Atmospheric Corrosion of Metals in Urban Area

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Abstract: Atmospheric corrosion rate depends on the content of the individual components in atmosphere, temperature of air, and refers primarily on the moisture content, the content of the various particles and the SOx and NOx gases. Washing out the pollutants from the atmosphere creates strong acids, bases and salts that can corrode various metal and non – metallic structures. The analysis of certain precipitation parameters, analysis of metal and alloy samples exposed to the atmosphere in Sarajevo and Kiseljak, and analysis of metal and alloy samples without atmospheric influence were carried out. The methods used for sample analysis are linear voltammetry and cyclic voltammetry. An iron plate, chrome coated iron plate with worn out surface, zinc coated iron plate with worn out surface and brass plate were used as a samples. It was observed that the corrosion of samples in Sarajevo is more intensive as compared to the corrosion of samples tested in the area of Kiseljak. Linear voltammetry measurements in a given range of potentials gave more pronounced corrosion currents in the samples from urban area. Cyclic voltammetry measurements gave pronounced reduction peak at -0.25 V for brass, and for chrome coated iron plate at -0.05 V. For the zinc coated iron plate sample, potentials were shifted to negative values that are characteristics of zinc pair. For chrome coated iron plate, reduction peak was detected at -0.75 V. The cyclic voltammogram for zinc coated iron plate with worn out surface is similar to the cyclic voltammogram for zinc coated iron plate. Urban area of Sarajevo is heavily polluted by different pollutants which can affect all aspects of life and environment. The occurrence of acid rains is intensified, which increases the corrosion of material of which the constructions are made.

INTRODUCTION

Atmospheric corrosion is the degradation of materials under the chemical and electrochemical influence of the atmosphere.

This type of corrosion is mostly prevalent. The largest number of metal structures is corroded by moisture caused by condensation of water vapor when exposed to atmospheric air. The rate of atmospheric corrosion depends on the atmospheric conditions to which metal structures are exposed, atmospheric effects on the metal, the nature of the metal, and the state of the metal surface. (Milenković, Mladenović and Vučković, 1996)

When it comes to the content of individual atmospheric components that have a significant influence on corrosion, it is primarily about the content of moisture, various particles and SOx and NOx gases.

These pollutants are emitted into the atmosphere as a direct or indirect consequence of human activity. The distribution of pollutants depends directly on meteorological conditions. If there is no wind, the transmission of the pollutant away from their source is slow, so that the reduction in local concentrations of air pollutants emitted by air dilution is slow. The direction of the pollutants movement and their distribution on a local and global scale depends on the direction, intensity and length of wind currents. In addition, rinsing

pollutants from the atmosphere by precipitation decreases their concentration.

In recent years, the increase in SO_2 concentration has been recorded in Sarajevo due to temperature inversion resulting in the absence of airflow, the use of fuel of extremely poor quality, increased number of vehicles, unplanned construction, (Đuković, 2001).

Sulfur dioxide and a much more reactive product of its conversion, sulfuric acid is very destructive in the contact with metals, construction materials, and leather, paper, and textile materials.

The main sources of nitrogen oxides occurring in the air are natural sources, whose emissions are globally estimated at around 450×10^6 t/year and sources of anthropogenic origin, whose emission is estimated at 45×10^6 t/year. (Miyazaki, Eskes and Sudo, 2012).

Although the emissions of nitrogen oxides of anthropogenic origin make up about 1/10 of total emissions, it is very important for air pollution, especially urban and industrial areas, where nitrogen oxides production is mainly concentrated. Basic stationary sources are: steam generators with conventional fuels, power plants, domestic heating, incinerators, heating processes, emissions from other sources (chemical production). In addition to stationary nitrogen oxide sources, significant sources are motor vehicles. Nitrogen oxides in the combustion process are formed thermally - in the flames of the present nitrogen and oxygen and by the oxidation of nitrogen compounds containing fuel. The degree of conversion of nitrogen compounds from coal to nitrogen oxides depends on the fuel / air ratio and temperature, if standard burners are used. Increase in air volume leads to increased nitrogen oxide emissions. The amount of nitrogen oxide produced from fuels such as coal and oil derivatives can exceed 50%. The fraction of the nitrogen oxide is produced in some industrial processes, among which the processes of electric metal application are, metal cleaning, by nitric acid production, refineries, and similar process. The content of nitrogen oxides in urban areas is much higher than in non-urban areas. (Đuković, 2000).

