste u industriji nerđajućeg čelika. [13]

U industriji hladnog kovanja, kvalitet proizvoda i cena kalupa za kovanje značajno utiču na performanse kalupa. Iz tog razloga, činjeno je mnogo napora za poboljšanje performansi kalupa. [3] Nažalost, ispitivanja sa različitim površinskim tretmanima nisu uspela da dobiju plodonosne rezultate u mnogim zemljama. U Japanskoj industriji hladnog kovanja, primetan uspeh ostvaren je zahvaljujući upotrebi dve vrste postupka oblaganja karbidom. Jedan od njih je sloj titanijum karbida (TiC) proizveden postupkom hemijske depozicije iz parne faze, koji je razvijen u zapadnoj nemačkoj, a zatim predstavljen u Japanu. Drugi je sloj vanadijum karbida proizveden upotrebom rastopljenog sonog kupatila. Ovaj proces, nazvan TD procesom, razvijen je od strane *Toyota Central Research and Development Labs of Japan*, i predstavljen različitim japanskim industrijama počevši od 1971. godine.

Prema profesoru Božidaru Matijeviću [14], postupak ima jedan nedostatak: parcijalno (delimično) razugljeničenje čelične površine ispod sloja karbida smanjuje tvrdoću i kapacitet opterećenja površine. Ovaj nedostatak je eliminisan od strane razvijenog i patentiranog dupleks postupka, prethodno uvođenje cementacije kako bi se sprečilo razugljeničenje i formirao otvrdnuti podsloj ispod sloja karbida. Novo razvijeni proces bi trebalo da doprinese širokoj primeni difuzione karbidne obloge u automobilskoj industriji.

Industrijska primena difuzionog vanadiranja u većem obimu, počela je u Japanu a zatim se proširila na ostale industrijski razvijene zemlje, usled odličnih triboloških svojstava površinskih slojeva vanadijum karbida. Primena vanadiranja na strukturne elemente i alate u različitim granama inženjerstva doprinosi značajnom povećanju njihove dugotrajnosti u eksploataciji. Primena vanadiranja u proizvodnji alata je proizvela odlične rezultate sa brojnim vrstama alata koji su u svojoj eksploataciji izloženi athezivnom i tribohemijskom mehanizmu habanja. Za abrazivni mehanizam habanja, vanadiranje je pravi izbor za tretiranje delova alata koji su izloženi habanju tvrdim abrazivnim česticama. Površinski sloj vanadijum karbida

produžava životni vek alata za nekoliko puta. Tipičan primer su delovi alata za sabijanje praha i delovi za ekstrudiranje.

Što se tiče athezivnog mehanizma habanja, vanadiranje se primenjuje na alate za procese oblikovanja metala, kao što su ekstruzija, kovanje i izvlačenje [1]. Koliko god je tribokorozivni mehanizam habanja u pitanju, vanadijum karbidni površinski sloj efikasno štiti alate koji se koriste u veoma agresivnim sredinama, čak i u HCL (hlorovodonična kiselina) i HNO_3 (azotna kiselina) [1]. Karbidni sloj se posebno koristi u reaktivnom spajanju za delove alata za livenje aluminijuma. Proces ima široki spektar primene, od pojila (hranitelja) do formiranja probojaca i kalupa, i pruža značajno poboljšanje performansi. Najveća industrijska primena su probojci za pirsing i ekstrudiranje [1]. Primena na različitim čelicima za kalupe takođe je evidentna. U mnogim slučajevima, vanadijum karbid je obložen na čeliku za kalupe i brzoreznom čeliku. Međutim, vanadijum karbid se takođe koristi na kovačkim kalupima od volfram karbida, sa značajnim unapređenjem veka trajanja kalupa. Postupak se, takođe, uspešno koristi u kovanju nerđajućeg čelika, na čelicima za kuglične ležajeve, i obojenim metalima. Kalupi koji se koriste kod toplog kovanja nerđajućeg čelika se, takođe, tretiraju ovim postupkom. Sloj vanadijum karbida se stalno primenjuje čak i za kalupe za toplo kovanje.

Povećanje životnog veka od nekoliko puta nije neuobičajeno, usled eliminacije problema habanja. Kao rezultat toga, u industriji su postignute velike uštede u potrošnji kalupa. Dodatne prednosti, u nekim slučajevima su bile daleko veće.

5. ZAKLJUČCI

U ovom poglavlju rada učinjen je pokušaj da se proceni značaj sprovedene analize i da se pronađe odgovarajuće mesto predočenih rešenja u okviru šireg pogleda na oblast termoreaktivnog postupka vanadiranja. Daje se osvrt na raspoložive podatke i sumira znanje iz oblasti inženjerstva površina. Objektivno sprovedeno istraživanje i analiza podataka pokazalo je osnovne zakonitosti i postavke, mogućnosti i ograničenja postupka vanadiranja.

Tekst ovog rada je imao za zadatak da objektivno pokaže prednosti i mane vanadijum karbidnog sloja. Sve u svemu, zaključeno je da prednosti vanadiranja nadmašuju njegove mane. Takođe je pokazana opravdanost izbora ove vrste rešenja za probleme abnormalnog trošenja delova u dodiru sa okolnom agresivnom sredinom. TD postupak znatno povećava otpornost prema habanju čeličnih kao i kalupa za hladno kovanje od volfram karbida, bez složene procedure i komplikovane opreme.

Na osnovu postavljenog cilja ovog rada i definisanog sadržaja istraživanja, kao i na osnovu obrađenih literaturnih podataka, može se zaključiti da difuziono formiranje tvrdih karbidnih slojeva nudi nove mogućnosti alatima za obradu, čime se značajno povećava otpornost prema habanju, omogućava duži životni vek u eksploataciji i shodno tome veća ekonomičnost primene. Iz navedenog, nedvosmisleno se može zaključiti da postupak vanadiranja predstavlja obećavajući metod za poboljšanje osobina različitih vrsta čelika pošto daje slojeve odličnog kvaliteta i ujednačenosti, visoke tvrdoće i dubine, glatke i kompaktne morfologije.

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ABSTRACT

APPLICATION PROCESS OF VANADIZING IN THE FUNCTION
OF EXTENSION WORKING LIFE OF PARTS

This paper gives review of literature data about the research influence of vanadium carbide layer formed by thermal-reactive diffusion on the surface of the tool steel and die for casting and forging. In western scientific and professional literature (USA and Japan) exists a lot of information about the vanadized layers obtained on tool steel and dies, while in our scientific and professional circles, and beside of the superior qualities whose layer provides in the process of exploitation, the process remained almost unknown. As the procedure of vanadizing still largely unknown our broader scientific and professional public, therefore, in the paper are systematized knowledge and described the basic principles, advantages and disadvantages of the procedure of vanadizing, with emphasis on specific examples of its application on current level of knowledge. Considering that the extremely hard layer formed by procedure of vanadizing possesses excellent properties, of which should be singled out: very high resistance to the abrasion and adhesion mechanism, good tribo-chemical properties and very low coefficient of friction, the authors belive that the data in this paper serve as a useful reference for the expansion of application this procedure in our manufacturing facilities, as the usual treatment process.

Key words: *vanadizing, abrasion, adhesion, tribo-corrosion, tool steel, dies*

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PETRONIJA J. JEVTIC

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Quality of wood surface finished with polyurethane coating

Comparative analysis of some properties of various wood coatings is performed in this paper. A special attention is paid to polyurethane coating and several different types were taken into consideration. Their properties are compared with those of nitrocellulose and acid curing coatings. Resistance to liquids, heat resistance and scratch resistance were examined.

Key words: *wood coatings, polyurethane coatings, resistance to liquids, heat resistance, scratch resistance*

1. INTRODUCTION

There are various types of coatings at disposal, for final wood products finishing. Which of them and when are to be applied, depends on economical an environmental factors, but first of all on the quality of finished surface. Economical factor, mostly, is not decisive, if high quality coatings are used. Environmental factors, in working and exploitation conditions, are still not dedisive, too, so that in the market conventional coatings are dominant, including nitrocellulose, polyurethane, acid curing and polyesther (classic) coatings. The most diffuse are polyurethane coatings [6] which are characterized by high quality. Disadventage of polyurethane systems for wood protection is relatively high content of organic solvents, making them environmentaly suitable. However, the use of polyurethane coatings has many adventages, such as: lower content of volatiles (comparing with nitrocellulose coatings), no reactive products are produced when applied, high resistance to mechanical action, hiogh resistance to chemicals, excellent cold-check resistance, possibility of finishing all substrate types, different decorative effects can be achieved.

Two-component polyurethanes cure through the reaction between isocyanate compound and polyol. By adequate formulation of various polymers (resins) and isocyanates, the coatings of excellent flexibility, hardness, abrasion resistance and resistance to chemicals are obtained.

On the polyol side, various hydrofunctional resins can be used. In the field of wood protection, the resins based on polyesters or polyesters modified with fatty acids. So far hardly used hydroxyfuncional polyacrilate types are ever more in use, while polyether types are not used for wood coatings. In many cases, adequate alkyd resins can be applied, where usually short chain oil types are used.

Author's address: Dr Petronija J. Jevtić, Graduate School of Applied Professional Studies,Vranje, Serbia

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The use of alkyd resins enables the coating production at reasonable price. Acrilate modified alkyds combine with aliphatic polyisocyanate. Adding copolymerizate such as cellulose esther, rapidly sandable polyurethane coatings are obtained. These are flesible, well resistant, light stable and solvent resistant. Coating of higher quality is obtained if, under two component coating on acrilate alkyd base, UV walz-base coat.

Abrasion resistance is particularly demanded for floor finishes. The investigations showed that abrasion resistance of polyurethane coatings cannot be achieved with no other classic system. It is hown that alkyd coatings after 100 cycles on Taber-abraser lost over 100 mg, acid curing - 50 mg, and polyurethane coatings from 10 to 25 mg. This is proved in service.

