PITTING CORROSION BEHAVIOUR OF ST 37 STRUCTURAL STEEL IN SEVERAL CORROSIVE ENVIRONMENTS

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ABSTRACT: St37 is constructional steel having maximum 0.17 % carbon ratio, and its fracture strength is between 360-510 MPa. It is used to increase the mechanical properties as rebar material in composite concrete systems. Pitting corrosion is one of the most dangerous detrimental mechanisms for the reinforcing rebar because it is widespread, difficult to control and it has degrading effects in the material. For these reasons, the pitting corrosion behavior of St37 is investigated with respect to the salinity rate of the Black Sea and the Mediterranean Sea to observe the influence of salt to the reinforcing rebars of buildings used in these regions. Several standards such as EN, ASTM or ISO could be used for the pitting corrosion experiments but the authors have decided to develop their own procedure to become as standard protocol for this research. Cutting from plate, St37 dogbone specimens are prepared two for pristine, two for 3.5 % NaCl solution and two for 1.8 % NaCl solution and they are sanded with sandpapers to obtain clean surfaces. To observe corrosion distinctly and giving ID numbers to the pits, the corrosion exposed area is adjusted to 1 mm^2 and the rest of the specimens are painted with nail polish. 1.8 % and 3.5 % are the salinity rates of the Black Sea and the Mediterranean Sea respectively, two different solutions are prepared and the dogbone specimens are immersed into these solutions based on the determined corrosion protocols. Pre-corroded specimens are then investigated under optical microscope to identify and measure the corrosion pits and these specimens are put to tensile test to obtain the stress-strain curves of the same specimens. The surfaces of the specimens are characterized by using Scanning Electron Microscope (SEM) to identify where the fracture originated from. The %3.5

salinity rate results more pits on the surface, deeper pits from the surface and the 1.8 % salinity rate results less pits on the surface and shallower from the surface. Moreover, it is observed that increase in salinity rate decrease the mechanical properties after tensile testing results.

Key words: Construction, Steel, Salinity, Pitting Corrosion

INTRODUCTION

Due to the low cost and availability of materials, steel-reinforced concrete composites are the most commonly used structural materials. The most important parts of these composite systems are reinforced steel rebars because of their load carrying capabilities. The steel is selected from structural steels and the most used one is St37. In this paper, pitting morphology and mechanical strength of St37 steel is investigated with respect to the salinity rate of the solution. The mechanical properties of steel rebars are strong, but the service problems influence negatively to the permanency of them. For example, due to the wear of concrete, steel rebars may contact with air and they can corrode. Similarly, storing of steel rebars for a long time may result corrosion before servicing of them. According to the ASTM, chemical or electrochemical reaction between a metal and its environment produces a deterioration of material and its properties and this is called corrosion [1]. Pitting corrosion is localized accelerated dissolution of the metal which occurs result of a breakdown of the protective passive film on the metal surface. The metal is not corroded uniformly, but deep pits are produced and these pits reduce the surface area and enhance the stress concentration. The most destructive environments for the pitting corrosion of the structural steels are coastal areas because the structures are subjected to extreme exposure to saline water and this results intrinsic tensions and crackings [2-4]. However, due to the high alkaline properties and passive film layer on metal surface, reinforced steel can bear to the corrosion for a long time. Furthermore, a well pressed concrete has lower permeability and the compounds which are the reason of the corrosion (oxygen, water and chloride) cannot penetrate into the concrete and so cannot reach to the rebars. When the alkalinity level starts to decrease, the material is exposed to the corrosive environment in a higher degree.

The corrosion pits decrease the effective area of the surface that sustain the loads and due to the stress concentration at the bottom of the pits, the cracks will possibly form from these regions. The volume of the corroded rebar expands and makes the reason for the parallel cracks on the rebars inside the concrete. Once these cracks and voids form, concrete is more exposed to atmospheric conditions and the structural member complete its life very rapidly [5-7].

The most important reason of the corrosion of the steel rebar is the penetration of the chloride ions to the concrete. The chloride ions can penetrate to the concrete with the salt inside the sea water or the salt that concrete contains. Although the material loss is very low comparing to the other homogenous corrosion types, the parts of the material may become unusable very rapidly. The pitting corrosion is one the most dangerous corrosion types because detection and prediction of it is very difficult [8-10].

The main purpose of this work is to analyze the effect of the salinity to the corrosion formation of St37 metal.

In the scope of this research project, some specimens are subjected to NaCl solutions with different concentration levels and some pristine specimens are used for comparison reason. The solutions used in this study include 1,8 % NaCl concentration and 3.5 % NaCl concentration respectively. The 1,8 % NaCl concentration represents the salinity rate of Black Sea and the 3.5 % NaCl concentration represents the salinity rate of Mediterranean Sea. After specimens immersed to the solutions, the specimens are taken out to investigate pitting morphology of them. Then, tensile tests are applied to compare the strength of the pre-corroded specimens with the pristine specimens. Lastly, fractured specimens are observed under Scanning Electron Microscope (SEM) to detect the crack initiation points.

METHODS

General Design Considerations

To make this research some standards are obtained such as TS 5731 EN ISO 8044 (corrosion of metals and alloys - basic terms and definitions), TS EN ISO 11130 (corrosion of metals and alloys - alternate immersion test in salt solution), TS EN ISO 11463 (corrosion of metals and alloys - evaluation of pitting corrosion) and TS ISO 11845 (corrosion of metals and alloys- general principles for corrosion testing). However, in this research in house developed protocols have become standards benefitting from these international standards with the decision of the authors to develop their own procedure for the time and labor savings. Therefore, the corrosion procedure of this study was developed by the master students and assistant professors at the Ankara Yildirim Beyazit University Department of Materials Engineering.