The aim of this paper is to examine the corrosion behavior of metals, metal coatings and alloys, both visually and electrochemically. Our goal is to examine their behavior in different environments and compare them with different atmospheric constituents in those environments. (Presuel-Moreno *et al.*, 2008).

EXPERIMENTAL

As samples an iron plate, chrome coated iron plate with worn out surface, zinc coated iron plate with worn out surface and brass plate were used.

The methods used were: visual examination, linear voltammetry and cyclic voltammetry (Geler *et al.*, 1997).

RESULTS AND DISCUSSION

Setting up a meteorological station

Due to the great influence of meteorological parameters on the content of individual components in the atmosphere and, consequently, on the processes of atmospheric corrosion, the first meteorological station was installed at the Department of Chemistry for the purposes of this research. The meteorological station was used to measure parameters such as pressure, temperature, rainfall, humidity, wind speed and wind direction, and is equipped with data acquisition and storage. The weather station was set up to measure these parameters every 30 minutes.

Sampling of precipitation

Sampling of precipitation was done on the roof of the Faculty of Science in Sarajevo and from the area of Kiseljak. Location of the measurement station on the roof of the Faculty is a typical urban area that is about 20 meters away from the main road. The location in Kiseljak represents an area that is much less urban sampling location. Precipitation patterns were used to test the pH value and electrical conductivity. Also, the sampling of precipitation was performed at a same time when the samples were exposed to the atmosphere.

Determination of pH value and conductivity

The pH value represents the chemical quality indicator of atmospheric water. The pH value of a natural, unpolluted rainfall is between 5 and 6.

The following table shows the measured values of pH and electrical conductivity in precipitation samples.

Table 1. Measured values of pH and electrical conductivity in the area of Sarajevo

Sample	Date	pH	κ (mS/cm)
1.	27.11.2017.	4,93	0,0620
2.	3.12.2017.	5,02	0,0480
3.	9.12-10.12. 2017.	6,40	0,1480
4.	13.12.2017.	6,04	0,0630
5.	15.12 - 8.12. 2017.	5,28	0,0650
6.	29.12.2017.	7,55	0,0719
7.	3.1.2018.	6,60	0,0526
8.	10.1.2018.	6,20	0,0334
9.	14.1.2018.	6,35	0,0471
10.	17.1.2018.	5,92	0,0250
11.	21.1.2018.	6,50	0,0260
12.	23.1.2018.	6,60	0,0460
13.	3.2.2018.	6,50	0,0402
14.	7.2.2018.	6,70	0,0379

Table 2. Measured values of pH and electrical conductivity in the area of Kiseljak

Sample	Date	pH	κ (mS/cm)
1.	3. 11. 2017.	5,30	0,0102
2.	9. 12. 2017.	5,33	0,0278
3.	11. 12. 2017.	6,17	0,0376
4.	19. 12. 2017.	6,66	0,0458

The acidity of the rainwater ranges from 5 to 6.5 and there is no major deviation. Electrical conductivity represents an indirect measure for the total amount of dissolved substances in water. No significant changes where observed here also.

Samples of metals and alloys and their exposure to the atmosphere

The thickness of the coating of chromium and zinc applied to the plates was determined by the x - ray diffraction method. Tables 3 and 4 show the results.

Table 3. Chromium, nickel and copper coating thickness

#	Sample	Cr (μm)	Ni (μm)	Cu (μm)
1	Chrome coated iron plate with worn out surface – desiccator	0,585	4,39	5,04
2	Chrome coated iron plate with worn out surface – Sarajevo	0,626	4,98	4,93
3	Chrome coated iron plate with worn out surface – Kiseljak	0,477	14,10	8,36

Table 4. Zinc coating thickness

#	Sample	Zn (μm)
1	Zinc coated iron plate with worn out surface - desiccator	5,32
2	Zinc coated iron plate – Sarajevo	6,03
3	Zinc coated iron plate with worn out surface – Sarajevo	6,02
4	Zinc coated iron plate with worn out surface – Kiseljak	5,81

The samples were placed in acetone, where there were no visible signs of corrosion and were placed in three different "atmospheres". The first set of samples was placed in a desiccator, so it was not exposed to external influences of the atmosphere. The second set of samples was set up on the roof of the Natural and Mathematical Faculty and exposed to the atmosphere. The third series of samples were placed in the area of Kiseljak. Samples were exposed to the atmosphere in period from 14.11.2017. to 26.3.2018.

