REDUCING OIL PIPES CORROSION
BY (ZN-NI) ALLOY COATING ON LOW CARBON STEEL
SUBSTRATE BY SUSTAINABLE PROCESS

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Abstract

The problem of corrosion is quite risky and costly. There is always the possibility of bridges and buildings collapsing, oil pipelines bursting, chemical plants leaking, and bathroom flooding. Corroded medical implants might result in blood poisoning, corroded electrical connections could start fires and cause other problems, and worldwide air pollution could damage artwork. Corrosion threatens the safe disposal of radioactive waste that should be stored in containers for millennia. This study makes an effort to enhance further the electroplated layer's (Zn-Ni) alloy characteristics. In this study, samples of low-carbon steel are electrodeposited with layers of varying thicknesses of (Zn-Ni) from an alkaline solution throughout various coating times (15, 30, and 60 minutes). The mechanical and corrosion characteristics of the electrodeposits layer are determined using X-ray fluorescence (XRF), which is also utilized to analyse the microhardness and corrosion test results of the (Zn-Ni) deposited layer.

Keywords: Corrosion test, Different thickness coated, Electrodeposited, Electroplated, Microhardness, XRF, (Zn-Ni) Coated layer,

1. Introduction

Corrosion is a potentially dangerous natural hazard connected to oil and gas production and transportation infrastructure and is a destructive assault on material via contact with its environment [1]. Corrosion in gas and oil production, processing, and transportation systems under several complicated situations may be promoted in almost any aquatic environment [2]. The electrolyte, cathode, and anode are the three parts of this process. The electrolyte is the corrosive solution that permits the flow of electrons from the anode to the negative electrode and creates the electrically conducting cathode in the cell, which is not consumed in the corrosion process. The positive electrode is where the metal gets eroded [3].

Several compounds that are corrosive and heavy in impurities may be transported in natural gas and crude oil. These very corrosive media include carbon dioxide (CO_2), hydrogen sulfide (H_2S), and free water in the case of wells for oil and gas and pipelines [4]. The inside surfaces of gas and oil components may experience the impacts of corrosion over time due to the constant extraction of free water, carbon dioxide, and carbon dioxide. Because of changes in fluid compositions, well tension over time, and adjustments in operating parameters like pressures and temperatures, lines and line-forming fixtures would be vulnerable to material deterioration with changing well conditions. The mechanical characteristics of the material, such as strength, ductility, and impact strength, are lost as a consequence of this material deterioration. This results in material loss, decreased thickness, and even complete failure. The component can sometimes cease functioning altogether, necessitating the assembly replacement while the manufacturing is halted. The severe effects of the erosion process have emerged as a significant issue on a worldwide scale [5].

In contemporary society, corrosion is one of the oil sector's most significant and challenging issues. Most industrial designs must always consider the impact of corrosion on the equipment's lifespan. According to recent industrial catastrophes, erosion has cost numerous sectors several billion dollars. Reports worldwide clarified that certain oil companies had ruptured their pipelines because of corrosion and that an oil spill had happened, contaminating the environment. Furthermore, resources were lost cleaning up this environmental mess, and the extensive environmental damage caused by corrosion eventually impacts [6]. The engineers and chemists in the petroleum, chemical, and mechanical fields were very concerned about the risk of corrosion in an industrial facility. It is now understood that corrosion may change the chemistry of the chosen process and that the corrosion product can influence the purity and reactivity of the reaction products.

Various kinds of degradation a metal could experience in such situations: Uniform, Pitting, Crevice, Intergranular Corrosion, Stress Corrosion Cracking (SCC), and Galvanic Corrosion [7]. The most prevalent kind of corrosion is uniform corrosion. It is also the most benign since the attack's magnitude and influence on material performance can be reliably reproduced and tested. This sort of corrosion usually affects huge surfaces [8]. Although challenging to forecast, detect, and define, pitting is among the most damaging kinds of corrosion. Pitting is a localized corrosion that creates a tiny depletion layer with the normal surrounding surface [9]. Pits evolve into "holes" or "cavities" of various forms. Pits usually go vertically down. Pitting corrosion may result from a temporary rupture

in the protective oxide layer, coating, or metal structural non-uniformities. Pitting is problematic because it may induce structural failure with little metal loss [10].