St 37 sheet metal was obtained and cut according to the ASTM standards as dogbone specimen shape. Then, the specimens were sanded with sandpapers 120,240,400 and 800 meshes to get smooth surface. After that, they were cleaned with the acetone in the ultrasonic cleaner and designated with ID numbers. In figure 1 (a), the sanded then ultrasonic bathed specimens are showed. The designations of the specimens with the ID numbers are illustrated in figure 1 (b). Some pilot tests were done before the final protocol was established. Six specimens were used firstly, two for 1.8 % salinity rate, two for 3.5% salinity rate and two specimens as pristine. Two pristine specimens were machined and put to the tensile test to compare the mechanical strength with the pre-corroded specimens. The weight of other four specimens was measured to observe the corrosion effect on weights. The specimens were measured with caliper and 1 mm^2 areas were marked at the center of the specimens, representatively showed in figure 2. Except the 1 mm^2 center, the cleaned specimens were applied nail polish.

The reason is to have the corrosion only at the center for examining easily. Oktem [3] and Frantziskonis et al. [11], used the nail polish for the pitting corrosion detection, they made an area which was corroded and remain parts were polished. This shows that nail polish is used in scientific studies to protect the material from corrosion. Polish was applied three layers with 20 minutes drying periods. Drying of the specimens is illustrated in figure 3. Afterward, the solutions were prepared with the precision scales. To immerse four specimens in different beakers, four solutions were prepared, two of them with 3.5 % NaCl and the other two with 1.8 % NaCl. The solutions with 3.5 % NaCl were prepared using 250 ml of distilled water with 15 % H_2O_2 (hydrogen peroxide). The solutions with 1.8 % NaCl were prepared using 250 ml of distilled water with 15 % H_2O_2. The solution pH could change with the specimen corrosion. Hence, the pH values of the solutions were measured before the specimens were immersed.

Next, the specimens were immersed to these solutions 15 minutes periods, after each period the specimens were observed with optical microscope and the process was repeated three times. The immersion procedure and the corroded area are showed in figure 4. End of the process, the pH values of solutions were measured. Then, the specimens put to the ultrasonic cleaner and the nail polish was removed from the specimens. The weight of each cleaned specimen was measured after process. Cleaned four specimens observed with optical microscope. After the solution process, four corroded specimens and two pristine specimens were applied tensile test. Tensile test was applied to them with 2500 N capacity, 0.1 N precision calibrated universal tester. The specimens were pulled with 1 mm/min velocity and the data were recorded. Then, the four fractured specimens were investigated with Scanning Electron Microscope. The relation between the pits and the fracture points were examined by this way. A summary for the experimental procedure is showed in table 1.

Table 1. A Summary of the Experimental Procedure in This Study.

Experiments	Specimen ID	Explanations
Pit Morphology Observation-1	1.8 ID 1	Pitting Morphologies Observed with Optical Microscope in the First Part of The Study.
	1.8 ID 2	
	3.5 ID 1	
	3.5 ID 2	
Tensile Test	PS ID 1	Four Corroded and Two Pristine Specimens were
	PS ID 2	

	1.8 ID 1	Applied Tensile Tests. The Reason is to Investigate The Effect of Corrosion to the Strength.
	1.8 ID 2	
	3.5 ID 1	
	3.5 ID 2	
Scanning Electron Microscope Observation	1.8 ID 1	Four Corroded Specimens were Observed with Scanning Electron Microscope. The reason is to Investigate the Relation of Fracture Points with the Pits.
	1.8 ID 2	
	3.5 ID 1	
	3.5 ID 2	

In table 1, specimen ID designations and experiments with explanations are given. According to the table 1, the 1.8 ID 1 and 1.8 ID 2 are the specimens immersed to 1.8 % NaCl solution and 3.5 ID 1 and 3.5 ID 2 specimens are the specimens immersed to 3.5 % NaCl solution. The PS ID 1 and PS ID 2 specimens are the pristine specimens for tensile test comparisons.

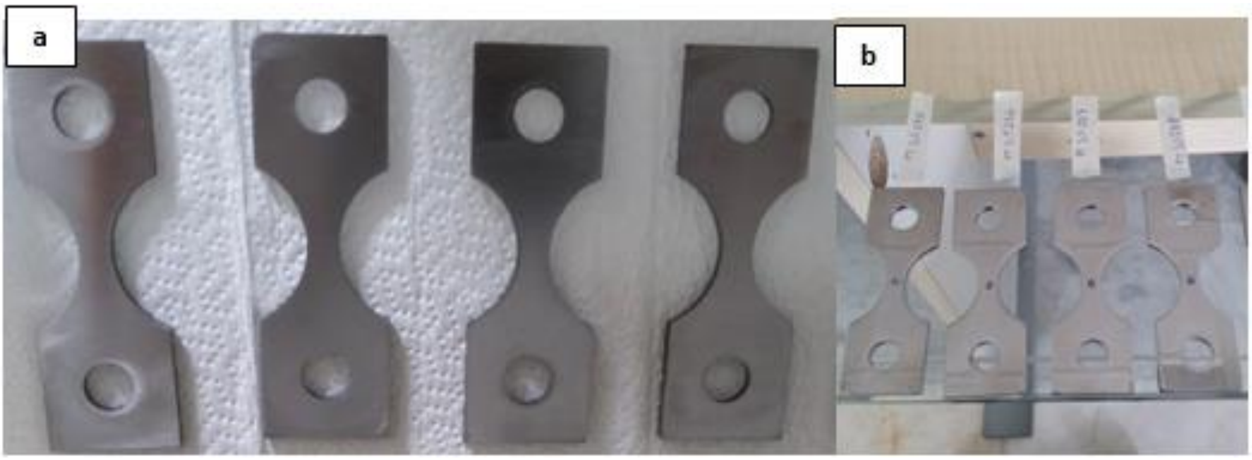


Figure 1. (a) Sanded and Ultrasonic Bathed Specimens (b) ID Numbered Specimens For 3.5 % Salinity Rate Solution