Iron   Brass

Chrome coated iron plate with worn out surface

Zinc coated iron plate with worn out surface

Figure 1. Samples before exposure in Sarajevo area

Analysis of samples

The analysis of the samples was performed after exposure to the outside environment in the period of time from 14.11.2017. to 26.3.2018. The methods used were: visual method and electrochemical methods.

Visual method

After the samples were removed from the outside environment, a visual examination method was performed. The images show iron samples after removal from the outside.

As can be seen from the figures, the iron that was in the desiccator has no visible corrosion products. Also, one can notice the color difference of corrosion products between the iron samples exhibited in the Kiseljak area and the iron that was exposed to the atmospheric conditions in the area of Sarajevo. This difference can be attributed to the different content of the individual components of the atmosphere in which these samples were exposed. It is evident that the corrosion of objects in Sarajevo is more intense.

Figures show that the brass from the desiccator has no visible corrosion products. The sample of brass that was exposed to atmosphere in Kiseljak, showed corrosion. This result can be explained by the brass characteristics and its reaction to the environment. The difference between the corrosion products between the brass which was exposed in the area of Kiseljak and the brass that was exposed in the area of Sarajevo, when excluding the experimental error, cannot be visually determined. The possible reason for this is that patina can be formed in environments that are not burdened with pollutants.

Chrome coated iron plate with worn out surface exposed to the atmosphere: it can be seen that the sample has no visible signs of corrosion. The difference between chrome coated iron samples that were exposed in two different atmospheres can be seen in the color of corrosion products. Also, the chrome coated iron that was exposed in the area of Sarajevo was more intensely corroded on other parts of the plate as well as on the part where it was worn out. Since the compactness of the chrome coating has been damaged, iron corrosion has occurred since iron pair potential is more negative than chrome pair potential. Iron behaved as anode and oxidized in a given conditions.

The samples of zinc coated iron with worn out surface that were exposed to atmospheric effect are shown: from figures it can be seen that zinc coated iron from the desiccator has no visible signs of corrosion. The difference between the samples that were exposed in two different atmospheric environments is seen in the corrosion intensity and color of the products of corrosion. Even when the zinc-coated layer was worn out, corrosion was not detected because zinc had a good protective role.

Sample	Desiccator	Kiseljak	Sarajevo
Iron			
Brass			
Chrome coated iron plate with worn out surface			
Zinc coated iron plate with worn out surface			

Figure 2. Samples after exposure to the atmosphere

Electrochemical methods

Electrochemical methods used for sample analysis were linear voltammetry and cyclic voltammetry. After the atmosphere exposure, the samples were prepared by isolating the surface of plate, except 1 cm² which was the active surface for electrochemical measurements. (Korać et al, 2013)

Linear voltammetry

Potentiodynamic measurements were performed by linear voltammetry in a given range of potentials depending on the sample type at a scan rate of 0.166 mV/s and 1 mV/s. The measurements were performed in a three electrode system, where sample was working electrode, Ag/AgCl reference electrode, and platinum electrode as a counter electrode providing the current flow through the cell. As electrolyte, 3% NaCl solution was used. The cell is connected to the

Potentiostat/Galvanostat PAR 263A instrument with PowerCV controlled software (Korać et al, 2012).

Tafel extrapolation of voltammograms for each sample gave the values of Tafel constants βa and βc, corrosion potential E_{corr}, corrosion current i_{corr} and the value of the polarization resistance Rp. Based on the polarization resistance it is possible to calculate the rate of corrosion.