Crevice corrosion is confined. In a static microenvironment, two metal regions have different ion concentrations. Oxygen-restricted spaces beneath washers, bolt heads, gaskets, etc., cause crevice corrosion. These tiny spaces enable corrosive agents to enter but do not allow adequate circulation, depleting oxygen and preventing re-passivation. pH rises in stationary solutions [11]. This mismatch between the fissure (microenvironment) and the exterior surface (bulk environment) increases corrosion. Crevice corrosion occurs at lower temps than pitting. Joint design reduces crevice corrosion. However, the microstructure of metal shows the grains and grain boundaries that occur during alloy solidification. Impurities or alloying element depletion or enrichment at grain boundaries may produce intergranular corrosion. Intergranular corrosion affects the metal's mechanical characteristics while leaving the bulk undamaged [12].

Tensile tension and corrosivity at high temperatures cause stress corrosion cracking (SCC). Tensile stresses or sudden temperature fluctuations may cause stress corrosion [13]. Residual tension from grinding, machining, welding, cold forming, etc., might cause it. Stress corrosion leaves much surface intact, but microscopic fractures make it hard to detect. Brittle fractures occur and spread perpendicular to the tension. Selecting materials for a specific environment (temp and external stresses) helps reduce SCC-related catastrophic failure [14]. Finally, galvanic corrosion happens when two electrochemically different metals are electrically connected in an electrolytic environment, such as copper and steel in seawater. Even if these three parameters are fulfilled, additional variables like metal temperature and surface polish might affect corrosion [15]. Large engineering systems of multiple metals and fasteners may galvanize if not appropriately designed. Selecting metals as near as possible on the galvanic series reduces galvanic corrosion [16].

Around 3 to 5 percent of the developed nations' oil companies calculated the expenditures associated with corrosion damages [17]. According to estimates, corrosion costs the oil and gas production sector $1.372 billion annually, broken down into $463 million in yearly downhole pipe expenses, $589 million in the surface pipeline and utility costs, and another $320 million in corrosion-related capital expenditures [18]. Each year, corrosion costs the oil and gas sector tens of billions of dollars in processing costs and lost revenue [19]. The oil and gas sector is responsible for more than half the estimated $170 billion yearly expenses associated with corrosion incurred by US industries alone [20]. Temp, carbon dioxide and carbon dioxide concentration, water chemistry, flow rate, and steel surface condition all impact internal corrosion in pipelines and wells [21]. Component life may be significantly increased by drastically lowering the wear rate (mm/year), which has more significant advantages like lower maintenance costs. Nowadays, many parts utilized in oil and gas extraction are made of carbon steel alloys. Organizations are now aiming to replace these alloy types with a more expensive alloy that offers greater corrosion resistance.

Zinc (Zn) and Zn-alloy coatings are finding multiple uses as sacrificial metallic coatings to protect steel components in various sectors such as automotive, electrical, and aerospace [22]. For years, electroplated thick Zn coatings provided affordable corrosion protection for metallic objects. However, these coatings are

gradually being replaced by alloys owing to their ineffectiveness in hostile or high-temperature conditions [23]. Zn alloys containing nobler Fe group metals (Ni, Co, and Fe) may outperform pure Zn coatings in protective effectiveness [24]. Furthermore, compared to pure Zn coatings, alloys such as Zn-Ni may impart excellent mechanical qualities, including hardness and wear resistance [25]. As a result, it is commonly acknowledged as an environmentally safe alternative to hazardous coatings such as cadmium.