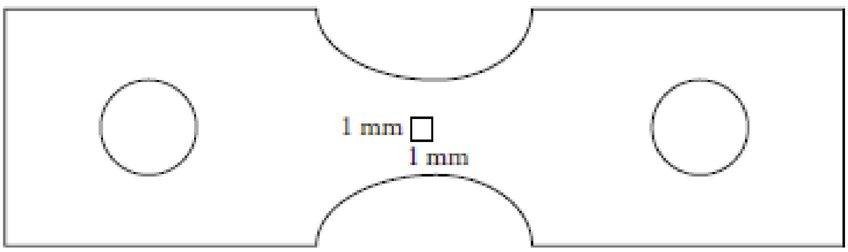


Figure 2. Representative Schematic Specimen and 1 mm^2 Area at the Center

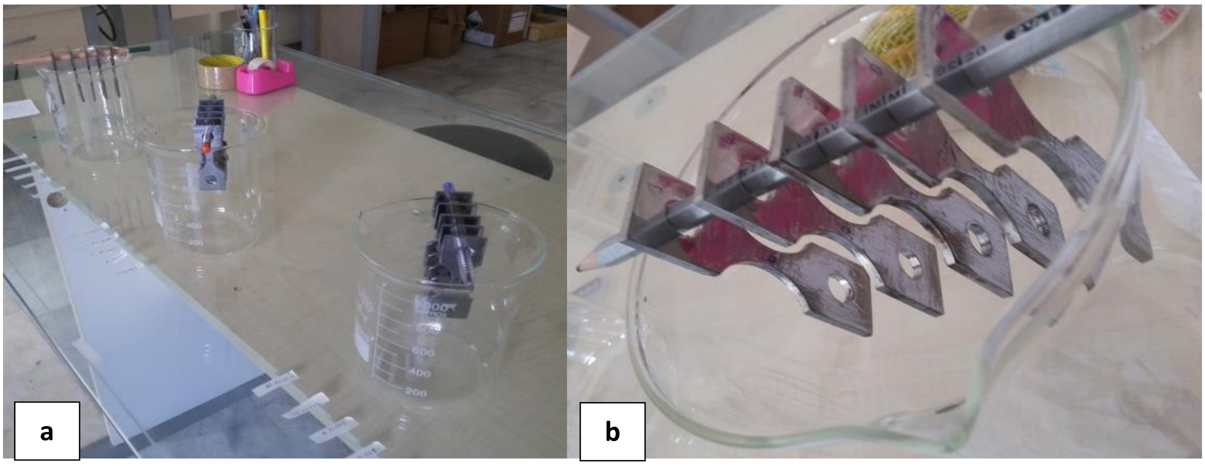


Figure 3. (a) Polished With Nail Polish and Dried Specimens (b) Zoom in Image

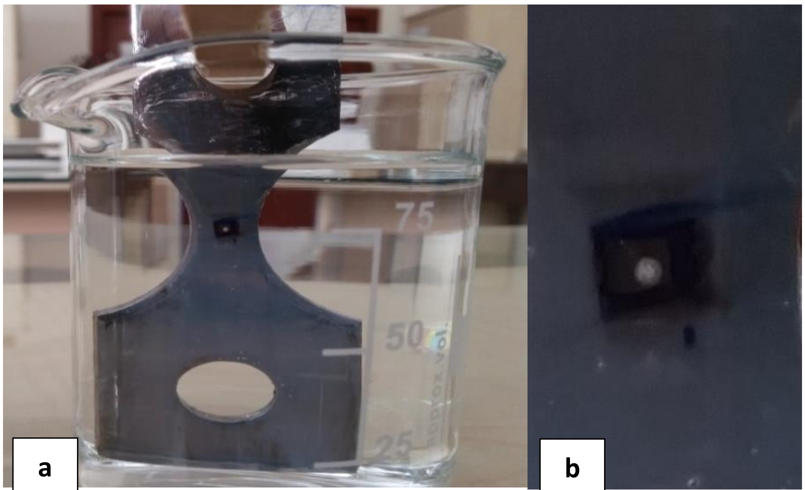


Figure 4. (a) An Immersed Specimen in a Prepared Solution (b) Zoom of the Corroded Area

RESULTS AND FINDINGS

Effect of Pitting Corrosion on Weight

The effects of the pitting corrosion on the reinforced steel St37 are investigated and experiments explained in the methods. The pitting corrosion is a localized corrosion and they are seen on the optical microscope as small hollows. These hollows are progressed to vertical direction to the material inside. Pitting corrosion can propagate until out of service and it may not be even noticed. As mentioned in methods section, there were only four specimens for solutions and two specimens for pristine. For these four specimens material loss was investigated. The table 2 shows this material loss study. According to the table 2, the material loss is almost zero, which means very low material loss, was observed. Thus, there is no possibility to comment this result for pitting corrosion formation. Angst et al. [12] made the weight loss in their article and they also stated that to detect the mass difference, a significant amount of pitting corrosion should be already taken place.

Table 2. Material Losses of Specimens as Percentage

Specimen	% Loss
1.8 ID 1	0,0009
1.8 ID 2	0,0006
3.5 ID 1	0,0006
3.5 ID 2	0,0025

Effect of Pitting Corrosion on Solution pH

One of another factor that can affect the pitting corrosion is the pH value. The change of the pH value was also investigated in this study. The structural metal St37 was immersed to the solutions and pH value difference of the solutions were observed after the specimens were corroded. In table 3, the pH values are illustrated and according to this table there is no significant change of the pH values. Glass et al. [13] have reported that the inhibitive properties of the concrete cannot be expressed only by the OH^- concentration because also a lot of other factors such as alkaline reserves affect to the concrete. Moreover, Page et al. [14] also stated that the chloride relation with pH is not a reliable parameter since the effect of the other factors may change the pH. Hence, the pH change may not be a significant parameter on the pitting corrosion. However, the reason of the little change may be the short immersion time of specimens.