The obtained results of electrochemical methods are shown in the Tafel diagrams in Figures 3,4,5 and 6. From these curves the corrosion parameters shown in Table 5 are derived.
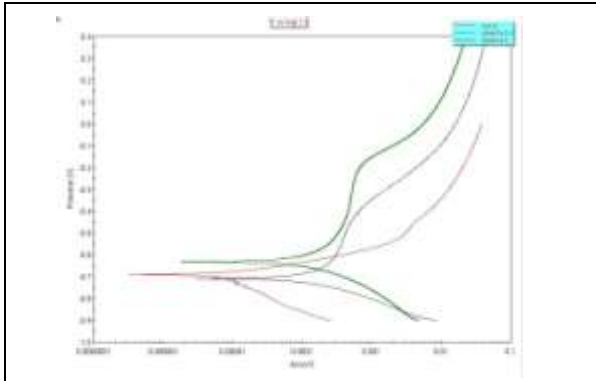
Figure 3. Tafel plots of iron samples from 3 different environments. Red – Desiccator, Green – Sarajevo, Black – Kiseljak.
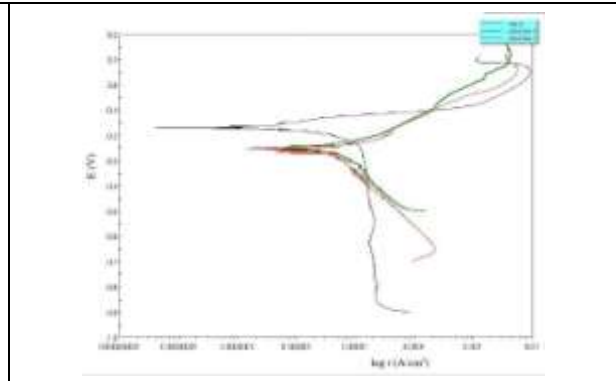

Figure 4. Tafel plots of brass samples from 3 different environments. Black – Desiccator, Green – Sarajevo, Red – Kiseljak.
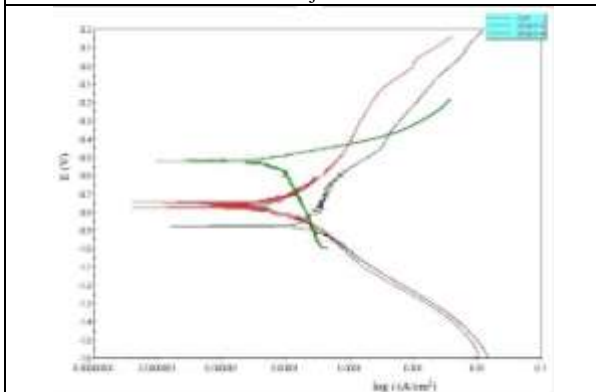

Figure 5. Tafel plots of chrome coated iron with worn out surface samples from 3 different environments. Green – Desiccator, Black – Sarajevo, Red – Kiseljak.
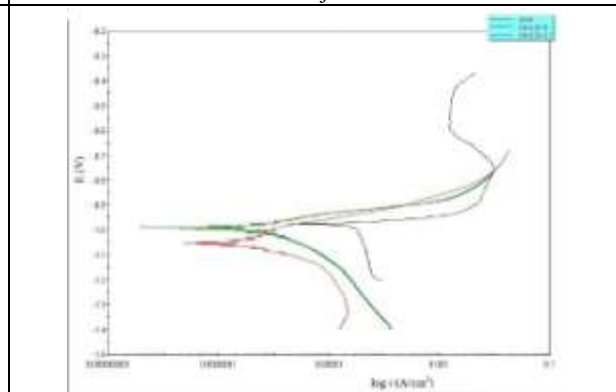

Figure 6. Tafel plots of zinc coated iron with worn out surface samples from 3 different environments. Black – Desiccator, Green – Sarajevo, Red – Kiseljak.

Table 5. Values of Corrosion Potential, Current, Tafels Constants and Polarization Resistance

Sample	Atmosphere	E_{corr} (mV)	I_{corr} (µA)	βc (mV)	βa (mV)	Rp (Ω)
Iron	Desiccator	-695,288	7,802	161,095	60,768	3202,690
	Kiseljak	-705,605	24,750	99,223	130,618	818,570
	Sarajevo	-631,916	20,860	89,355	147,490	1542,990
Brass	Desiccator	-153,151	2,03	60,88	30,106	10950,97
	Kiseljak	-256,096	3,763	223,057	92,198	9689,935
	Sarajevo	-248,947	3,804	169,495	64,586	6510,677
Chrome coated iron with worn out surface	Desiccator	-517,563	4,356	190,274	62,609	20861,723
	Kiseljak	-756,595	9,859	264,045	277,250	4683,620
	Sarajevo	-854,572	6,240	236,306	660,776	3009,945
Zinc coated iron with worn out surface	Desiccator	-981,415	8,907	625,970	25,098	6947,269
	Kiseljak	-1053,536	1,050	60,747	89,264	10686,568
	Sarajevo	-982,829	2,100	102,552	46,956	18906,150