In this paper, resistance to liquids - alcohol, acetone, water, coffee, coca cola; heat resistance and scratch resistance were examined. Various types of polyurethane coatings are comparatively analyzed, and then, results were compared with those obtained for nitrocellulose and acid curing coatings - the other two types of the most used classic coatings. In this way, the possibility of applying these materials in various fields of exploitation is examined.

2. METHODS AND MATERIAL

For the investigation, the following types of coatings are used: nitrocellulose transparent opaque coatint, acid curing transparent glossy, polyurethane transparent opaque, polyurethane white glossy and polyurethane white opaque. The coatings are taken from different manufacturers. As substrate, MDF board of 4 mm thickness was used. The coating was applied by spraying in the system: three base coats and one top coat.

Resistance to liquids is tested according to the international and serbian standard ISO 4211 and SRPS D.E8.218. Filter paper of 25 mm diameter is immersed in the chosen test liquids and then placed on the tested area, where remained the following test periods: 10 s, 2 min, 1 h and 6 h. Test periods

correspond the real exploitation cases of liquid removal from the surface as shown in the Table 1.

Table 1 - Test periods

Period	Removal
10 s	Immediate removal
2 min	Immediate removal
10 min	After a short time
1 h	After a meal or similar
6 h	After work or other activity
16 h	As soon as possible next day
24 h	After one day
7 days	After one week
28 days	Long-term action

Chosen test liquids are: distilled water, ethanol, acetone, coca cola, coffee. These are chosen as the liquids in domestic use that can have considerable destructive action against coatings on wood surfaces, as some studies showed [2, 3, 4]. The changes on the surface are rated according to the above mentioned ISO and SRPS standards from 5 to 1 after cleaning and conditioning of the surface in the period of 24 h.

The heat resistance is determined according to Serbian standard (SRPS.D.E8.220). The method applies aluminium cup filled with mineral oil. The cup was heated and placed on the surface and left for 30 min. The applied temperatures are: 100°C, 130°C, 150°C, 180°C. 24 hours after removing the cup, the surfaces were examined under the light from different angles and any change or defect on the surface was determined.

Scratch resistance was determined by hardness test rod - Erichsen (model 318) with marking stylus 1 mm diameter. The spring tension is set with the help of the slider. The assesment of the resistance is made according to the standard DIN 68861/4. The criterion is the lowest applied force which produce the scratch.

3. RESULTS AND DISCUSSION

The results of deterimation of resitance to liquids are shown in Table 2, scratch resistance in Table 3 and heat resistance in Table 4.

Table 2 - Results of determination of resistance to liquids

Liquid	Coating	NC transp.	SH transp.	PU transp. (1)	PU transp. (2)	PU transp. (3)	PU pigmen. (1)	PU pigmen. (2)
	Test period	**Resistance to liquids (according to ISO)**						
Acetone	10 s	2	5	5	5	5	5	5
	2 min	2	5	5	4	4	4	4
	10 min	2	5	4	3	4	3	3
	1 h	1	4	3	3	3	3	3
	6 h	1	4	3	3	2	3	3
Alcohol	10 s	4	5	5	5	5	5	5
	2 min	4	5	5	4	4	5	5
	10 min	3	5	5	4	4	5	5
	1 h	3	5	5	4	4	5	5
	6 h	2	4	5	4	4	4	5
Distilled water	10 s	5	5	5	5	5	5	5
	2 min	5	5	5	5	5	5	5
	10 min	5	5	5	5	5	5	5
	1 h	5	5	5	5	5	5	5
	6 h	5	5	5	5	5	5	5
Coffee	10 s	5	5	5	5	5	5	5
	2 min	5	5	5	5	5	5	5
	10 min	5	5	5	5	5	5	5
	1 h	5	5	5	5	5	5	5
	6 h	5	5	5	5	5	5	5

Coca Cola	10 s	5	5	5	5	5	5	5
	2 min	5	5	5	5	5	5	5
	10 min	5	5	5	5	5	5	5
	1 h	5	5	5	5	5	5	5
	6 h	5	5	5	5	5	5	5

Table 3 - Results of scratch resistance determination

Coating	NC transp.	SH transp.	PU transp. (1)	PU transp. (2)	PU transp. (3)	PU pigmen. (1)	PU pigmen. (2)
Applied force (N)	8.0	12.0	11.0	13.0	13.0	11.0	14.0
Class (DIN)	A	A	A	A	A	A	A

The results shown in Table 2, showed that all applied types of coating are resistant to water, coffee and coca cola, both, in shor-term and long-term action, and when the liquid remains on the surface even 6 hours will not cause any damage or change on the surface. Nitrocellulose coating is much more sensitive to alcohol and acetone in opposite to acid curing and polyurethane coatings and the changes on the surface are noticed already after 10 s. Acetone even in short period causes the changes in the structure of the surface. Alcohol (ethanol) does not produce any visible chanhges, not even the change in lustre, on acid curing and polyurethane coatings, if removed in 2 minutes. In longer periods sliight marks with change in lustre remain on the surface of some polyurethanes. Acetone, on the same coating types, after 2 min causes the change of lustre, and after 10 min slightly visible marks, but without change in the structure of the coating. According to the alcohol action, acid curing and polyurethane coatings had similar behaviour, while according to the acetone action acid curing coating was more resistant.

According to DIN standard, all applied coatings: nitrocellulose, acid curing and polyurethane, regarding the scratch resistance, belong to, and so can be considered as high resistant coatings. If these coatings are compared, it could be noticed that nitrocellulose coatings give more resistant surfaces with similar values.

Regarding the heat action, polyurethane coatings show excellent resistance and higher one comparing with other types of coatings. Namely, the changes of surfaces are not induced neither by the temperature of 180°C. On acid curing coating, the changes are noticable only at 180°C, as slightly noticable marks. Slightly noticable marks, visible from various direction, on nitrocellulose coating are observed at temperature of 150°C, what still can be considered as good resistance.

Table 4 -Results of heat resistance determination

Applied temp. (°C)	NC transp.	SH transp.	PU transp. (1)	PU transp. (2)	PU transp. (3)	PU pigmen. (1)	PU pigmen. (2)
100	-	-	-	-	-	-	-
130	-	-	-	-	-	-	-
150	3	-	-	-	-	-	-
180	3	3	-	-	-	-	-

Results of some investigations [5] showed that, generally speaking, polyurethane coatings and decorative materials have similar behaviour under the heat action, i.e. that belong to the same resistance class and that can be used in the same exploitation conditions, where these resistances are decisive, such as for top boards. Both materials vary from medium resitant to high resistant. The highest resistance is observed at some laminates and some types of polyurethanes. PVC foils and decorative papers are less resistant.

Polyurethane coatings on alkyd base show good properties for use in furniture finishing. Sensibility to the action of some liquids - alcohol and acetone limits

them partly the use for horizontal surfaces such as kitchen tops and tables. According to [1] it comprises the furniture groupsfrom C to F. For groups A and B, i.e. for special uses such as kitchen tops, bathroom furniture, table tops, bars etc., decorative materials - laminates or coatings as polyurethane, wherin the resin (polyol) is modified and special catalyst is applied, are to be used [5, 7,8].

4. CONCLUSION

From the investigated coatings - nitrocellulose, acid curing and polyurethane, nitrocellulose coatings, according to heat resistance, scratch resistance and resistant to acetone and alcohol show the lowest values, while acid curing and polyurethane coatings show sufficient properties for use for furniture finishing. The analysis of various polyurethane coatings deriving from different producers indicates that they do not differ a lot. For special use, i.e. in extremely severe conditions, decorative materials - laminates or specially modified polyurethane coatings are to be applied. In other, normal exploitation conditions, polyurethanes on alkyd base give good results.

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IZVOD

KVALITET POVRŠINE DRVETA OBRAĐENOG POLIURETANSKIM PREMAZOM

U ovom radu ispitivana je otpornost na tečnosti - alkohol, aceton, vodu, kafu, Coca Colu; otpornost na toplotu i otpornost na grebanje. Komparativno su ispitivani različiti tipovi poliuretanskih premaza, a zatim su rezultati upoređeni sa rezultatima dobijenim za nitroceluloze i kiselinski-očvršćavajuće premaze - druga dva tipa najčešće korišćenih klasičnih premaza. Na ovaj način je ispitana mogućnost primene ovih materijala u različitim oblastima eksploatacije. Nitrocelulozni premazi pokazali su najniže vrednosti, dok su kiselinski-očvršćavajući i poliuretanski premazi pokazali zadovoljavajuća svojstva za upotrebu za obradu nameštaja.

***Ključne reči**: premazi za drvo, poliuretanski premazi, otpornost na tečnosti, otpornost na toplotu, otpornost na grebanje*

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Scientific paper

DRAGAN UGRINOV
ALEKSANDER STOJANOV

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Zakonodavni okvir i nadležnosti u oblasti upravljanja medicinskim otpadom

Medicinski otpad u zdravstvenim ustanovama u Republici Srbiji se stvara u neravnomernim količinama, u zavisnosti od tipa ustanove, broja kreveta, vrste i prirode oboljelja i stanja koje se zbrinjavaju, kao i vrste i kvaliteta usluga koje se u ustanovama pružaju. Medicinski otpad se smatra potencijalno opasnim otpadom za ljudsko zdravlje i upravljanje otpadom se razlikuje od zemlje do zemlje, zavisno do stepena razvijenosti, geografskih uslova i kulture. Svaka zemlja može imati svoje Pravilnike i vodiče za upravljanje medicinskim otpadom, ali se većina zasniva na dokumentima koja je dala Svetska zdravstvena organizacija (SZO). U poslednjoj deceniji se intenzivno radi na rešavanju ovog problema u svetu.

***Ključne reči** : medicinski otpad, zakon, pravilnik, upravljanje*

1. UVOD

Medicinski otpad predstavlja sav onaj otpad koji je nastao u zdravstvenim ustanovama, a vezan je za obavljanje zdravstvene delatnosti, bez obzira da li se radi o primarnoj,sekundarnoj ili tercijalnoj zdravstvenoj zaštiti ili veterinarskoj medicini. A takodje je vezan za dijagnostiku ili lečenje oboljenja, stanja i povreda kao i naučno istraživačke delatnost u humanoj ili veterinarskoj medicini i farmaciji.