Table 3. pH Change of Specimens Before and After Corrosion

Specimen	Before Corrosion	After Corrosion
1.8 ID 1	3,94	3,92
1.8 ID 2	3,94	4,00
3.5 ID 1	3,97	4,03
3.5 ID 2	3,97	4,02

Pitting Morphology Observations

After specimens immersed to the solutions, they were taken out each 15 minutes period. They were observed under optical microscope whether pits occurred or not. Then, for each period images were captured until the specimens cleaned with acetone. Lastly, the cleaned specimens again observed with optical microscope to detect whether the pits continued or not. Hence, the pitting morphology figures include the pits at 15 minutes, 30 minutes, and 45 minutes and cleaned with acetone. They were zoomed to a pit and the growing of this pit was observed.

From figure 5 to figure 8 shows the pit morphologies of the specimens used in this study. Each 15 minutes the pits in the corroded area grows. These figures cropped from the whole images to show the pits only. Especially pits grow with first 15 minutes for all specimens. However, after first 15 minutes the depths of pits increase instead of the size of them. This means that the sizes of the pits are almost same after 15 minutes. In addition, the pits are tending to be more circular.

The size of the pit in figure 5 (a) is 7096 μm^2, in figure 5 (b) is 10752 μm^2, in figure 5 (c) is 12584 μm^2 and in figure 5 (d) is 11650 μm^2. The reason of decrease in figure 5 (d) is due to the acetone addition.

The size of the pit in figure 6 (a) is 12150 μm^2, in figure 6 (b) is 12520 μm^2, in figure 6 (c) is 12864 μm^2 and in figure 6 (d) is 13650 μm^2. Thus, the size of pit increases with time.
The size of the pit in figure 7 (a) is 6315 μm^2, in figure 7 (b) is 7562 μm^2, in figure 7 (c) is 8624 μm^2 and in figure 7 (d) is 9150 μm^2. In this pit, these size belong figure 7 (a). Figure 7 (b), figure 7 (c) and figure 7(d) has two more circular pits. This shows that these two new pits were formed and they were grown.

The size of the pits in figure 8 (a) is 8132 μm^2, in figure 8 (b) is 9545 μm^2, in figure 8 (c) is 10584 μm^2 and in figure 8 (d) is 10225 μm^2. The reason of decrease in figure 8 (d) is due to the acetone addition. In this figure there is more than one pit.

Specimen 1.8 ID 1

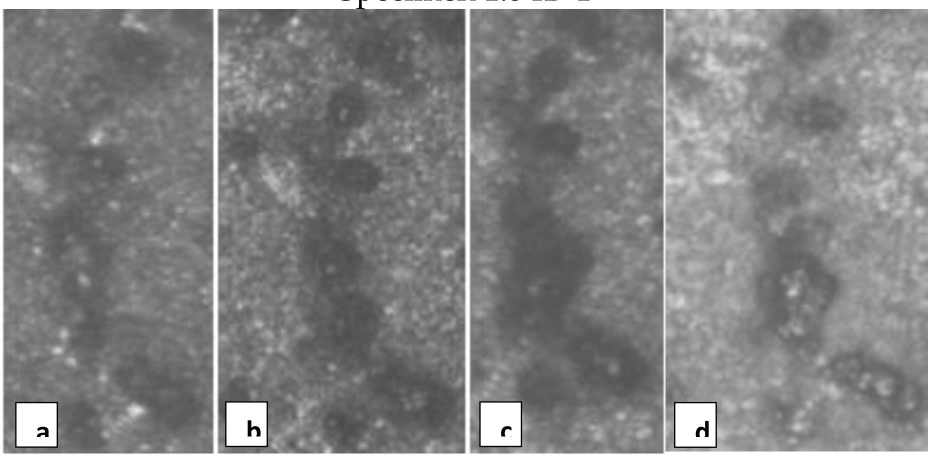


Figure 5. The Change in the Pit Morphology of Specimen 1.8 ID 1 at (a) 15 min. (b) 30 min. (c) 45 min. (d) Cleaned with Acetone

Specimen 1.8 ID 2

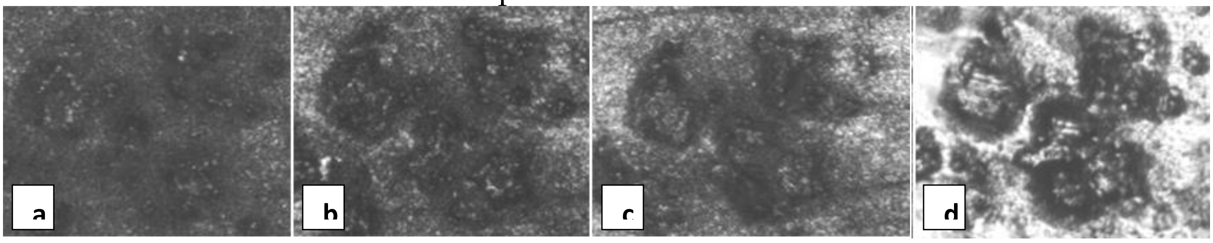


Figure 6. The Change in the Pit Morphology of Specimen 1.8 ID 2 at (a) 15 min. (b) 30 min. (c) 45 min. (d) Cleaned with Acetone