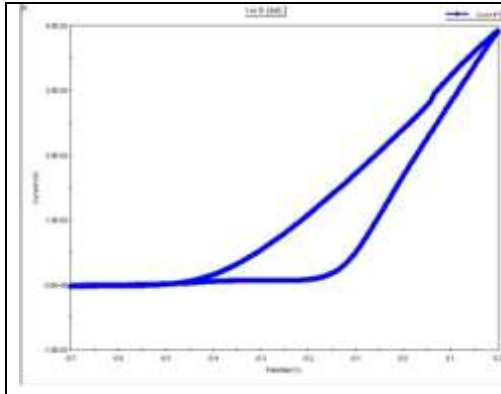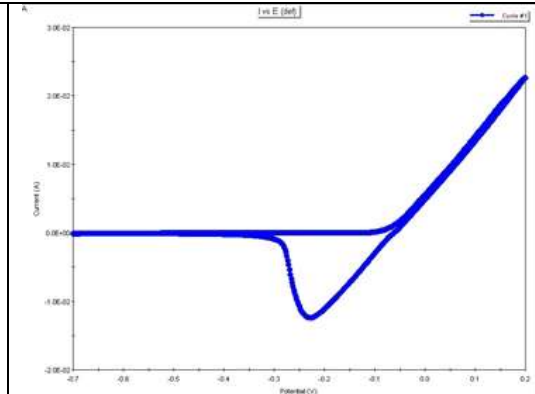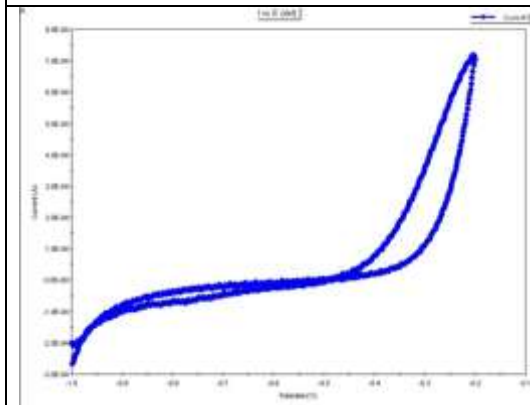| **Figure 7.** Cyclic voltammogram of iron sample from desiccator	**Figure 8.** Cyclic voltammogram of brass sample from desiccator

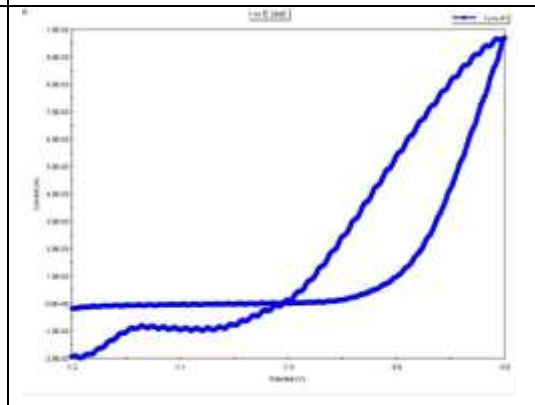| **Figure 9.** Cyclic voltammogram of chrome coated iron with worn out surface sample	**Figure 10.** Cyclic voltammogram zinc coated iron with worn out surface

Table 6. Values of pitting potential and repassivation potential

Sample	Location	E_{pit} (mV)	E_{rp} (mV)
Iron	Desiccator	-0,1938	-0,5098
Brass	Desiccator	-0,03139	-0,8467
Chrome coated iron with worn out surface	Desiccator	-0,3932	-0,4965
Zinc coated iron with worn out surface	Desiccator	-0,9393	-1,007

Iron

First, a voltammogram of iron that was exposed in the desiccator was recorded at a scan rate of **0.166 mV**/s with a potential range between -0.95 and 0.4 V, and then samples of iron were exposed in Kiseljak and Sarajevo area were recorded at the scan rate of 0.**166 mV/s** the in potential range between -0.95 and 0.4 V.