Odlaganje različitih kategorija medicinskog otpada u Srbiji se do 2008. godine obavljalo na različite načine u različitim zdravstvenim ustanovama. Ministarstvo zdravlja Republike Srbije je 2007. godine započelo specifične aktivnosti na uvođenju uniformnog sistema upravljanja medicinskim otpadom, a posebno infektivnog medicinskog otpada, kao kategorijom opasnog otpada.U tom duhu intenzivno se radilo na definisanju Zakonske procedure u ovoj oblasti.

2. OPŠTI DEO

2.1. Definicija i klasifikacija medicinskog otpada

Medicinski otpad se definiše kao sav otpad koji se generiše u zdravstvenim institucijama, istraživačkim ustanovama i laboratorijama i predstavlja heterogenu mešavinu otpada koji ima karakteristike komunalnog i visoko rizičnog/opasnog otpada.

Klasifikacija medicinskog otpada u Evropskoj Uniji određena je Evropskim katalogom otpada [4] (Tabela 1). Ovaj katalog je inače u primeni u Republici Srbiji od 2005. godine a njegove kategorije otpada preuzete su objavljivanjem domaćeg kataloga otpada [5], s malim razlikama.

Tabela 1 - Klasifikacija medicinskog otpada prema EU direktivi 75/442/EEC

18 00 00	Otpad iz zdravstvene zaštite ljudi i životinja i/ili s tim povezanog istraživanja (isključujući otpad iz kuhinja i restorana koji ne potiče od neposredne zdravstvene zaštite).
18 01 00	Otpad iz porodilišta, dijagnostike, tretmana ili prevencije bolesti ljudi
18 01 01	Oštri instrumenti (skalpeli, lancete, igle, makaze i sl.)
18 01 02	Delovi tela i organi uključujući i vrećice s krvlju i produktima krvi
18 01 03	Ostali otpad čije sakupljanje i odlaganje podleže posebnim zahtevima radi sprečavanja nastanka infekcije
18 01 04	Otpad čije sakupljanje i odlaganje ne podleže posebnim zahtevima radi sprečavanja infekcije (napr. zavoji, gipsevi, posteljina, odeća koja se baca, pelene)
18 01 06	Hemikalije koje se sastoje ili sadrže opasne materijale
18 01 07	Hemikalije drugačije od navedenih u 18 01 06
18 01 08	Citotoksični i citostatični lekovi
18 01 09	Lekovi drugačiji od navedenih u 18 01 08
18 01 10	Otpadni amalgam iz stomatologije

Medicinski otpad obuhvata sledeće kategorije visoko rizičnog – opasnog otpada [6]:

- **Infektivni otpad** – otpad koji sadrži patogene biološke agense koji zbog svog tipa, koncentracije ili broja mogu izazvati bolesti kod ljudi koji su im izloženi:

  - kulture i rastvori infektivnih agenasa nastalih u laboratoriji;

Adrese autora: [1]Zavod za javno zdravlje, Pančevo, [2]Direkcija za građevinsko zemljište i izgradnju Beograd, J.P., Beograd

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- otpad koji je rezultat hirurških intervencija i autopsija na pacijentima sa infekti-vnim bolestima (tkiva, materijali ili oprema koja je bila u kontaktu sa krvlju ili drugim telesnim tečnostima); otpad koji je bio u kontaktu sa zaraženim pacijentima podvrgnutim hemodijalizi (oprema za dijalizu i dr.);

- otpad od zaraženih pacijenata iz karantina (ekskreti, kontaminirana odeća ...); otpad od zaraženih eksperimentalnih životinja, kao i bilo koji drugi materijali i instrumenti koji dolaze u kontakt sa zaraženim osobama ili životinjama.

- **Patoanatomski otpad** – delovi ljudskog tela – amputati, tkiva i organi odstranjeni tokom hirurških zahvata, tkiva uzeta u dijagnostičke svrhe, placente i fetusi, eksperimentalne životinje i njihovi delovi, krv i druge telesne tečnosti.
- **Oštri predmeti** – igle, lancete, skalpeli i drugi oštri instrumenti i predmeti koji mogu izazvati ubod ili posekotine.
- **Farmaceutski otpad** – uključuje farmaceutske proizvode, lekove, vakcine, serume s isteklim rokom trajanja, neupotrebljeni ili kontaminirani, kao i opremu koja se koristi pri rukovanju (boce, kutije, rukavice, maske, epruvete i sl.)
- **Hemijski otpad** – hemikalije koje se upotrebljavaju pri medicinskim, dijagnostičkim ili eksperimentalnim postupcima, čišćenju i dezinfekciji. Deli se na opasan hemijski otpad – toksične, korozivne, lako zapaljive, reaktivne i genitoksične materijale i inertni hemijski otpad.
- **Otpad sa visokim sadržajem teških metala** – otpad onečišćen jedinjenjima žive, olova, arsena i drugi teških metala (termometri, aparati za merenje krvnog pritiska, baterije, rezidue iz stomatološke prakse...).
- **Posude pod pritiskom** - gasni cilindri (anestetički gasovi, gasovi za sterilizaciju, gasovi za inhalaciju), aerosol boce (sadrže inertne gasove pod pritiskom pomešane s aktivnim materijama – antibiotik, dezinficijens, insekticid itd.).
- **Radioaktivni otpad** – otpad kontaminiran radionukleidima, uglavnom niskog i srednjeg intenziteta zračenja, koji se koriste u dijagnostici, terapiji i istraživanju (kontaminirani materijal, oprema, rastvori, ekskreti pacijenata tretiranih ili dijagnostikovanih uz pomoć izvora zračenja, leševi eksperimentalnih životinja, kontaminirani scintilacioni fluidi i dr.).

2.2. Medicinski otpad kao rizik po zdravlje ljudi i životnu sredinu

Medicinski otpad je neophodno tretirati jer nosi rizik po zdravlje ljudi i životnu sredinu. Rizik zavisi od vrste medicinskog otpada i načina rukovanja i zbrinjavanja. Izlaganje opasnom medicinskom otpadu može imati za posledicu bolest ili povredu. Smatra opasnim ako:

- sadrži infektivne agense, žive organizme ili njihove spore ili toksine za koje se zna ili sumnja da uzrokuju bolesti ljudi i životinja;
- je genotoksičan, tj. ako sadrži materijale koje ako se inhaliraju, progutaju ili penetriraju u kožu mogu indukovati pojavu raka ili pogodovati njegovom rasprostranjivanju;
- sadrži toksične ili opasne hemijske supstance ili lekove koji u slučaju da su inhalirani, progutani ili su penetrirali u kožu mogu izazvati akutne ili hronične posledice po zdravlje;
- je radioaktivan;
- sadrži oštre predmete.

Prema Zakonu o potvrđivanju Bazelske konvencije o prekograničnom kretanju opasnih otpada i njihovom odlaganju medicinski i farmaceutski otpad se definiše kao:

- **Y1** – klinički otpad od medicinske nege u bolnicama, zdravstvenim centrima i klinikama;
- **Y2** – Otpad koji potiče iz proizvodnje i pripreme farmaceutskih proizvoda;
- **Y3** – Otpad od farmaceutskih proizvoda, droga i lekova;
- **Y4** – Otpad iz proizvodnje, formulacije i korišćenja biocida i fitofarmaceutskih proizvoda.

Neodgovarajuće upravljanje medicinskim otpadom može imati direktni uticaj na zajednicu, osobe koje rade u zdravstvenim ustanovama i na životnu sredinu.

Rizici po zajednicu uključuju namernu i nenamernu ekspoziciju usled nepostojanja sigurnog sistema upravljanja otpadom. Namerna ekspozicija se odnosi na praksu ponovne upotrebe iskorišćenih igala ili otpadnog materija koja dovodi do transmisije virusa hepatitisa B i C i HIV-a. Nenamerne povrede se mogu javiti kada postoji ekspozicija neadekvano odloženom otpadu, napr. pri čišćenju ili razdvajanju otpada na smetlištima. ***Rizici za zdravstvene radnike*** i radnike koji dolaze u kontakt s medicinskim otpadom nastaju usled nepropisnog rukovanja iglama nakon intervencija (vraćanja zaštite na iglu) i njihovog neadekvatnog odlaganja (u tanke kese i sl.).

Rizici po životnu sredinu i zdravlje stanovništva se ogledaju i u zagađenju vazduha dioksinima i furanima koji nastaju kod neadekvatnog tretmana otpada visokom temperaturom (insineracijom).

2.3. Pregled propisa koji se odnose na upravljanje medicinskim otpadom

2.3.1. Pregled nacionalne regulative

2.3.1.1. Nacionalni zakoni

- Zakon o postupanju sa otpadnim materijama (Službeni glasnik RS br. 25/96, 36/96) – reguliše rukovanje otpadnim materijama koje mogu da se koriste kao sekundarne sirovine, postupak prikupljanja otpada, uslove njegove obrade i skladištenja, kao i rukovanje otpadnim materijama koje nemaju upotrebnu vrednost i ne mogu da se koriste kao sekundarne sirovine.
- Zakon o potvrđivanju Bazelske konvencije o prekograničnom kretanju opasnih otpada i njihovom odlaganju (Službeni list SRJ, medjunarodni ugovori, br.

2/99) – uredjuje način postupanja s opasnim materijama, način vodjenja evidencije o vrsti i količini opasnih materija u proizvodnji, upotrebi, prevozu, prometu, skladištenju i odlaganju. Prema ovom Pravilniku obradu opasnog otpada obavlja generator otpada ili preduzeće koje ima odgovarajuću tehnologiju, uredjaje i opremu. Opasni otpad se sakuplja, privremeno skladišti, prevozi i obrađuje u posebno obezbedjenim objektima.