Specimen 3.5 ID 1

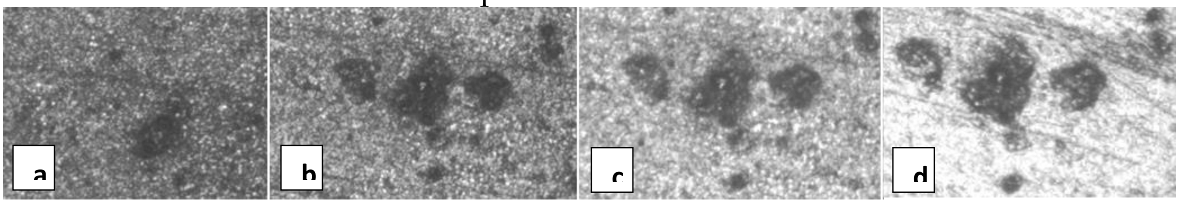


Figure 7. The Change in the Pit Morphology of Specimen 3.5 ID 1 at (a) 15 min. (b) 30 min. (c) 45 min. (d) Cleaned with Acetone

Specimen 3.5 ID 2

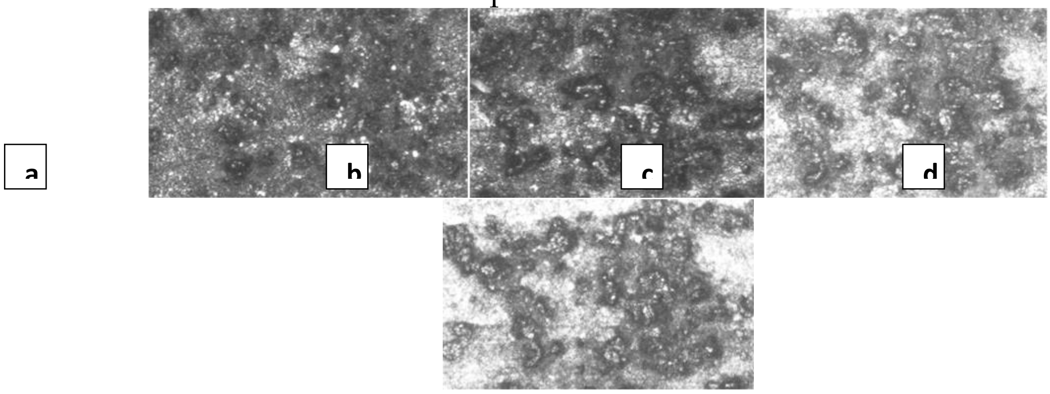


Figure 8. The Change in the Pit Morphology of Specimen 3.5 ID 2 at (a) 15 min. (b) 30 min. (c) 45 min. (d) Cleaned with Acetone

Tensile Test Results

Tensile test is used to observe the durability of the material under static forces and other mechanical properties. The studies shows that the tensile test applied on metallic materials, the physical detriments such as scratches or cracks of the materials affect negatively the strength. The maximum tensions concentrate to the small thicknesses, the notches or holes that locate on the materials; this is valid for the St 37 metal. [15]

From figure 9 to figure 14 are the tensile test graphs and the results of the tensile tests are showed in table 4. According to the results, the specimens immersed to the 1.8 % NaCl solution showed higher strength than the specimens immersed to the 3.5 % NaCl solution as expected. The reason of this result is that the specimens immersed to the 1.8 % solution have lower number of pits on their surfaces after they were corroded and the pits were formed on surface, they were not deep. In other words, the specimens immersed to 3.5% solution have deeper pits and this result decrease the strength of them. Furthermore, strain rates are close to each other and this is unexpected. The reason may be the increase of brittleness in the material because of test conditions or a fault in the test machine about placing the specimen or measuring the strain of it. Nakai et al. [16] stated that increase pitting corrosion decrease the tensile strength and total elongation drastically. The results of pristine specimens are between the literature intervals and they are enough to compare.

Table 4. Results of the Tensile Tests

Specimen	Tensile Strength [N/mm²]	Fracture Strength [N]	Strain Rate [%]
PS ID 1	486,28	6291,5	26,7
PS ID 2	521,60	6853,4	25,8
1,8 ID 1	483,14	6389,7	26,3
1,8 ID 2	513,64	6275,5	26,0
3,5 ID 1	470,64	6227,6	25,8
3,5 ID 2	435,64	5982,9	26,5

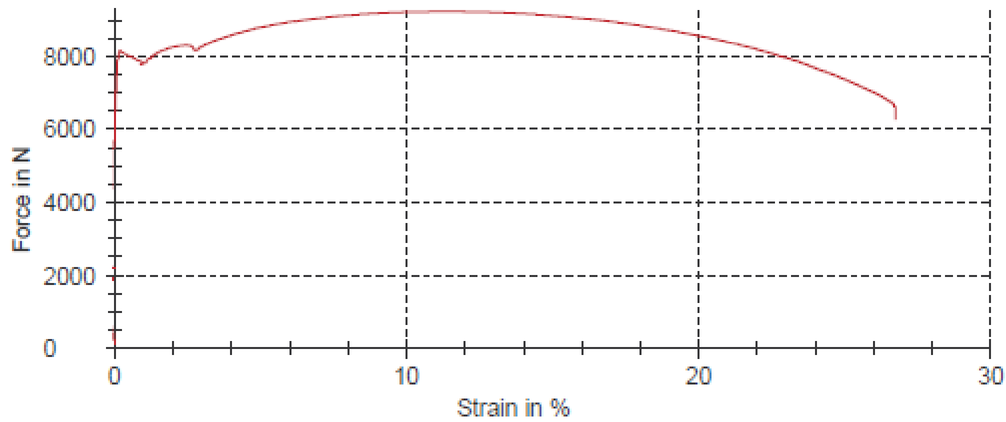


Figure 9. The Tensile Test Graph of PS ID 1 as Force (N) to Strain (%).