Electroplating with corrosion-resistant materials is considered one of the advanced technologies that contribute significantly to reducing the problem of corrosion. It is an ideal method for coating metals with a thin surface layer with specifications that exceed the base metal [26]. Electroplating also has particular importance in complementary processes by giving it good specifications for resistance to corrosion and abrasion. Sometimes the coating is used to adjust the dimensions of the coated part depending on Caporali et al. [21]. It is essential for creating a smooth surface, precision in dimensions, surface uniformity, and a beautiful look. The research was undertaken to enhance the coating layers' performance by enhancing their plasticity, adhesion, and mechanical characteristics [27, 28].

Among all the frequently electroplated alloys, Zn-Ni is the most widely used in commercial applications [29]. Several data exist on the corrosion-resistant efficacy of Zn-Ni alloy coatings [30-33]. However, these coatings seem prone to severe sacrificial dissolution to some extent owing to the low Ni content of the deposits based on Eliaz et al. [25]. Electroplating with (Zn-Ni) alloy has gained great importance and wide applications in protecting steel due to its good resistance against corrosion in most corrosive media. Especially if the percentage of nickel in the alloy (Zn-Ni) is approximately (10%), and this percentage gives a clear improvement in the mechanical properties as mentioned by Karahan et al. [26], and the resistance against corrosion of this alloy exceeds the corrosion resistance of cadmium and titanium by more than four times. It is also free from toxicity and has no destructive environmental impact compared to cadmium and chromium [34].

The present study aims to mitigate the corrosion problems that the pumps suffer from, whether they are gas or gasoline pumps, to reduce the impact of these problems on the efficient functioning of these pumps by using electroplating chemical coating methods with (Zn-Ni) alloys.

2. Practical Part

The specimens used are (L.C.S) Low carbon steel, whose chemical composition is demonstrated in Table 1. The chemical analysis has been carried out utilizing a metal spectrophotometer (to identify the chemical composition of the sample shown in Table 1) in the General Company for Mechanical Industries in Alexandria, Babylon, Iraq.

**Table 1. Percentages of the
chemical analysis of the carbon steel specimens.**

| Fe	Cr	Mn	Si	C
Rem	0.04	0.65	0.17	0.12

The specimens were prepared in the form of discs with a thickness of (2 mm) and a diameter of (15 mm), meaning that their total surface area is (447,677 mm²).

The surfaces of the samples were prepared in the following manner. The process of smoothing was done entirely using Grit silicon carbide papers, which were gradual as follows (220, 240, 400, 600, 800, 1000, 1200). Then the surfaces of the samples were cleaned with an alkaline solution (10%NaOH) and an acidic solution (30%HCl). The electroplating process of the samples was carried out according to the required coating time for each sample.

2.1. Equipment for the electroplating process

The electroplating process was carried out in a basin made of polyethylene in the form of a rectangular prism with dimensions (29x21x18) cm. In the coating process, a power supply could give a current ranging from A(0-6), and the given voltage varies (0-20) V.

Figure 1 shows a graphic diagram of the electroplating cell, showing the locations of the electrodes. The positive poles (Anodes) are suspended by (Hooks) of copper, which represents the poles of zinc in the form of a plate (plate) dimensions mm (35 x 20 x 5) containing a hole with a diameter of (2 mm) for the possibility of hanging the copper brackets. The negative electrode (Cathode) represents the specimens used and is made of carbon steel, whose composition is shown in Table 1 and is attached to a hook holder made of copper. The distance between the negative electrode and the positive electrode is about (70 mm).
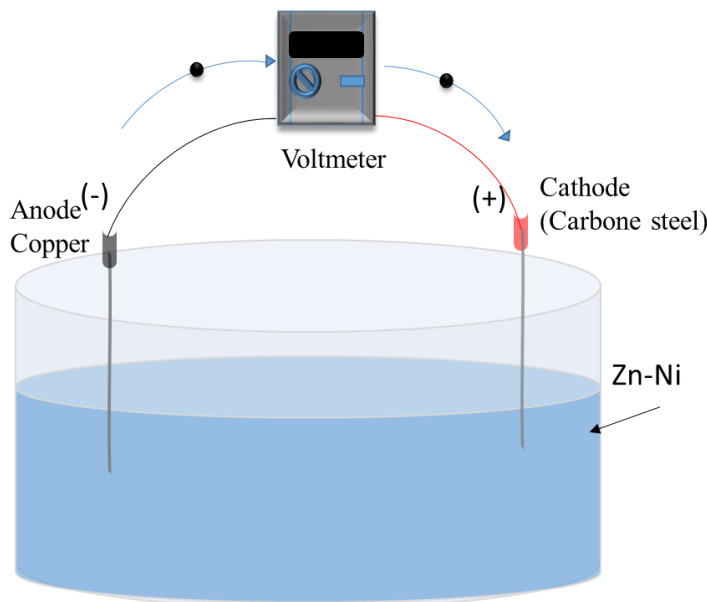
Fig. 1. A graphic diagram of the electroplating cell.