- Zakon o proizvodnji i prometu lekova (Službeni list SRJ br. 18/93, 24/94, 28/96, 21/99, 36/99, 23/2002).
- Zakon o proizvodnji i prometu otrovnih materija (Službeni list SRJ br. 15/95, 28/96, 37/02).
- Zakon o prevozu opasnih materija (Službeni list SFRJ br. 27/90, 45/90, 24/94, 28/96, 21/99, 44/99, 68/02).
- Zakon o lekovima i medicinskim proizvodima (Službeni glasnik RS br. 84/04).
- Zakon o zaštiti stanovništva od infektivnih bolesti (Službeni glasnik RS br. 125/04) – reguliše proceduru i mere čiji je cilj sprečavanje i kontrola ovih bolesti u medicinskim ustanovama. Program koji se odnosi na zaštitu stanovništva od infektivnih bolesti zahteva nadzor nad primenom predviđenih higijenskih mera (uključujući sterilizaciju i dezinfekciju kako bi se infekcija držala pod kontrolom).
- Zakon o sanitarnom nadzoru (Službeni glasnik RS br. 125/04) – predviđa uvođenje aktivnosti sanitarnog nadzora, reguliše pitanja procedure i načina obavljanja sanitarnog nadzora i definiše oblasti i ustanove koje će biti podložne tom nadzoru, sanitarne zahteve koje ustanove treba da ispune, kao i ovlašćenja, prava i obaveze sanitarnih inspektora u sprovođenju aktivnosti sanitarnog nadzora.
- Zakon o zaštiti životne sredine (Službeni glasnik RS, br. 66/91, 83/92, 53/93, 67/93, 48/94, 44/95, 53/95, 135/04) – daje osnove za upravljanje otpadom.
- Zakon o sahranjivanju i grobljima (Službeni list SRS br. 20/77, 24/85, 6/89 i Sl. glasnik RS br. 53/93, 67/93, 48/94, 101/2005 – drugi zakoni).
- Zakon o zdravstvenoj zaštiti (Službeni glasnik RS br. 17/92, 26/92, 50/92, 52/93, 53/93, 67/93, 48/94, 25/96, čl. 77a-77e i čl. 78 – 85, 107/05).

2.3.1.2. Nacionalni pravilnici

- Pravilnik o načinu uništavanja neupotrebljenih otrova i ambalaže koja je upotrebljena za pakovanje otrova i o načinu povlačenja otrova iz prometa (Službeni list SFRJ br. 7/83).
- Pravilnik o kriterijumima za razvrstavanje otrova u grupe i o metodama za određivanje stepena otrovnosti pojedinih otrova (Službeni list SFRJ br. 79/91).
- Pravilnik o kriterijumima za određivanje lokacije i uređenje deponija otpadnih materija (Službeni glasnik RS br. 54/92).
- Pravilnik o načinu uništavanja lekova, pomoćnih lekovitih sredstava i medicinskih sredstava (Službeni list SRJ br. 16/94, 22/94).
- Pravilnik o načinu postupanja s otpacima koji imaju svojstva opasnih materija (Službeni glasnik RS br: 12/95) – daje kategorizaciju opasnog otpada; reguliše način rukovanja izvesnim vrstama otpada koji imaju osobine opasnih materija, način vođenja beleški o tipovima i količinama opasnih materija u proizvodnji, korišćenju, transportu, prometu, skladištenju i odlaganju otpada.
- Pravilnik o načinu i postupku za utvrđivanje vremena i uzroka smrti, za obdukciju leša kao i za postupanje sa odstranjenim delovima ljudskog tela (Službeni glasnik RS br. 9/99, 10/99).
- Pravilnik o dokumentaciji koja se podnosi uz zahtev za izdavanje dozvole za uvoz, izvoz i tranzit otpada (Službeni list SRJ, br. 69/99).
- Pravilnik o uslovima i načinu razvrstavanja, pakovanja i čuvanja sekundarnih sirovina (Službeni glasnik RS, br. 55/01) – daje proceduru za postupanje otpadom u smislu razvrstavanja, obeležavanja i dokumentovanog prosledjivanja do mesta odlaganja, reciklaže ili uništavanja. Pravilnik sadrži katalog otpada u kome su nabrojane vrste otpada prema njihovim svojstvima i poreklu i koji je u potpunosti usklađen sa Evropskim katalogom otpada. Kategorizaciju otpada vrši Gradski zavod za javno zdravlje Beograd. Za otpad koji ima upotrebnu vrednost donosi se rešenje kojim se određuje način postupanja i otpad se upućuje na reciklažu.
- Uredba o transportu opasnih materija u drumskom i železničkom saobraćaju (Službeni glasnik RS br. 53/2002).

2.3.1.3. Drugi zakoni

- Zakon o komunalnim delatnostima (Službeni glasnik RS br. 16/97, 42/98).
- Zakon o određivanju posebnih nadležnosti autonomne pokrajine (Službeni glasnik RS br. 6/02)
- Zakon o lokalnoj samoupravi (Službeni glasnik RS br. 9/2002, 33/2004, 135/2004)
- Predlog zakona o upravljanju otpadom – član 56. – upravljanje otpadom iz zdravstvenih ustanova. Zabranjeno je mešati opasni otpad s otpadom koji nije opasan u okviru zdravstvenih ustanova. Menadžeri koji se pominju u stavu br. 1 ovog člana treba da usvoje plan upravljanja, ministarstvo koje je nadležno za aktivnosti zdravstvene zaštite u saradnji sa Ministarstvom zaštite životne sredine treba da odobre plan upravljanja otpadom iz zdravstvenih ustanova koje proizvode više od 500 kg opasnog otpada godišnje.

2.3.1.4. Propisi koji definišu pitanja bezbednosti na radu

- Zakon o bezbednosti i zdravlju na radu (Službeni glasnik RS br. 101/05).
- Pravilnik o postupku utvrđivanja ispunjenosti propisanih uslova u oblasti bezbednosti i zdarvlja na radu (Službeni glasnik RS br. 60/06).
- Pravilnik o sadržaju i načinu izdavanja obrasca izveštaja o povredi na radu, profesionalnom oboljenju i

oboljenju u vezi sa radom (Službeni glasnik RS br. 72/06, 84/06).

- Pravilnik o načinu i postupku procene rizika na radnom mestu i u radnoj okolini (Službeni glasnik RS br. 72/06, 84/06).
- Pravilnik o postupku pregleda i ispitivanja opreme za rad i ispitivanja uslova radne okoline (Službeni glasnik RS br. 94/06, 108/06).
- Bezbedno upravljanje medicinskim otpadom – Nacionalni vodič za bezbedno upravljanje medicinskim otpadom. Ministarstvo zdravlja RS, septembar, 2008.

Očekuje se uskoro usvajanje Zakona o upravljanju otpadom i donošenje podzakonskih regulativa za medicinski otpad. U nacrtu ovog zakona uvedena su osnovna načela upravljanja otpadom: načelo predostrožnosti, «zagađivač plaća», hijerarhija, primena najpraktičnijih opcija za životnu sredinu, odgovornost proizvođača i sl. Predviđeno je da se lokacija i izgradnja postrojenja za tretman medicinskog otpada određuje na osnovu regionalnih planova i Nacionalne strategije upravljanja otpadom [3] uz odgovarajuće tehničko-tehnološke uslove i dozvole koje izdaju nadležni organi za zaštitu životne sredine Republike i Pokrajine. Dokumentacija koja je potrebna za dobijanje dozvole sadrži: procenu uticaja na životnu sredinu, saglasnost na procenu uticaja, mišljenje organizacije lokane samouprave i mišljenje javnosti. Za sada se odustalo od ideje izgradnje postrojenja za uništavanje medicinskog otpada nakon sprovedenih pilot studija, tako da su prihvaćene druge metode. Zakon definiše i način finansiranja upravljanja otpadom i kaznene odredbe.

2.4. Uloge ministarstava

2.4.1. Ministarstvo zdravlja Republike Srbije

- Uvodi jedinstven sistem upravljanja medicinskim otpadom u zdravstvenim ustanovama državnog i privatnog sektora u Republici Srbiji u saradnji sa nadležnim organima državne uprave na svim nivoima (Republika, Pokrajina, lokalne samouprave).
- Uvodi obavezu razdvajanja infektivnog medicinskog otpada od ostalih kategorija otpada u dnevnom radu i obezbeđivanja tretmana istog do pretvaranja u komunalni, bezopasni otpad.
- Uvodi jedinstven sistem obeležavanja i pakovanja infektivnog medicinskog otpada prema preporukama Nacionalnog vodiča za bezbedno upravljanje medicinskim otpadom.
- Obezbeđuje primenu preporuka u procesu razvrstavanja, pakovanja i obeležavanja medicinskog otpada (Nacionalni vodič za bezbedno upravljanje medicinskim otpadom).
- Realizuje projekat *Tehnička podrška u upravljanju medicinskim otpadom* i obezbeđuje njegovu održivost, sa ciljem unapređenja upravljanja medicinskim otpadom, u saradnji sa nadležnim organima državne uprave na svim nivoima (Republika, Pokrajina, lokalna samouprava).
- Kontroliše upravljanje medicinskim otpadom i primenu propisa kojima se reguliše ova oblast.
- Odobrava planove upravljanja medicinskim otpadom za postrojenja za obradu otpada u okviru bolnica ili drugih ustanova koje su imenovane u centralna i lokalna mesta tretmana infektivnog medicinskog otpada, na teritoriji administrativno upravnih okruga.
- Odobrava planove za upravljanje medicinskim otpadom u drugim zdravstvenim ustanovama, koje ne poseduju autoklave za tretman infektivnog medicinskog otpada.
- Uspostavlja partnerske odnose sa drugim organima državne uprave koji učestvuju u upravljanju medicinskim otpadom.
- Institucionalizuje obuku za potrebe kvalitetnog upravljanja medicinskim otpadom.
- Obezbeđuje održivost ostvarenih rezultata uvođenjem modela okruga i primenom tehnologije toplotnog tretmana infektivnog medicinskog otpada u zdravstvenim ustanovama u Srbiji.
- Prati primenu domaće zakonske regulative i usaglašavanje iste sa EU zakonodavstvom, sa ciljem bezbednog i kvalitetnog upravljanja medicinskim otpadom u zdravstvenom sistemu u Republici Srbiji.