From the obtained values, it can be concluded that the sample from Kiseljak shows the lowest polarization resistance, and the highest value of the corrosion current. The iron that was exposed in the desiccator shows the highest value of polarization resistance, and the lowest corrosion current.

Brass

Desiccator brass was recorded in a potential range between -0.9 and 0.2 V at a scan rate of 0.166 mV/s. Brass samples that were exposed in the area of Sarajevo and Kiseljak were recorded in the potential range between -0.7 and 0.2 V at a scan rate of 0.166 mV/s.

From the obtained values it can be concluded that the brass exposed in the area of Sarajevo has the lowest value of the polarization resistance and the highest value of the corrosion current. The Tafel diagrams show clearly the section of passivating properties of the corrosion products.

Chrome coated iron whose surface is worn out

Samples of chrome coated iron whose surface was worn out were recorded in the potential range between -1.6 and 0.2 V. The sample from the desiccator was recorded at a scan rate of 0.166 mV/s, while the samples that were exposed in the area of Kiseljak and Sarajevo were recorded at a scan rate of 0.166 mV/s. From these obtained values it can be concluded that the chrome coated iron sample whose surface is worn out from the desiccator has the highest value of the polarization resistance and the lowest value of the corrosion current. The corrosion potential of the sample from the desiccator is most positive – it can be attributed to

chromium. The other two are those in which the iron oxidation process begins and slowly reaches the potential of iron, which is more negative.

Zinc coated iron whose surface is worn out
Samples of zinc coated iron whose surface was worn out were recorded in the range of potentials from -1.4 to -0.4 V. The sample from the desiccator was recorded at a scan rate of 0.166 mV/s, while the samples that were exposed in the area of Kiseljak and Sarajevo recorded at a scan rate of 0,166 mV/s. From the obtained values of corrosion potentials, it can be concluded that there are no significant changes in the corrosion parameters. There was no critical degradation of zinc, so it retained protector properties.Also, these samples show no significant changes in corrosion parameters.

Cyclic voltammetry
Samples for measuring this method were prepared in the same way as for linear voltammetry. This method was used to capture samples that were exposed in the desiccator.
The results obtained by this method are shown in the cyclovoltammograms in Figures 7, 8, 9 and 10. The corrosion parameters shown in Table 6 are derived from these voltammograms.

Iron
A sample of iron from the desiccator was recorded in the potential range of -0.7 - 0.2 V, at a scan rate of 1 mV/s. Cyclic voltammogram (CV) shows no peaks obtained in the selected range of potentials.

Brass
The brass sample from the desiccator was recorded in the potential range of -0.7 - 0.2 V at a scan rate of 1 mV/s. On voltammograms of brass, there is a defined reduction peak at about -0.25 V, which corresponds to processes related to the reduction of oxidized species of copper.

Chrome coated iron whit worn out surface
The CV of sample of chrome coated iron whit worn out surface is recorded in the potential range of -1.0 V to -0.1 V at a scan rate of 1 mV/s. On this voltammogram, peaks occur at potentials of around -0.75 V. This may suggest that chrome coating no longer protects iron. The compactness of the coating is disturbed, and iron, as a more negative one, gets the role of anode and corrodes.

Zinc coated iron whit worn out surface
A CV of a zinc coated iron sample whose surface is worn out is recorded in a potential range of -1.2 V to -0.8 V at a scan rate of 1 mV/s. The cyclic voltammogram of this sample is similar to the sample of a not worn out one. There was no disturbance in the zinc protective properties, even though it is worn out.