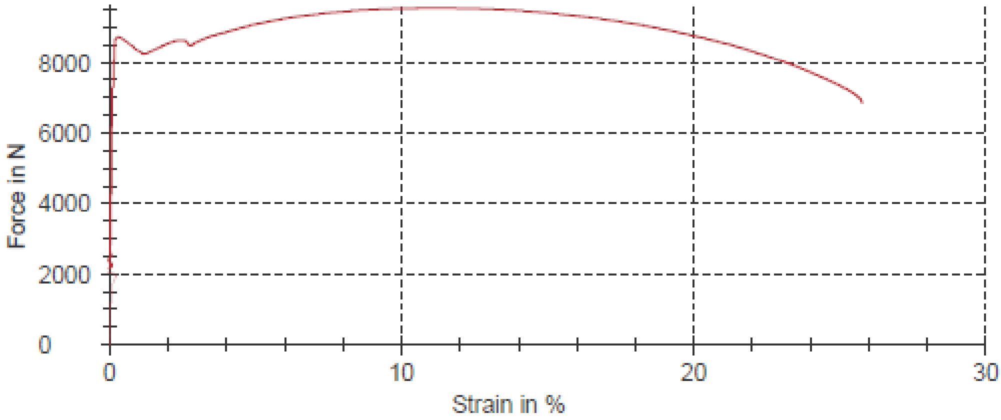


Figure 10. The Tensile Test Graph of PS ID 2 as Force (N) to Strain (%).

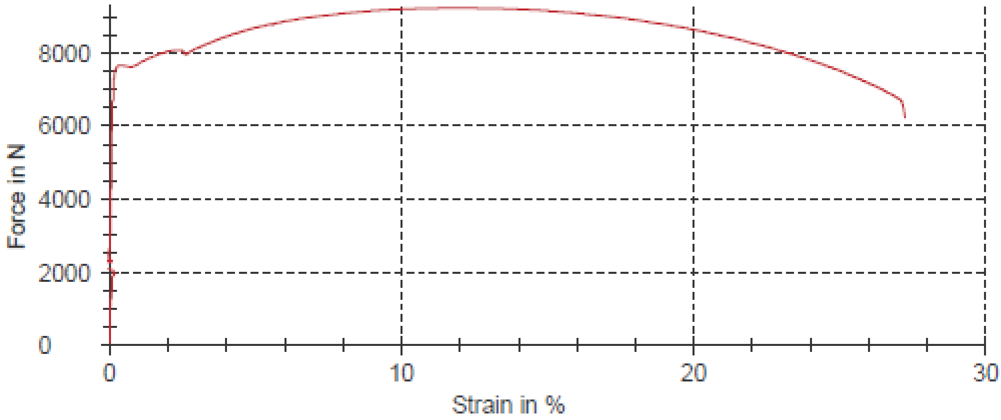


Figure 11. The Tensile Test Graph of 1.8 ID 1 as Force (N) to Strain (%).

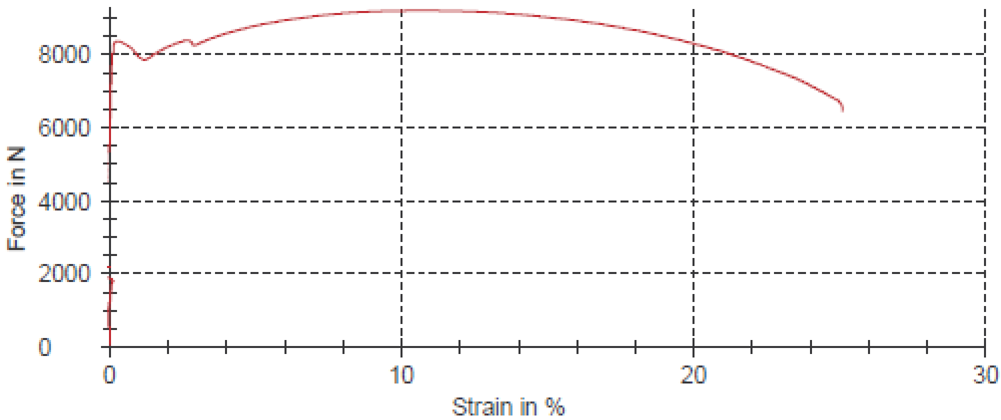


Figure 12. The Tensile Test Graph of 1.8 ID 2 as Force (N) to Strain (%).

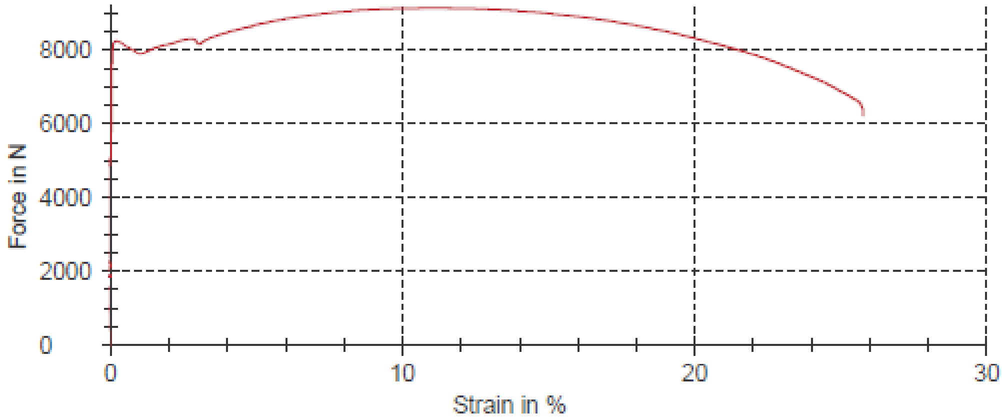


Figure 13. The Tensile Test Graph of 3.5 ID 1 as Force (N) to Strain (%).