A coating basin containing an alloy (Zn-Ni) solution was used during the research period. Table 2 shows the components of the coating basin and its operating conditions [35].

The positive electrodes and the coated samples were fixed, and the basin was equipped with the required current and voltage at the temperature required for the

coating process. After the period required for depositing a certain thickness of the coating on the metal, the samples are extracted from the coating basin, washed with distilled water, then alcohol, and dried with a stream of hot air. Afterward, weight readings are taken, and the samples are kept in glass desiccators to remove corrosive moisture.

**Table 2. Proportions of the components
of the coating solution used in the current study.**

Solution	Chemical compositions	Deposition conditions
Zn-Ni	ZnO=6-12 g/l NiCl2.6H2O=1-1.5 g/l NaOH=100-120 g/l	pH = 12.5 Temperature = 25 degrees centigrade. Coating time=15, 30, 60 min. Current Density= (2.5) Amp/dm²

3. Tests

In the current study, the following tests have been conducted to assess the performance of (Zn-Ni) coating layers on low-carbon steel substrate:

3.1. Measurement Of Coating Thickness

In (Babylon/College of the Material Engineering/ University of Babylon), the thickness measurement instrument has been conducted to assess the thickness of (Zn-Ni) coating films on low-carbon steel substrates.

In the current research, the device's accuracy was (± 0.1 µm) using a coating thickness gauge. The principle of operation of the device is based on ultrasonic waves.

3.2. X-Ray Fluorescence (XRF)

The ratios of the components of the (Zn-Ni) coating layers were found using an X-ray fluorescence technique (X-MET 3000 TX, horizon 600 series, model 2004). The quantitative method was adopted in the examination of the research samples.

3.3. Surface roughness test

The (Zn-Ni) alloy's roughness of surface plated on low carbon steel has been determined utilizing the University of Babylon's Department of Materials Engineering's (TR-100 surface roughness testing machine). The gadget measures the surface roughness by passing over the surface of the specimen. The gadget features a sensor that measures the surface roughness of the specimen and displays the data on its screen, the instrument's precision ($\pm$ mµ0.01).

3.4. Surface topographic test

Grain limits are characterized by their comprehensive measurement and identification of the phase's structure and particle size. Each of them has unique qualities. The microstructure was analysed utilizing a Japanese-made Olympus microscope at 1000x magnification. Testing was conducted on low and low-carbon steel samples coated with a layer of (Zn-Ni) with varying coating times.

3.5. Microhardness test

Vickers Hardness (TH-717 Digital Micro Vickers Hardness Tester) measured the hardness of (Zn-Ni) coated layers by different coating times, at load (100 g) and holding time of 15 seconds (college of Material engineering/University of Babylon).

3.6. Corrosion test

The weight loss method is the simplest method for measuring the corrosion rate or what is called the simple immersion method, where steel samples without coating and steel samples coated with an alloy (Zn-Ni) with different coating times (15, 30, and 60) min were immersed in the following corrosive media (tap water properties shown in Table 3, a salt solution of sodium chloride with a concentration of (3% NaCl) by weight, A solution of hydrochloric acid with a concentration of (3% HCl) by volume.