CONCLUSIONS

An iron plate, chrome coated iron plate with worn out surface, zinc coated iron plate with worn out surface and brass plate were used as samples.
The analysis of the samples was carried out after exposure to the outside environment in the period between 14.November 2017 to 26.March 2018. The methods used are: visual method and electrochemical methods. Based on the obtained results, the following conclusions are:
• Iron in the desiccator has no visible corrosion products, while the samples from Sarajevo and Kiseljak show more corrosion
• The brass that was in the desiccator has no visible corrosion products. On brass sample, from both tested areas of Kiseljak and of Sarajevo, layer of patina was seen;
• The chromium-iron sample whose coating was frozen, has no visible signs of corrosion. The difference between samples of chromium iron exposed in two different atmospheres can be seen in the color of corrosion products;
• Galvanized iron with a sealed coat kept in desiccator has no visible signs of corrosion. Even when the zinc-coated layer was not corrosive, zinc had a good protective role.
Tafel extrapolation of the shown voltammograms for each sample determined the values of Tafel constants βa and βc, corrosion potential E_{corr}, corrosion current i_{corr} and the value of the polarization resistance Rp. Based on the polarization resistance it is possible to calculate the rate of corrosion.
• Iron sample from Kiseljak shows the lowest polarization resistance, and thus the highest value of corrosion. The iron that was kept in the desiccator shows the highest value of the polarization resistance, and thus the lowest corrosion current.
• From the obtained values, it can be concluded that the brass exposed in the area of Sarajevo has the lowest value of the polarization resistance and the highest value of the corrosion current. On the Tafel plots, it is possible to clearly see the sections showing the passivating properties of the products of corrosion.
• Chrome coated iron sample whose surface is worn out from the desiccator has the highest value of the polarization resistance and the highest value of the corrosion potential. The corrosion potential of the sample from the desiccator is the most positive - belongs to the chromium. The other two are those in which the iron oxidation process begins and slowly reaches the potential of iron, which is more negative.
• The zinc coated iron sample from the desiccator has the highest value of corrosion current and the lowest value of the polarization resistance. Also, in these samples there are no significant changes in corrosion parameters. There was no critical degradation of zinc, so it retained protective properties.

Cyclic voltammetry provides following data:
• CV of iron shows no detected peaks in the selected potential range.

• CV of brass shows a defined reduction peak at a value of about -0.25 V, which corresponds to processes related to the reduction of oxidized species of copper.

• CV of chrome coated iron shows the peak at a value of about -0.75V. This suggests that chrome coating no longer protects iron. The compactness of the coating is disturbed, and iron, as a more negative one, gets the role of anode and corrodes.

• CV of zinc coated iron with worn out surface is similar to that which has no worn out surface. There was no disturbance in the zinc protective properties, even though it is worn out.

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Summary/Sažetak

Brzina atmosferske korozije je funkcija sadržaja pojedinih komponenata u atmosferi i temperature vazduha, prvenstveno se misli na sadržaj vlage, različitih čestica i gasova SOx i NOx. Ispiranjem polutanata nastaju jake kiseline, baze i soli koje mogu da nagrizaju različite metalne i nemetalne konstrukcije.

Izvršena je analiza određenih parametara kvaliteta padavina, analiza uzoraka metala i legura koji su bili izloženi atmosferi na području Sarajeva i Kiseljaka, te analiza uzoraka metala i legura bez atmosferskog uticaja. Metode analize uzoraka koje su korištene su linearna voltametrija i ciklična voltametrija. Kao uzorci su korištene pločice željeza, hromiranog željeza, pocinčanog željeza, hromiranog željeza čija je površina bila zaparana, pocinčanog željeza čija je površina bila zaparana i pločica mesinga.Vidljivo je da je intenzivnija korozija predmeta u Sarajevu. Nešto manje je u području Kiseljaka. Linearna voltametrija u određenom rasponu potencijala dala su izraženije korozione struje u urbanoj sredini.

Ciklična voltametrija kod mesinga je javlja izraženi redukcioni pik na vrijednosti od oko -0,25 V. Kod hromiranog željeza se javlja na -0,05 V. Kod pocinčanog željeza potencijali su pomjereni prema negativnijim vrijednostima koji pripadaju cinku. Na ciklovoltamogramu kod zaparane hromne prevlake je na -0,75V. Ciklični voltamogram zaparanog cinka je sličan onom koji nije zaparan. Urbano područje Sarajeva, značajno opterećeno polutantima koji mogu uticati na sve aspekte života i okoline. Izražena je pojava kiselih kiša, što pojačava korozione osobine materijala od kojih su izgrađene konstrukcije.