2.4.2. Ministarstvo životne sredine i prostornog planiranja

- Priprema nacionalnu strategiju upravljanja otpadom i podnosi je na odobravanje Vladi Republike Srbije.
- Koordinira postupcima upravljanja otpadom, vrši monitoring, inspekcijski nadzor u skladu sa postojećom zakonskom regulativom.
- Odgovorno je za primenu međunarodnih sporazuma i ugovora u oblasti životne sredine.
- Obavlja poslove državne uprave koji se odnose na proizvodnju i promet otrova i drugih opasnih materija, upravljanje hemikalijama, upravljanje otpadom, izuzev radioaktivnim otpadom.
- Formira informacioni sistem o otpadu na teritoriji Republike i izveštava o stanju životne sredine

Agencija za zaštitu životne sredine

- Izdaje saglasnost na elaborate o proceni uticaja na životnu sredinu.

U Odeljenju za upravljanje otpadom obavljaju se poslovi koji se odnose na:

- Pripremu stručnih osnova za izradu zakona i drugih propisa u oblasti upravljanja otpadom;
- Izradu i sprovođenje strateških dokumenata za integrisano upravljanje otpadom i njihovo povezivanje sa drugim strateškim dokumentima;
- Razvoj operativnih planova za posebne tokove otpada;
- Praćenje rada i učestvovanje u radnim telima vezanim za Bazelsku konvenciju, Stokholmsku konvenciju u delu koji se odnosi na upravljanje otpadom i Program UN za životnu sredinu;

- Razvoj održivog sistema za stalno pružanje pomoći privrednim subjektima i drugim subjektima za sprovođenje propisa iz oblasti upravljanja otpadom
- Sprovođenje Bazelske konvencije;
- Upravljanje industrijskim otpadom;
- Upravljanje komunalnim otpadom i posebnim tokovima otpada;
- Prekogranično kretanje otpada, izdavanje dozvola za uvoz, izvoz i tranzit otpada (lista potrebne dokumentacije kao i informacija o proceduri za izdavanje dozvola, nalazi se na sajtu ovog ministarstva www.ekoserb.sr.gov.rs).

Vezano za procenu rizika u oblasti upravljanja otpadom može se konstatovati da s obzirom na to da se opasan otpad u Republici Srbiji samo privremeno skladišti i izvozi, Ministarstvo životne sredine i prostornog planiranja upućuje na postupanje sa opasnim otpadom u skladu sa:

A) Uredbom o prevozu opasnih materija u drumskom i železničkom saobraćaju (Službeni glasnik Republike Srbije, br.53/2002) vezano za prevoz;

B) Zakonom o zaštiti životne sredine (Službeni glasnik Republike Srbije, br.135/04) u tački 3.2. Postupanje sa opasnim materijama i članu 38. Procena opasnosti od udesa;

V) Saglasnošću na Studiju o proceni uticaja na životnu sredinu vezano za skladištenje.

Zakonom o utvrđivanju određenih nadležnosti autonomne pokrajine (Službeni glasnik Republike Srbije, br.6/02) bliže se definišu nadležnosti AP Vojvodine, posebno u oblastima u kojima Republika uređuje sistem, između ostalih i u oblastima zdravstva i zaštite životne sredine. Vršenje poverenih poslova u ovim oblastima AP Vojvodina obezbeđuje preko Pokrajinskog sekretarijata za zdravstvo i Pokrajinskog sekretarijata za zaštitu životne sredine i održivi razvoj.

2.4.3. Pokrajinski sekretarijat za zdravstvo

- Kontroliše upravljanje medicinskim otpadom i primenu propisa kojima se reguliše ova oblast u zdravstvenim ustanovama u državnom sektoru na teritoriji APV čiji je ona osnivač, kao i u privatnom sektoru.
- Uspostavlja partnerske odnose sa drugim organima državne uprave koji učestvuju u upravljanju medicinskim otpadom (Republika i lokalne samouprave).
- Učestvuje u uvođenju jedinstvenog sistema upravljanja medicinskim otpadom u zdravstvenim ustanovama državnog sektora na teritoriji APV čiji je ona osnivač, kao i u privatnom sektoru.
- Učestvuje u realizaciji projekta *Tehnička podrška u upravljanju medicinskim otpadom*, sa ciljem unapređenja upravljanja medicinskim otpadom, za teritoriju APV.

2.4.4. Pokrajinski sekretarijat za zaštitu životne sredine i održivi razvoj

- Obezbeđuje praćenje stanja činilaca životne sredine na teritoriji APV, između ostalog i u oblasti upravljanja otpadom.
- Daje saglasnost na studije o proceni uticaja projekata na životnu sredinu, za projekte za koje građevinsku dozvolu izdaje nadležni organ APV.
- Obrazuje informacioni podsistem za zaštitu i unapređenje životne sredine za teritoriju APV koji obuhvata i oblast upravljanja otpadom, kao deo jedinstvenog informacionog sistema Republike.
- Vrši inspekcijski nadzor u oblasti upravljanja otpadom na teritoriji APV.
- Uspostavlja partnerske odnose sa drugim organima državne uprave koji učestvuju u upravljanju otpadom.
- Kontroliše upravljanje otpadom uključujući i medicinski otpad, kao i primenu propisa kojima se reguliše ova oblast na teritoriji APV.
- Učestvuje u uvođenju jedinstvenog sistema upravljanja medicinskim otpadom u zdravstvenim ustanovama državnog sektora na teritoriji APV čiji je ona osnivač, kao i u privatnom sektoru.
- Učestvuje u realizaciji projekta *Tehnička podrška u upravljanju medicinskim otpadom*, sa ciljem unapređenja upravljanja medicinskim otpadom, za teritoriju APV.

2.4.5. Organi lokalne samouprave

- Usvajaju lokalno zakonodavstvo u oblasti upravljanja komunalnim čvrstim otpadom.
- Definišu lokalnu politiku i usvajaju akcione planove za teritoriju opštine u oblasti upravljanja otpadom.
- Izdaju dozvole za sakupljanje i tretman komunalnog otpada i građevinskog otpada.
- Sprovode inspekcijski nadzor radi provere usaglašenosti sa zahtevima u izdatoj dozvoli.
- Kontrolišu aktivnosti preduzeća sa kojima su ugovorili usluge o sakupljanju, prevozu i odlaganju komunalnog čvrstog otpada.
- Upravljaju ukupnom organizacijom u pružanju usluga za komunalni čvrsti otpad, uključujući sakupljanje razdvojenog otpada.
- Ustanovljavaju takse i kazne u oblasti upravljanja komunalnim čvrstim otpadom.
- Uspostavljaju partnerske odnose sa drugim organima državne uprave koji učestvuju u upravljanju otpadom.
- Učestvuju u realizaciji projekta *Tehnička podrška u upravljanju medicinskim otpadom*, sa ciljem unapređenja upravljanja medicinskim otpadom, za teritoriju lokalne samouprave.

2.4.6. Generatori medicinskog otpada /zdravstvene ustanove

- Preduzimaju mere upravljanja generisanim otpadom u smislu sprečavanja ili smanjenja nastajanja, ponovne upotrebe ili reciklaže, izdavajanja sekundarnih sirovina i korišćenja kao energenta, odnosno njegovog konačnog odlaganja (u skladu sa osnovnim načelima zaštite životne sredine, načelom prevencije i predostrožnosti, načelom odgovornosti zagađivača i njegovog pravnog sledbenika, načelom „zagađivač plaća“).

- Dostavljaju propisane podatke Agenciji za zaštitu životne sredine za izradu integralnog katastra zagađivača.
- Učestvuju u realizaciji projekta *Tehnička podrška u upravljanju medicinskim otpadom*, sa ciljem unapređenja upravljanja medicinskim otpadom.