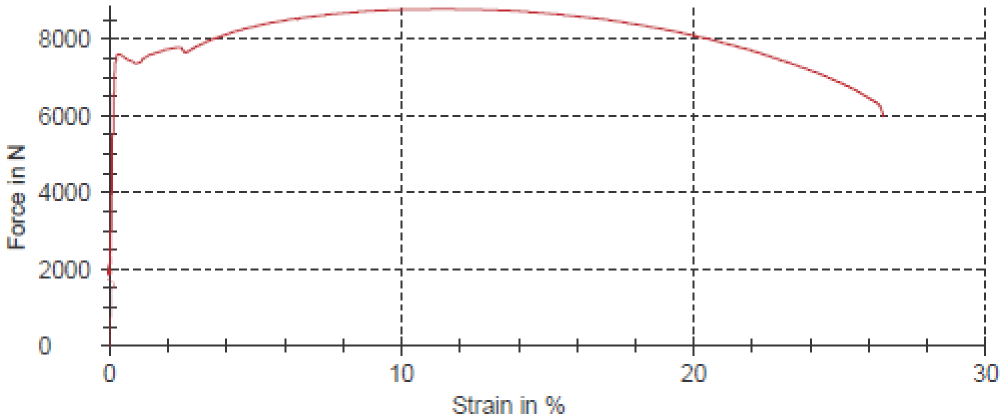


Figure 14. The Tensile Test Graph of 3.5 ID 2 as Force (N) to Strain (%).

Scanning Electron Microscope (SEM) Results

When we observe the images of the Scanning Electron Microscope, the specimens immersed to the 3.5 % NaCl solution have corroded pits wider area on the surface than the specimens immersed to the 1.8 % NaCl solution. Moreover, in cross-sectional view of the specimens immersed to 3.5% NaCl solution have deeper pits than the specimens immersed to the 1.8 % NaCl solution. The figure 15 shows the pits on the surface and the figure 16 shows the pits on cross-section to detect the depth of them.

However, the corroded pits were formed in a narrower area for the specimens immersed to 1.8 % NaCl solution. Moreover, they did not propagate along cross-section. When Fong Yuan Ma [9] observed in his study the corrosive effects of chloride on metals, he also used the Scanning Electron Microscope to determine the pitting corrosions.

In this study, the purpose of using the Scanning Electron Microscope is to determine whether the fractures started from the pits or not.

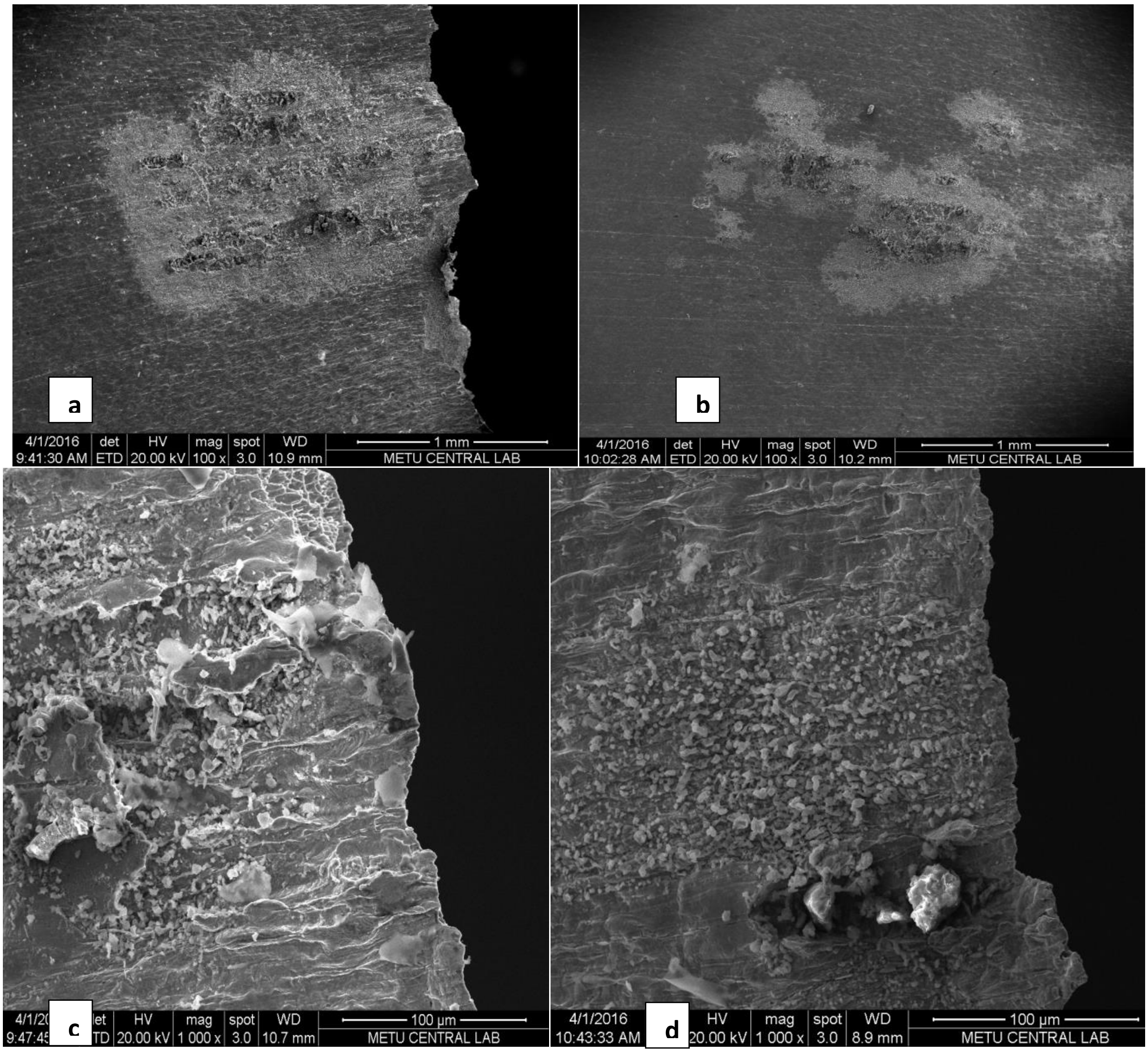
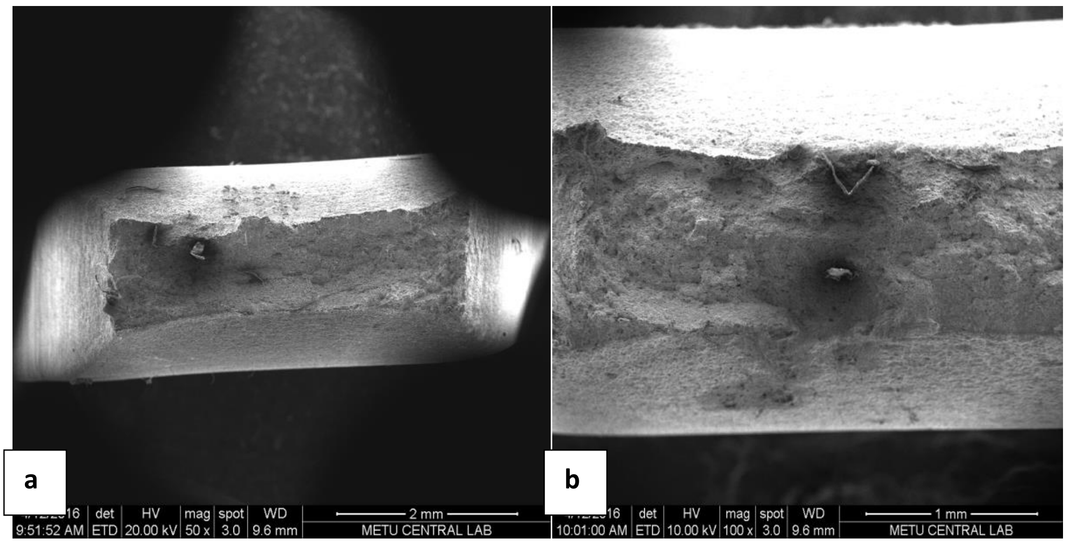


