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EVALUATION OF CORROSION BEHAVIOUR BY GRAVIMETRIC METHOD

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ABSTRACT

The study aims to evaluate the corrosion behaviour of two steels: BL245 and S235JR, produced at Liberty Steel Galati. BL245 is an alloy used in the oil and gas industry to manufacture pipes for pipeline transportation systems. S235JR is used to make hot finished hollow sections for construction. Gasoline, diesel and a 3.5% sodium chloride solution were chosen as corrosion environments for this study, considering the field of use of the two alloys (oil and construction). Corrosion assessment was analysed using the gravimetric method, which is based on weighing the samples before and after they were immersed for 7, 14, and 35 days in the above-mentioned corrosion environments. Based on the initial weighing and those recorded after the immersion periods, the mass variation of the samples was determined, and the corrosion rate and penetration index were calculated.

KEYWORDS: corrosion, gravimetric method, corrosion rate, penetration index, steel

1. Introduction

The concept of corrosion includes all chemical, electrochemical and biochemical processes resulting in spontaneous and continuous degradation of metal and alloy surfaces [1]. Chemical corrosion is triggered in dry gases, at high temperatures and in non-electrolyte solutions (corrosion is not accompanied by the appearance of an electric current) [2]. Electrochemical corrosion follows the laws of electrochemical kinetics and is accompanied by the appearance of an electric current (corrosion in electrolyte solutions or wet gases) [3]. Microbiological corrosion is a form of corrosion produced by living micro-organisms (bacteria, algae or fungi) often associated with the presence of organic substances and often accompanies electrochemical corrosion [4].

Corrosion is one of the most serious problems of modern society and an important scientific research topic. Corrosion of metals and materials is also an important problem both industrially and economically [5], with losses of billions of dollars every year [1]. A study published in 2016 on the cost of corrosion worldwide shows that the highest costs due to corrosion are found in Europe (28%), followed by the USA and China, as shown in Figure 1 [6].

Corrosion, as a chemical, electrochemical and biochemical process, has been studied over the years by several scientists, who have analysed in their experiments different alloys used in several branches of industry, using various methods and materials.

***Fig. 1.** The cost of corrosion in the world in 2016* [6]

Some authors have analysed the corrosion behaviour of two types of carbon steel (OLC-45 and OL-37), used in the shipyards of Galati and Constanta. Two natural seawater salts collected from the Black Sea (Constanta area) and the Aegean Sea

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(Athen's area) were used as corrosion environments. By gravimetric method, following the calculations, it was found that the corrosion rate increases linearly with time and then remains constant, indicating that the corrosion product film formed on the surface of these two materials is more compact and provides better corrosion protection [1]. The results obtained throughout the study also revealed that the Aegean Sea, where both chloride and sulphate concentrations are almost double that of the Black Sea (indicating higher salinity) is a more corrosive environment compared to the Black Sea [7].

Some researchers have studied the behaviour of equipment in refineries and petrochemical plants in working environments. Samples of the steels from which refinery equipment is made were immersed in diesel fuel with sulphur compounds in a nitrogen atmosphere. The tests showed lower corrosion rates than measured and observed in the presence of air, which demonstrated the contribution of oxygen in the process fluid to the corrosion intensification, due to increased acidity caused by the oxidation reactions [8].

Another study on the corrosion of steels used in the manufacture of drill pipes and water-carrying pipes accompanying natural gas fields in contact with reservoir waters shows the salts dissolved in these waters greatly favour corrosion [9]. The retention time of the samples in the immersion environments was between 24-336 h. The results obtained indicate that the corrosion rate decreases with time and that the reservoir waters, due to the chlorides in their composition, show a high corrosion effect on the steel [10].

2. Materials and methods

The materials under investigation in this experiment are two types of steel manufactured at Liberty Steel Galati for industrial use: BL245 used in the oil industry to manufacture pipes for transportation systems and S235JR used in construction. According to the analysis bulletins issued by Total Materia, the chemical composition is shown in Table 1.

Table 1. *The chemical composition of steels BL245 and S235JR (%)* [11]

Proba	C	Cu	Mn	N	P	S	Si	V	Ti
BL245	0.22	-	1.20	0.05	0.025	0.015	0.45	0.05	0.04
S235JR	0.17	0.55	1.5	0.01	0.05	0.05	0.03	-	-

The corrosion environments gasoline, diesel and 3.5% NaCl solution were chosen for this study because of the areas in which the two types of steels are used, thus evaluating their corrosion resistance.