2.5. Pregled evropske regulative

- Direktiva Saveta 75/442/EEC o otpadu (okvirna direktiva) – određuje nadležni organ koji će vršiti nadzor u postupku uklanjanja otpada; uređuje staranje o tome da ovlašćeni organi utvrđuju planove o uklanjanju otpada; utvrđuje režim prethodne dozvole za uređaje za preradu, skladištenje i odlaganje otpada za račun trećih lica; dosledno primenjuje načelo «zagađivač plaća».
- Direktiva 75/439/EEC o odlaganju otpadnih ulja – zabranjuje bacanje upotrebljenih ulja u sve unutrašnje površinske i podzemne vode i kanalizaciju; zebranjuje odlaganje i/ili bacanje upotrebljenih ulja čije je dejstvo štetno za zemljište i svako nekontrolisano bacanje otpada (taloga) koji nastaje u postupku obrade upotrebljenih ulja (za ponovno korišćenje, regeneraciju, spaljivanje); zabranjuje postupanje sa upotrebljenim uljima koje izaziva zagađivanje atmosfere iznad granice utvrđene propisima.
- Direktiva 84/631/EEC o nadzoru i kontroli prekograničnog prenosa opasnih otpada - zahteva da se prilagodi procedura koja se primenjuje, a odnosi se na upućivanje notifikacije u slučaju namere držaoca opasnih otpada da ih prenese preko granice druge države; zahteva da se izvrši revizija sadržine propisane prateće isprave; da se obezbede određeni uslovi u pogledu pakovanja i obeležavanja; da se propišu uputstva koje treba primeniti u slučaju opasnosti ili udesa.
- Direktiva 89/369/EEC o redukciji zagađenja iz novih gradskih postojenja za spaljivanje otpada i Direktiva 89/429/EEC o redukciji zagađenja iz postojećih gradskih postojenja za spaljivanje otpada.
- Direktiva 89/391/EEC – opšta direktiva o uvođenju mera za podsticanje poboljšanja bezbednosti i zdravlja radnika na radu koja definiše opšte principe prevencije.
- Direktiva 91/157/EEC o baterijama i akumulatorima koji sadrže opasne supstance - propisuje da se uvedu mere za kontrolu odlaganja potrošenih baterija i akumulatora koji sadrže opasne supstance; propisuje da se uvedu zabrane plasiranja na tržište određenih vrsta baterija i akumulatora.
- Direktiva 91/689/EEC o opasnom otpadu - propisuje sve potrebne mere kako bi se zabranilo nekontrolisano napuštanje, odbacivanje ili odlaganje opasnih otpada i njihov nekontrolisan prevoz; propisuje i preduzima sve mere za odvajanje opasnih otpada, kada je to potrebno, i propisuje i identifikuje svako mesto na kome je izvršeno odlaganje opasnih otpada; nalaže da se opasan otpad beleži i identifikuje, da se odlaganje otpada podvrgne režimu dozvola i periodičnoj inspekciji; zahteva donošenje programa za uklanjanje opasnih otpada; zahteva da se vodi registar sa odgovarajućim podacima o tim otpadima od strane preduzeća koja proizvode, drže ili uklanjaju opasne otpade, i da na zahtev nadležnih organa dostavljaju tim organima tražene podatke iz registra.
- Direktiva Saveta 94/62/EC o ambalaži i ambalažnom otpadu – propisuje da se sprečava stvaranje ambalažnog otpada, ponovo upotrebljava ambalaža i minimizuje konačno odlaganje takvog otpada; propisuje da se vrši prerada/reciklaža i energetsko spaljivanje, kao i organska reciklaža i odlaganje; propisuje da se ustanovi sistem garancija za povraćaj upotrebljene ambalaže i/ili ambalažnog papira.
- Direktiva 94/67/EC o insineraciji opasnog otpada.
- Direktiva 96/61/EEC o integralnoj prevenciji i kontroli zagađenja.
- Direktiva 97/11/EC o proceni uticaja određenih javnih i privatnih projekata na životnu sredinu kojom se menja i dopunjuje Direktiva 87/337/EEC.
- Direktiva Saveta 99/31/EC o deponijama otpada – ima za cilj da smanji količinu biorazgradivog komunalnog otpada koji se šalje na deponiju; metan iz novih i postojećih deponija treba da bude sakupljen i iskorišćen.
- Direktiva Saveta 2000/53/EC o istrošenim vozilima.
- Direktiva Saveta 2000/76/EC o spaljivanju otpada – propisuje da se uvede sistem dozvola za spaljivanje otpada i za ispuštanje otpadnih voda iz ovih postrojenja; propisuje da se primenjuju propisani uslovi u pogledu izgleda i rada postrojenja za spaljivanje, kao i propisane vrednosti emisije.
- Direktiva 2001/42/EC o proceni uticaja određenih planova i programa na životnu sredinu.
- Direktiva 2002/96 o otpadu od električne i elektronske opreme.
- Uredba Saveta 259/93/EEC o nadzoru i kontroli procesa otpada unutar i van Evropske zajednice.
- Uredba 2150/2002 Parlamenta i Saveta o statistici otpada.
- Bazelska konvencija o kontroli prekograničnog kretanja opasnog otpada i njegovog odlaganja (1989).
- Pravilnik o načinu i postupku za utvrđivanje vremena i uzroka smrti, za obdukciju leša kao i za postupanje sa odstranjenim delovima ljudskog tela (Službeni glasnik RS br. 9/99, 10/99).
- ISO 9001:2000 – medjunarodni standard za sistem upravljanja kvalitetom.
- ISO 14001 - medjunarodni standard za sistem upravljanja zaštitom životne sredine.
- OHSAS 18001 – specifikacija koja definiše sistem upravljanja zaštitom zdravlja i bezbednošću na radu.
- ISO/IEC 17025:2006 - medjunarodni standard za kompetentnost laboratorija za ispitivanje

2.6. EU- direktive

Osnovi politike upravljanja otpadom u Evropskoj uniji sadržani su u Rezoluciji veća Evrope o strategiji upravljanja otpadom (97/C76/01) koja se bazira na Okvirnoj direktivi o otpadu (75/442/EEC) i ostalim propisima o upravljanju otpadom u EU.

Utvrđeno je pet osnovnih načela:

- hijerarhija upravljanja otpadom,
- samoodrživa postrojenja za odlaganje,
- najbolja dostupna tehnologija,
- blizina odlaganja otpada i
- odgovornost proizvođača.

Uz navedena nastoje se ostvariti i sledeća načela: zajednička definicija otpada u svi državama članicama, podsticanje čistije proizvodnje i korišćenja čistih proizvoda, podsticanje korišćenja ekonomskih instrumenata, regulisanje transporta otpada, kao i zaštita životne sredine i unutrašnje tržište.

EU zakonodavni okvir koji obuhvata bezbedno upravljanje otpadom i zaštitu zdravlja i bezbednosti definisan je sledećim propisima:

- Direktiva 75/442/EEC o otpadu (Okvirna direktiva)
- Direktiva 99/31/EC o deponijama otpada
- Direktiva 94/62/EC o ambalaži i ambalažnom otpadu
- Direktiva 96/61/EEC o integralnoj prevenciji i kontroli zagađenja
- Direktiva 97/11/EC o proceni uticaja određenih javnih i privatnih projekata na životnu sredinu kojom se menja i dopunjuje Direktiva 87/337/EEC
- Direktiva 2001/42/EC o proceni uticaja određenih planova i programa na životnu sredinu
- Direktiva 91/689/EEC o opasnom otpadu izmenjena direktivom 94/31/EC
- Direktiva 2000/76/EC o spaljivanju otpada
- Direktiva 94/67/EC o spaljivanju opasnog otpada
- Direktiva 89/369/EEC o redukciji zagađenja iz novih gradskih postrojenja za spaljivanje otpada i Direktiva 89/429/EEC o redukciji zagađenja iz postojećih gradskih postrojenja za spaljivanje otpada
- Direktiva 2004/37/EC o zaštiti radnika od rizika povezanih sa izlaganjem karcinogenima ili mutagenima na radnom mestu
- Direktiva 2000/54/EC o zaštiti radnika od rizika povezanih sa izlaganjem biološkim sredstvima na radnom mestu
- Direktiva 98/24/EC o zaštiti zdravlja i bezbednosti radnika izloženih rizicima od hemijskih sredstava na radnom mestu
- Uredba 259/93/EEC o nadzoru i kontroli isporuka otpada unutar zemalja EZ, kao i pri ulasku i izlasku iz njih.
- Uredba 2150/2002 o statistici otpada.

2.7. Bazelska konvencija

Bazelska konvencija o kontroli prekograničnog kretanja opasnog otpada i njegovog odlaganja (1989) je jedan od najvažnijih međunarodno prihvaćenih pravnih akata u oblasti upravljanja opasnim otpadom, koji je u našoj zemlji na snazi od 1999. godine i koji, između ostalog, reguliše i prekogranično kretanje i odlaganje medicinskog otpada (kao vrste opasnog otpada). Sporazum je potpisalo preko 100 zemalja, koje su prihvatile princip da je jedini legitimni transport opasnog otpada, izvoz iz zemalja koje nemaju postrojenja ili stručni kadara za pouzdano odlaganje otpad, u zemlje koje imaju i postrojenja i stručni kadar.

2.8. Prilagođavanje međunarodnom zakonodavstvu

Postojeća zakonska regulativa ne obuhvata sve aspekte upravljanja medicinskim otpadom i ne daje preporuke za tretman posebnih tokova otpada, što predstavlja i medicinski otpad. Neophodno je njeno usaglašavanje sa evropskim direktivama i međunarodnim standardima, što podrazumeva jasno definisanje opasnog medicinskog otpada i njegovih različitih kategorija, uvođenje sistema integralnog upravljanja (razdvajanje, sakupljanje, skladištenje, postupanje, tretman, odlaganje, transport), sistema evidencije, principa pravne i finansijske odgovornosti generatora otpada, inspekcijskog sistema koji će obezbediti efikasno sprovođenje zakona, kao i kaznenih odredbi.

Takođe, upravljanje medicinskim otpadom mora biti usaglašeno sa ostalim relevantnim zakonima koji se odnose na upravljanje otpadom generalno, uticaje na javno zdravlje i životnu sredinu, kvalitet vazduha, prevenciju i kontrolu infektivnih bolesti i upravljanje radioaktivnim materijama.

Usvajanjem Predloga zakona o upravljanju otpadom, koji je u skupštinskoj proceduri, biće učinjen značajan pomak ka usklađivanju s pravnim nasleđem EU na području upravljanja otpadom, a proces će se nastaviti donošenjem niza propisa i dokumenata za njegovo sprovođenje. Celoviti proces usklađivanja nacionalnog zakonodavstva s pravnim sistemom EU, prema rokovima utvrđenim Predlogom zakona o upravljanju otpada, trebao bi biti završen do 2015. godine.

Član 56. Predloga zakona o upravljanju otpadom, koji se odnosi na upravljanje otpadom koji potiče iz zdravstvenih ustanova, uvodi obavezu "in situ" razdvajanja otpada na opasan i neopasan, izrade planova upravljanja, kao i evidentiranja količina opasnog otpada. Planove upravljanja za zdravstvene ustanove koje generišu više od 500 kg opasnog otpada na godišnjem nivou odobrava Ministarstvo zdravlja Republike Srbije, u saradnji sa Ministarstvom životne sredine i prostornog planiranja Republike Srbije.

3. UPRAVLJANJE MEDICINSKIM OTPADOM

Količina medicinskog otpada koja nastaje u nekoj zemlji zavisi od njene ekonomske moći i stepena razvoja zdravstvene službe. Što je zemlja bogatija, a zdravstvena služba razvijenija to je i količina otpada veća.