Table 3. Chemical composition of ordinary tap water.

Chemical Analyses	Amount (g/l)
PO_4	1.5
SO_4	230.6
Cl^-	71
pH	7.7

Low carbon steel samples were immersed in all the media mentioned above because carbon steel is affected by all electrolytic solutions but by varying degrees. The duration of immersion of samples in solutions also varied, depending on the type of electrolyte solution.

The sensitive balance measured the weights of the samples, and the surface area of each was calculated before immersion in the solutions; after different times, the samples were taken out of the solutions, cleaned with distilled water and alcohol, and dried, and the change is calculated by weight per unit area ($\frac{\Delta W}{A}$), where several readings are taken to reach the maximum period, the relationship between the weight change per unit area and the immersion time was drawn.

4. Results and Discussion

In the current research, the thickness of the coating layer was about (10, 25, and 35) μm, while the coating time was (15, 30, and 60) min, respectively. The coating thickness increases with increased coating time, i.e., coating thickness depending on the coating time, as shown in Fig. 2.

The chemical composition of (Zn-Ni) coated XRD analysis layer; the results are illustrated by two elements, zinc, and nickel, and to ensure that these proportions fall within the monophasic phase (δ), in which the proportion of nickel is about (10%) [35], as shown in Table 4.

Table 4. the proportions of the components of the coating layer (Zn-Ni).

Coating layer	Element	The weight percentage of the element
Zn-Ni	Zn	90.3
	Ni	9.7
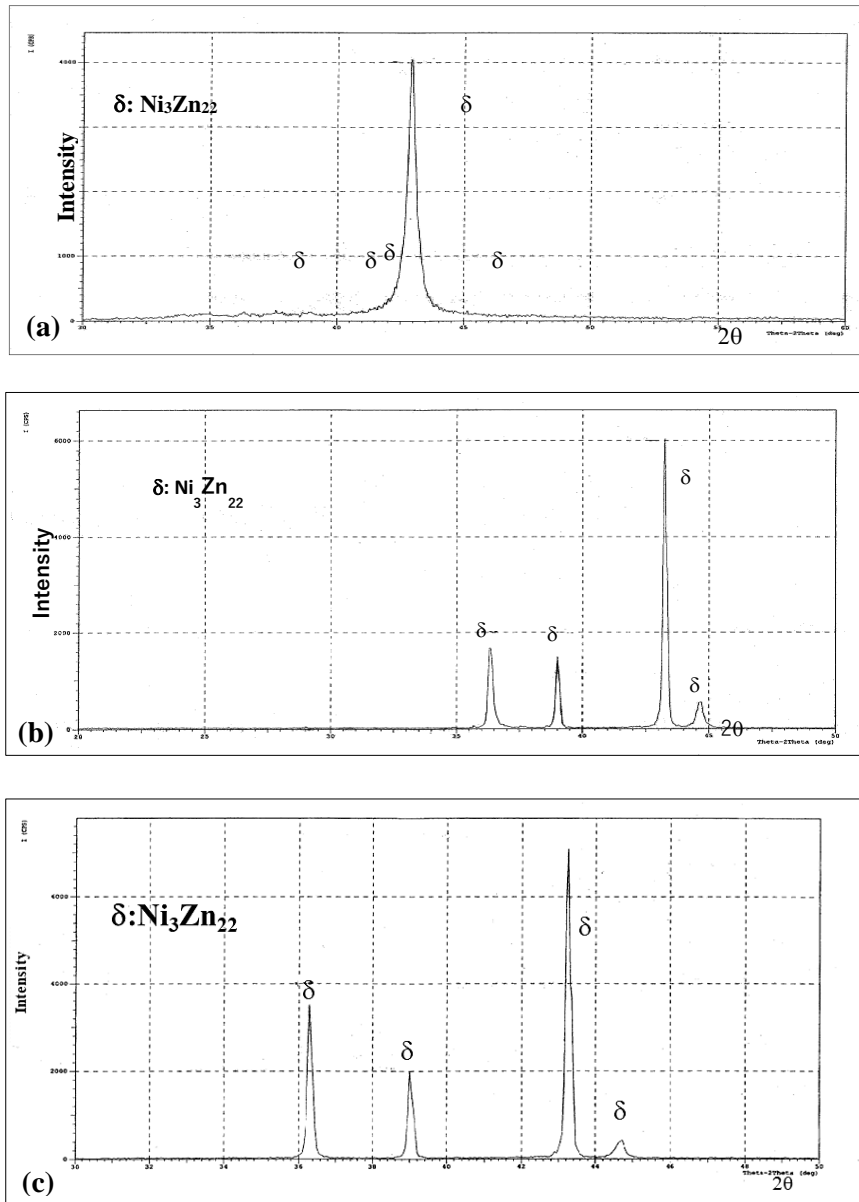
Fig. 2. The results of the X-ray diffraction test for a sample coated with a) 60 min (Zn-Ni) alloy, b) 30 min (Zn-Ni) alloy, and c) 15 min (Zn-Ni) alloy.