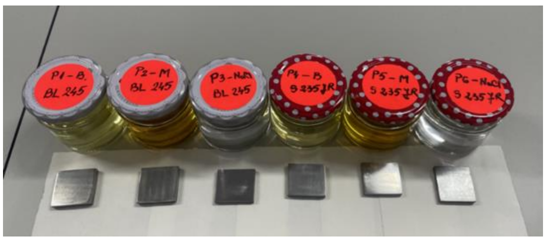

Fig. 2. *Samples prepared for immersion*

The first part of this experiment includes sample preparation. The six samples of the investigated materials have a parallelepiped shape and approximately equal dimensions (335 x 330 x 60 mm). Sanding was performed manually on three metallographic papers, starting with 800 grit, following 1000 grit and ending with 1200 grit. The purpose of sanding was to obtain perfectly flat, scratch-free, high-gloss surfaces. At the end of the sanding operation, the samples were washed under a water jet to remove traces of abrasive or metal dust, and then dried by wiping. The final stage of sample preparation included degreasing with acetone and blot drying with filter paper. Figure 2, below, illustrates the samples prepared for immersion.

The method chosen to assess corrosion compaction was gravimetric analysis. This method involves weighing the samples used in the experiment on an analytical balance before and after immersion in the corrosion environment [12]. Thus, the samples were weighed before and after each immersion period: 7, 14 and 35 days. Using the obtained data, after each weighing, the corrosion rate and penetration index were calculated using the formulas:

- corrosion rate:

$$V_{cor} = \frac{\Delta_m}{S \cdot t} \text{ [g/m}^2\text{h] [13]} \qquad (1)$$

where:

Δ_m - change in mass [g];
S - area of sample [m^2];
t - immersion period [h].

- penetration index with the formula:

$$P = \frac{24 \cdot 365 \cdot V_{cor}}{1000 \cdot \rho} \text{[mm/an] [13]} \qquad (2)$$

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V_{cor} - corrosion rate; ρ - density of steel, in our case, having the value of 7.4 g/cm³ for BL245 steel and 7.8 g/cm³ for S235JR.

3. Results and discussions

After calculations using the formulas for corrosion rate and penetration index, the results are shown in the graphs below.

From Figure 3, the BL245 alloy shows the corrosion rate with the highest value in 3.5% NaCl solution, regardless of the immersion period. It is also observed that in 3.5% NaCl solution, the corrosion rate is accelerated in the first immersion period of 7 days and then starts to decrease. In the case of gasoline, experimental data show an increase in the corrosion rate value with increasing immersion time. In diesel, a sharp increase in the corrosion values is observed in the second immersion period and then a decrease.

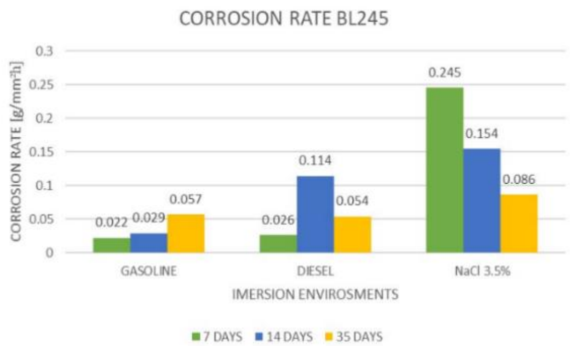


Fig. 3. *Corrosion rate values obtained for BL245*

Figure 4 shows the corrosion rate values obtained for the S235JR alloy. It can be seen that the corrosion rate is higher in the 3.5% NaCl solution that the other two environments in all immersion periods. In diesel, there was an increase in the first two immersion periods (7 and 14 days), followed by a sharp decrease in the third period (after 35 days). In gasoline, the corrosion rate is approximately equal, not exceeding a value of 0.027 [g/mm²*h].

Comparing the results obtained for the corrosion rate for the two materials, it is observed that the BL245 alloy shows a higher corrosion rate in all three environments, regardless of the immersion duration.

Figures 5 and 6 show the penetration index values for the two types of analysed steel in this study. Both graphs show that the highest values of the penetration index are recorded in the 3.5% NaCl solution in all immersion periods.