Osnovni zadaci upravljanja medicinskim otpadom (slika 1) su:

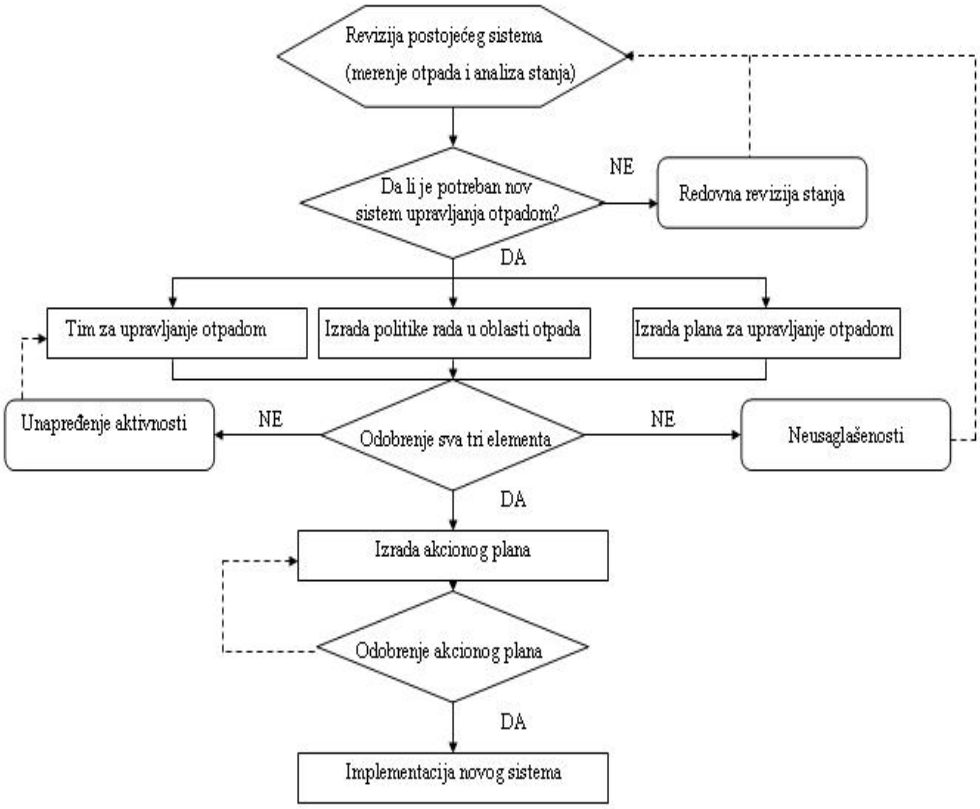
- Planiranje aktivnosti u vezi sa upravljanjem medicinskim otpadom (izrada plana upravljanja medicinskim otpadom za svaku zdravstvenu i ustanovu socijalne zaštite i sl.);
- Smanjivanje proizvodnje i količine medicinskog otpada;
- Uspostavljanje procesa razvrstavanja/razdvajanja otpada, u kome se otpad razdvaja prema različitim nači-

nima prerade i odlaganja i usmerava u pravcu različitih „tokova";
- Upravljanje otpadom na način kojim se ne ugrožava zdravlje ljudi i životna sredina;
- Organizovanje prerade i odlaganja otpada na najpogodniji način u okviru različitih tokova otpada;
- Priprema ili sanacija neuređenih privremenih ili trajnih skladišta otpada;
- Vođenje evidencije i dokumentacije o aktivnostima u vezi s upravljanjem medicinskim otpadom;
- Praćenje pokazatelja u vezi sa razvrstavanjem, odlaganjem i tretmanom otpada;
- Preduzimanje korektivnih mera u planiranju aktivnosti na godišnjem nivou;
- Obuka zaposlenih za poslove razvrstavanja, obeležavanja, pakovanja, odlaganja i tretmana medicinskog otpada;
- Motivisanje zaposlenih za efikasno upravljanje medicinskim otpadom;
- Razvoj svesti o upravljanju medicinskim otpadom;
- Multidisciplinarna saradnja u cilju uređivanja sistema upravljanja medicinskim otpadom, kako na nivou zdravstvene ustanove, tako i na teritoriji administrativnog okruga.

Za dobru praksu upravljanja otpadom od značaja je da zdravstveni radnici i saradnici tačno znaju šta se od njih očekuje u vezi razvrstavanja otpada, da budu motivisani i propisno obučeni za navedene aktivnosti, kao i da imaju adekvatnu saradnju s upravom zdravstvene ustanove.

Mehanizmi praćenja i kontrole aktivnosti u domenu upravljanja medicinskim otpadom u svakoj ustanovi koja generiše medicinski otpad su zasnovani na saradnji, multidisciplinarnosti i partnerskim odnosima u cilju uspostavljanja upravljanja medicinskim otpadom kako proizvođača medicinskog otpada, tako i lokalne samouprave, ekološkog sektora i svih subjekata upravljanja otpadom.

Pre početka planiranja aktivnosti u vezi upravljanja medicinskim otpadom neophodno je prvo sagledati koje se količine otpada generišu i kakva je kadrovska i organizaciona struktura zdravstvene zaštite u regionu.



Slika 1 - Dijagram procesa upravljanja medicinskim otpadom

3.1. Upravljanje medicinskim otpadom u svetu

U Nemačkoj se dnevno generiše 8 kg bolničkog infektivnog otpada po krevetu, a u Iranu manje od 4 kg.

Procena je da se u Turskoj generiše u bolnicama oko 22t/dan medicinskog otpada, što je u proseku 0.63kg/krevetu/dan. Od ove količine 59% je komunalni, a 41% opasni otpad, što pokazuje da se u oko 25% ustanova i dalje neadekvatno upravlja medicinskim otpadom.

U Tanzaniji, koja pripada zemljama u razvoju, 1995. godine je generisano 0,03 do 0,8 kg po pacijentu dne-

vno, u proseku 0,66kg/dan. Produkcija medicinskog bolničkog otpada je u proseku bila 200kg/dan. Što je bolnica modernija i bolje opremljena, veća je i produkcija otpada. Na primer bolnica Aga Khan generiše 1.3kg/pacijentu/dan čvrstog medicinskog otpada, što je 9 puta više od Temeke bolnice gde se generiše samo 0,15kg/pacijentu/dan. Učešće opasnog otpada je rangiralo od 53,9 do 70,0%, u proseku 60,2%, nasuprot visoko razvijenim zemljama (SAD) gde se generiše 4,5-9,1kg/krevetu/dan, što je oko 10% ukupne produkcije otpada [7].

U Jordanu prosečna količina generisanog medicinskog otpada iznosi 6,10kg/pacijentu/dan (3,49kg /krevetu/dan), 5,62kg/pacijentu/dan (3,14kg/krevetu/dan), 4,02kg/pacijentu/dan (1,88kg/krevetu/dan), u bolnicama, porodilištima i privatnim bolnicama respektivno. U državnim medicinskim laboratorijama te količine iznose 0,053-0,065kg/test-dan, odnosno 0,034-0,102kg/test-dan u privatnim laboratorijama [8].

U nekim drugim zemljama količine generisanog otpada su slične [9], što se vidi iz tabele 2. U Srbiji se godišnje generiše oko 10000 t medicinskog otpada [10].

Tabela 2 - Količine generisanog otpada po pacijentu [9]

Zemlja	Količina generisanog otpada (kg/pacijentu/dan)
Saudijska Arabija	1,1
Iran	2,7
Francuska	3,3
Španija	4,4
Velika Britanija	3,3
SAD	4,4

U Hrvatskoj u 2004. godini prijavljeno je 1616,5 t opasnog otpada koji nastaje prilikom zaštite zdravlja ljudi i životinja i/ili srodnih istraživanja, od čega se najveći deo (90%) odnosi na otpad čije je skupljanje i odlaganje podvrgnuto specijalnim zahtevima radi prevencije infekcije. Ministarstvo zdravstva Hrvatske izdalo je 2000. godine Naputak o postupanju s otpadom koji nastaje pri pružanju zdravstvene zaštite (NN 50/00), koji terminologijom i definicijama pojedinih vrsta medicinskog otpada nije u skladu s Katalogom otpada koji se nalazi u sklopu Pravilnika o vrstama otpada, ali uređuje upravljanje otpadom u pogledu razvrstavanja na mestu nastanka, skupljanja, prevoza, skladištenja i obrade. Veliki broj proizvođača otpada pod šifrom EKO *18 01 03 predaje ovaj otpad skupljaču, odnosno obrađivaču koji poseduje odobrenje za obavljanje delatnosti upravljanja opasnim otpadom od nadležnog ministarstva.

Farmaceutski i hemijski otpad trenutno ima rešenje u vidu izvoza u zemlje koje poseduju odgovarajuće uređaje za destrukciju u skladu sa propisima EU, jer kod nas takvi uređaji ne postoje. Takođe, ne treba menjati ni postojeći način postupanja sa radioaktivnim otpadom i patoanatomskim otpadom, jer su oni u skladu sa odgovarajućim propisima. Problem infektivnog medicinskog otpada se u svetu rešava primenom sledećih postupaka [11]:

- Prikupljanje i kontrolisano spaljivanje
- Prethodna selekcija, prikupljanje i kontrolisano spaljivanje
- Prethodna selekcija, sterilizacija i kontrolisano spaljivanje
- Prethodna selekcija, sterilizacija i odlaganje na komunalnu deponiju

Postoji čitav niz uređaja za sterilizaciju i spaljivanje medicinskog otpada koji rade na najrazličitijim principima ali je izuzetno važno da kod kontrolisanog spaljivanja mora da se postigne temperatura od 1200^{o}C i da postoji adekvatan tretman dimnih gasova i otpadnih voda, a kod sterilizacije da se postiže efikasnost, odnosno redukcija broja mikroorganizama, od minimum $6_{\log 10}$ [11]. Kao posledica nepotpunog sagorevanja u insineratorima dolazi do stvaranja kancerogenih dioksina i furana i kao ostatak tretmana javlja se pepeo, koji takođe ima karakteristike opasnog otpada, zbog čega ova vrsta tretmana nije prihvaćena u našoj zemlji.