The results of surface roughness of (Zn-Ni) coated layer on low carbon steel substrate by different coating times (15, 30, and 60) min. The surface roughness decreases with increasing coating time, as shown in Table 5.
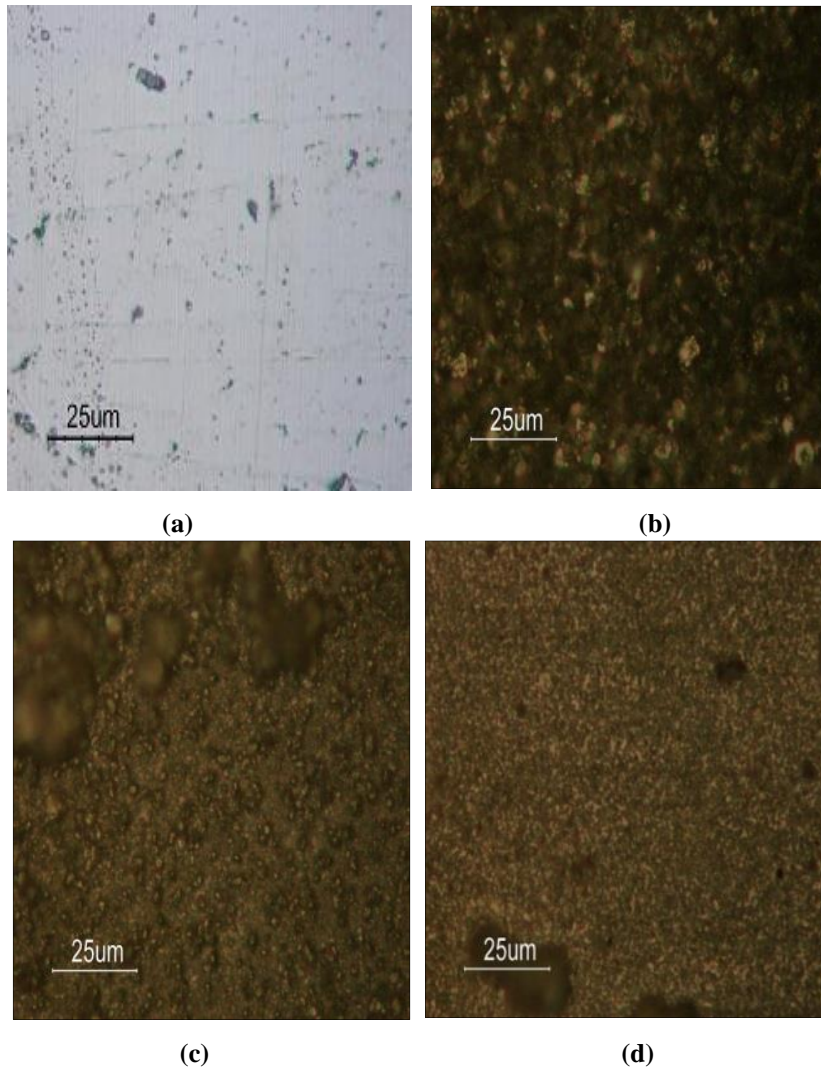
The topography of uncoated low-carbon steel samples and coated samples with (Zn-Ni) alloy by (15, 30, and 60) min have been identified. Utilizing the microscope magnification (1000x), as demonstrated in Fig. 3.