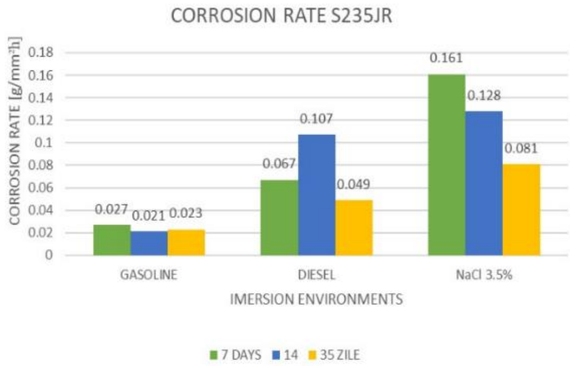


Fig. 4. *Corrosion rate values obtained for S235JR*

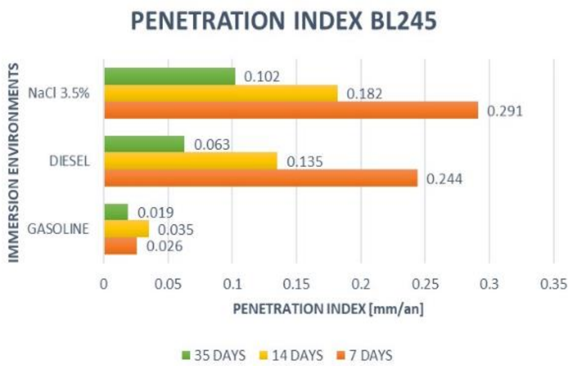


Fig. 5. *Penetration index values obtained for BL245*

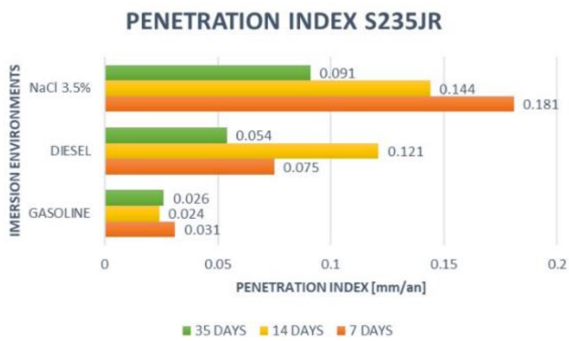


Fig. 6. *Penetration index values obtained for S235JR*

In comparison, it can be seen that the BL245 alloy shows the highest values, which increase with the immersion time. In diesel, the BL245 steel shows increasing values over time, while for the S235JR steel, the penetration index increases in value in the first two periods (7 and 14 days), sharply decreasing in the third period of the experiment. This may indicate the formation of continuous and adherent corrosion products on the surface of the material that provides better corrosion protection as concluded by other authors [1]. The same is observed for the BL245 steel in gasoline.

In order to determine whether the investigated materials are corrosion resistant, the conventional corrosion resistance scale for metals was consulted. Its values are: 0.001 mm/year for perfectly stable metals, 0.01-0.1 mm/year for stable metals, 0.1-1 mm/year for relatively stable metals and 10 mm/year for unstable metals [14]. The resulting values from graphs 5 and 6 indicate the following: both samples are stable in diesel, gasoline and relatively stable in 3.5% NaCl solution, as shown in Figure 7.

The corrosion products resulting from immersion in 3.5% NaCl solution are solid and adherent to the surface (which is also evident from the corrosion rate value which is higher in the first immersion period) shallow pitting type [13].

Also, for the samples immersed in NaCl 3.5%, the ferroxalic indicator was used to perform the drop test (Ewans), where the presence of Fe^{2+} ions and OH^{-} ions were detected. It was observed the variable and inhomogeneous appearance of pink and blue spots, indicating the following: the pink portion corresponds to the cathodic portion (presence of Fe^{2+} ions) and the blue portion to the anodic portion (presence of OH^{-} ions) [13], as shown in Figures 10 and 11.