Figure 15. From Surface View SEM Micrographs Of Specimens Immersed to the (a)&(c) 3.5 % NaCl and (b)&(d) 1.8 % NaCl solutions



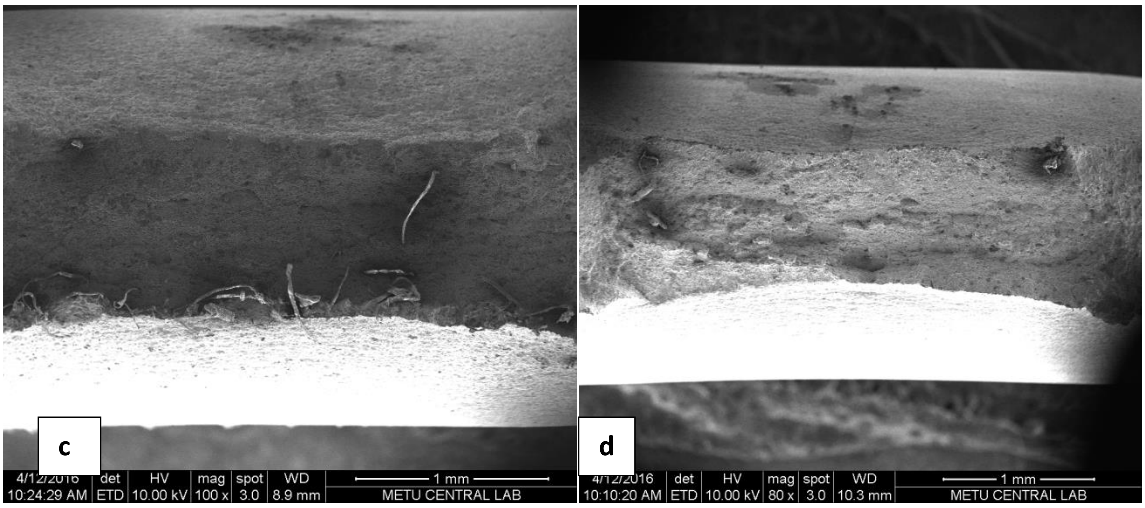


Figure 16. From Cross-Sectional View SEM Micrographs Of Specimens Immersed to the (a)&(b) 3.5 % NaCl and (c)&(d) 1.8 % NaCl solutions

CONCLUSIONS

Pitting corrosion behavior of structural steel St37 with several corrosive environments have been investigated in this study. Mainly, the effects of salinity rates are observed using two different solutions. According to this study, to detect the weight difference, a significant amount of pitting corrosion should be occurred. Thus, the weight of specimens did not change enough. The pH of solution did not change with specimen immersion.

The reason may be the short time immersion of the specimens. The corrosion pits form firstly circular and then they grow on surface with 15 minutes in the solution. After 15 minutes, the pits tend to be deeper, but the size of them tends to be stable. The tensile test results are decrease with increase of salinity as expected. Hence, the more the salinity rate the less the tensile strength of the St37 metal. Scanning electron microscope results show that the more the salinity rate, the deeper the corrosion pits. Also, the more the salinity rate means the more the surface corrosion pits.

RECOMMENDATIONS

The metal St 37, used for several structures, was investigated according to the corrosion resistance with experiments and to determine the most suitable environmental conditions was the main purpose. This purpose was tried to explain with some studies and supported with literature searches. Thus, selecting the material and environment conditions properly causes to increase the lifetime that results to decrease the effect of corrosion to the structural metals. Therefore, these precautions will contribute to the national economy. Similarly, avoiding the expensive repairs, economy can make savings from the labor force. To investigate pitting corrosion resistance, more specimens should be used; the pitting morphology of these specimens should be observed carefully. The depth of the pits should be measured separately. The relation of these pits and the fracture points should be evaluated with scanning electron microscope. To sum up, how the pitting corrosion can be prevented or how the lifetime of the structural reinforced bars can increase should be studied.

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