3.2. Upravljanje medicinskim otpadom u Srbiji

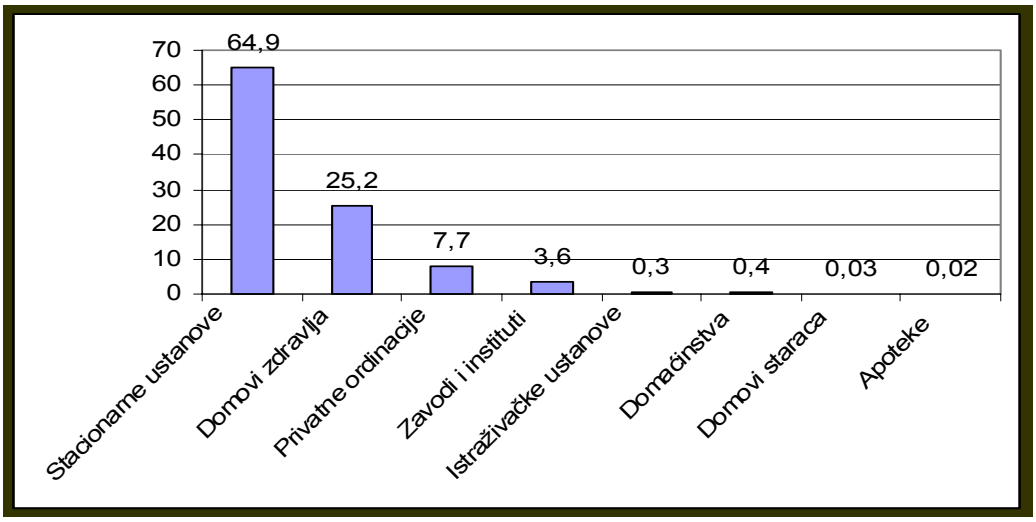
Prema procenama iz 2004. godine [12] u Srbiji nastaje oko 10000 tona medicinskog otpada (slika 2) i to u:

- Ustanovama sa stacionarom oko 6300 t (64,9%);
- Domovima zdravlja oko 2450 t (25,2%);
- Privatnim lekarskim, stomatološkim i laboratorijskim objektima 750 t (7,7%);
- Raznim zavodima i institutima 350 t (3,6%);
- Visoko specijalizovanim istraživačkim ustanovama 30 t (0,3%);
- Domaćinstvima sa hroničnim bolesnicima 40 t (0,4%);
- Domovima staraca i nezbrinutih lica oko 3 t (0,03%);
- Apotekarskim ustanovama 2 t (0,02%)

Početkom 2008. godine u Srbiji još uvek nije postojao sistem upravljanja medicinskim otpadom na način kako se to radi u EU ili kako preporučuje SZO. Za sada postoji samo jedna sanitarna deponija u Vranju, nekoliko je u izgradnji, dok nema ni jednog uređaja za destrukciju ili kontrolisano spaljivanje opasnog otpada ili posebno uređene deponije za opasan otpad.

Sa radiokativnim otpadom postupa se u skladu sa propisima Međunarodne Agencije za Atomsku Energiju (IAEA), a sa patoanatomskim otpadom u skladu sa domaćim propisima (kremiranje ili sahranjivanje) [12].

Farmaceutski i hemijski otpad uglavnom se ne razvrstavaju u skladu sa Katalogom otpada, već se odlažu i čuvaju u posebnim ormarima i prostorijama. Retko gde postoji evidencija o vrstama i količinama ovog otpada. Za sada samo Gradski zavod za javno zdravlja Beograd rešava ovaj problem u skladu sa propisima (izvoz na spaljivanje u zemlje EU).



Slika 2 - Generisanje medicinskog otpada u Srbiji prema vrsti ustanove [12]

U najvećem broju zdravstvenih ustanova sa medicinskim otpadom se postupalo kao s klasičnim komunalnim otpadom, a ne kao s opasnim otpadom. Ovo je posebno česta bila praksa u manjim zdravstvenim organizacijama i nerazvijenim sredinama. Samo je mali broj zdravstvenih ustanova (zavodi za javno zdravlje, Institut za transfuziju krvi, infektivne klinike i odeljenja za TBC) postupalo sa infektivnim medicinskim otpadom i korišćenim oštrim instrumentima u skladu sa higijenskim principima. Primenjivala sterilizacija vodenom parom pod povećanim pritiskom (autoklaviranje).

Realizacijom projekta Tehničke podrške u upravljanju medicinskim otpadom u Srbiji, krajem 2008. godine 78 zdravstvenih ustanova je dobilo aparate za sterilizaciju i drobljenje infektivnog čvrstog otpada. Izvesan broj ustanova je dobio i vozilo za prevoz otpada do centralnog mesta za tretman otpada. Izvršena je edukacija osoblja i radi se na uspostavljanju i pokretanju sistema upravljanja medicinskim otpadom.

4. ZAKLJUČAK

Modeli upravljanja medicinskim otpadom se razlikuju, najviše u zavisnosti od primenjene tehnologije tretmana otpada, ali i prema načinu upravljanja. Tako su u Americi i Kanadi [1] za rukovanje medicinskim otpadom zadužene posebne agencije, dok se u Srbiji (koja je tek u početnoj fazi implementacije planiranog sistema upravljanja) ovim poslovima i dalje bave zdravstvene ustanove. Reforma zdravstvenog sistema koja se očekuje će verovatno zahvatiti i ovaj segment zdravstva, tako da je ovaj rad osmišljen u tom pravcu, da pruži pomoć zainteresovanima za dalje rešavanje ove problematike.

U Srbiji još uvek postoji neadekvatna praksa upravljanja medicinskim otpadom. Produkcija ove vrste otpada sve više raste, kao i zdravstveni rizici (zaražavanje virusima HIV-a, hepatitisa B i C i druge bolesti koje se prenose putem krvi, kao i usled izlaganja toksičnim i genotoksičnim materijama - hemikalijama, lekovima, radionukleidima). Dokazano je da ne postoji metod tretmana otpada ili odlaganja koji u potpunosti eliminiše sve rizike koje medicinski otpad nosi u sebi za populaciju ili životnu sredinu.

Aktivnosti na unapređenju postojeće prakse upravljanja otpadom predstavljaju jedan od definisanih prioriteta Strategije zaštite životne sredine i održivog razvoja, u okviru Programa privrednog razvoja AP Vojvodine [2], kao i sastavni deo implementacije Nacionalne strategije upravljanja otpadom sa programom približavanja EU [3]. Nacionalnom strategijom se uredjuje upravljanje otpadom od njegovog nastanka do konačnog odlaganja, s ciljem uspostavljanja integralnog sistema upravljanja otpadom na teritoriji Republike Srbije, koji bi bio usklađen s evropskim standardima. Osnovna svrha ovog sistema upravljanja otpadom je da se maksimalno smanje količine generisanog otpada, da se smanji nepovoljan uticaj otpada na ljudsko zdravlje, životnu sredinu i klimu i da ceo sistem bude u skladu s načelima održivog razvoja. Ovo podrazumeva uspostavljanje zakonodavno-pravnog i institucionalnog okvira, hijerarhije upravljanja otpadom i ekonomskih instrumenata, kao i edukaciju i razvijanje javne svesti.

Pojedine zdravstvene ustanove koriste metod spaljivanja celokupnog otpada u postojećim sopstvenim spalionicama, kao osnovni i jedini metod zbrinjavanja medicinskog otpada. Pomenute spalionice najčešće rade na temperaturama koje nisu adekvatne za bezbedno spaljivanje medicinskog otpada, pa postoji tendencija njihove dodatne kontrole kvaliteta rada i zatvaranja. Ministarstvo zaštite životne sredine sprovodi nadzor nad radom pomenutih bolničkih spalionica.

Samo u određenom broju zdravstvenih ustanova u Srbiji se obavlja sterilizacija infektivnog medicinskog otpada, i to najčešće u autoklavima koji su vrlo stari, ali koji se redovno kontrolišu i održavaju. Ovakvu praksu imaju instituti i zavodi za javno zdravlje, kao i pojedine mikrobiološke laboratorije. Nakon sterilizacije, oštri

predmeti se odlažu u obične kontejnere za komunalni otpad. Juna 2007. godine Ministarstvo zdravlja Srbije uz pomoć finansija Evropske Unije je pokrenulo projekat Tehničke podrške u upravljanju medicinskim otpadom, čije su pripreme sprovedene u 2008. godini: distribuirana je oprema za tretman otpada, izvršena je obuka i očekuje se da se završi sa pripremom dokumetacije u svim ustanovama i da se uspostavi sistem upravljanja medicinskim otpadom na svim nivoima zdravstvene službe. Vodič dobre prakse za bezbedno pravljanje medicinskim otpadom je takođe još uvek u obliku radne verzije. Uspešno rešavanje problema upravljanja medicinskim otpadom je vrlo značajno zbog unapređenja zdravlja celokupne populacije kao i bolje zaštite životne sredine, pa se ovoj problematici mora posvetiti i posebna pažnja.

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ABSTRACT

LEGISLATION FRAMEWORK AND RESPONSIBILITIES IN MEDICAL WASTE MANAGEMENT

Medical waste in hospitals and appropriate institutions in Serbia is generated in huge amounts, in dependence of the type of institution, number of beds, type and nature of diseases and conditions to be treated, as well as kind and quality of services provided. Medical waste is treated as potentially harmful for human health and waste management is different from country to country, depending on development level, geographic conditions and culture. Each country could have appropriate Regulations and manuals for medical waste management, but majority of them is based on documents issued by World Health Organization (WHO). During the last decade, work on solving the problem is intensive throughout the world.

***Key words**: medical waste, law, regulation, management*

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