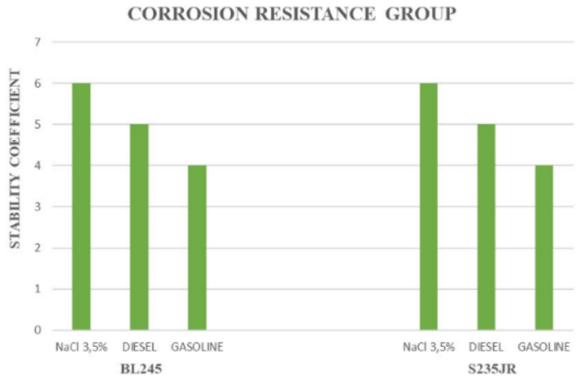
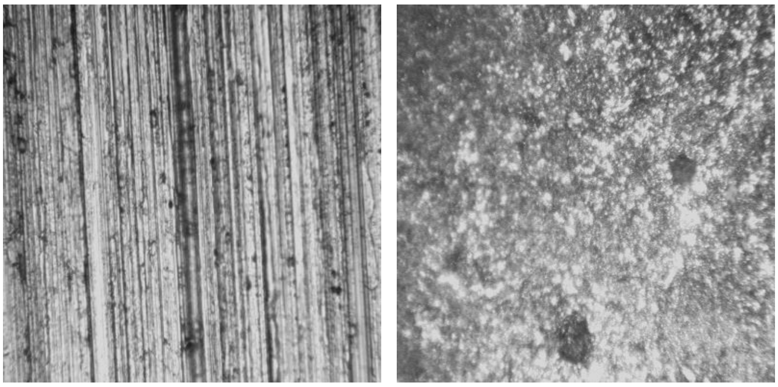


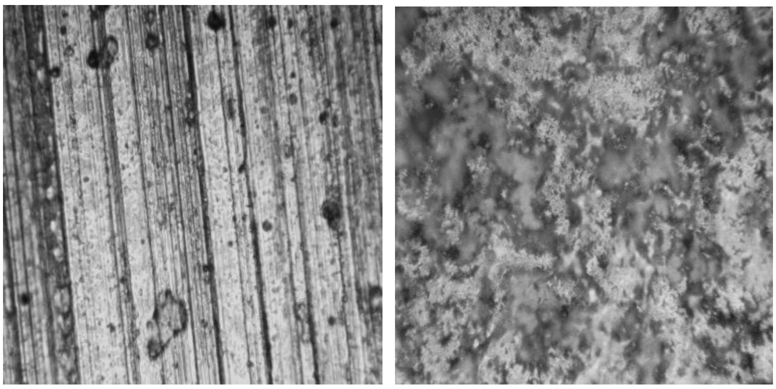
Fig. 7. *Corrosion resistace group for BL245 and S235JR*

Using the Kern optical microscope in the laboratory, optical scanning micrographs (X50) were taken of both samples undergoing the experiment, before and after 35 days of immersion in 3.5% NaCl solution, to better highlight the corrosion products, as shown in Figure 8 and 9.



a) b)

Fig. 8. *Optical scanning micrographs(X50) for BL245: a) initial; b) after 35 days in 3.5% NaCl*



a) b)

Fig. 9. *Optical scanning micrographs(X50) for S235JR: a) initial; b) after 35 days in 3.5 % NaCl*

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Fig. 10. *The presence of ions of Fe^{2+} and OH^- for BL245*

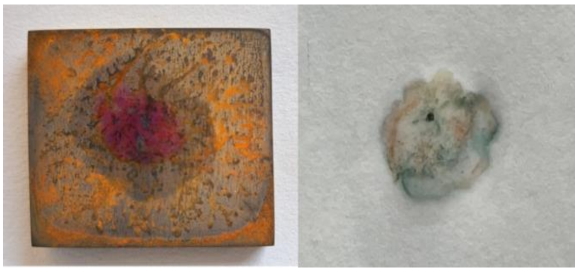

Fig. 11. *The presence of ions of Fe^{2+} and OH^- for S235JR*

4. Conclusions

In this experiment, the corrosion behaviour of the two steels BL245 and S235 JR, used in the oil industry and construction was studied. Gasoline, diesel and 3.5% NaCl solution were chosen as corrosion environments. Three immersion periods were established: 7, 14 and 35 days.

The gravimetric method was used for the study, calculating the corrosion rate and penetration index. After processing the obtained data, the following was discovered:

- the highest corrosion rate value is recorded after 7 days of immersion in 3.5% NaCl for the BL245 sample;
- the lowest corrosion rate value is recorded for the S235JR sample immersed in gasoline for 14 days;
- also, both alloys have a higher corrosion rate in 3.5% NaCl, regardless of the immersion period, indicating that the presence of chlorine in the immersion solution accelerates the corrosion rate;
- the highest penetration index values are observed for the BL245 alloy, regardless of the immersion time;
- the penetration index is higher in the 3.5% NaCl solution than in the other two immersion environments for all three periods of exposure to the corrosive environment;
- fitting the obtained data in the experiment in the conventional material strength scale, it is observed that both investigated steel alloys are stable in diesel and gasoline and relatively stable in 3.5% NaCl solution.

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