Table 5. surface roughness value.

Coating samples	surface roughness value(µm)
(Zn-Ni)15min.	1.975
(Zn-Ni) 30min.	1.547
(Zn-Ni) 60min	1.198

When the coating period is low, the researcher is compelled to increase the voltage of the coating to accelerate the coating process. The rapid coating process causes inhomogeneous coating with high roughness, shown in Fig. 3(c).

(a)

(b)

(c)

(d)

**Fig. 3. Topography of the sample surface at
a magnification of (1000x): a) carbon steel sample (b, c, and
d) carbon steel samples coated with (Zn-Ni) alloy by (15, 30, and 60) min.**

The results of the microhardness test clearly illustrated that the hardness increases with coating time increase as shown in Table 6

Table 6. Microhardness value.

Coating samples	microhardness value (g/mm^2)
Low carbon steel	198
(Zn-Ni) 15 min.	250
(Zn-Ni) 30 min.	273
(Zn-Ni) 60 min.	313

This test was conducted at room temp and in normal tap water, where the change in the sample weight was calculated for different exposure periods, and the lost weight per unit area was obtained. Figure 4 shows the effect of the exposure period to tap water on the lost weight of carbon steel specimens coated with an alloy (Zn-Ni) and a sample of steel without coating.

The base metal (low carbon steel) showed a continuous decrease in weight by increasing the exposure period to regular tap water, as shown in Fig. 4. This is because the corrosion products formed during this exposure period do not protect the steel surface [36], so it was necessary to search for a means to protect the steel surface.

For coated layers with a coating time of (15 and 30) min, they showed a continuous increase in weight at different rates with the increase in the immersion time in the water, and this is due to the presence of pores and cracks in different proportions in the layers of coating.

As for the coating layer with a coating time of (60 min), it did not show weight loss for up to three days, which can be attributed to the great protection provided by the corrosion products growing on the (Zn-Ni) alloy coating layer, followed by a weight loss after three days as it no longer forms the layer is an effective barrier to prevent the convergence of ions between the solution (tap water) and the surface of the steel samples. This study conducted the corrosion test in different acidic, basic, and neutral corrosion media (HCL, tap water, NaCl). A loss in the weight of the sample accompanies Soluble in the solution. As for the second type, it is not dissolved in the solution and sticks to the sample's surface, which causes an increase in the weight of the sample.

The corrosion test was conducted at room temp and in a solution of (3%NaCl) by weight, where the change in the sample weight was calculated for different exposure periods, and the lost weight per unit area was obtained. Figure 5 shows the effect of the exposure period for a solution of (3%NaCl) by weight on the lost weight of samples of carbon steel with an alloy (Zn-Ni) coated and uncoated steel sample [37].

The study of the two coating layers (15 and 30) min (Zn-Ni) and the carbon steel sample without coating showed a continuous decrease in weight in general with the increase in the exposure period to the saline solution (3%NaCl) by weight, except for the coating layer 60 min (Zn-Ni) which lost an increase By weight up to a time of exposure to the saline solution of three days, followed by weight loss. This behavior indicates the dissolution or dissolution of corrosion products in the saline solution. As for the continuous weight loss of (15 and 30) min (Zn-Ni) layers, this corresponds to the fact that the layers are the thin film contains a higher

percentage of porosity [38]; if this porosity represents sites or pathways for the movement of ions and then an increase in the rate of loss as shown in Fig. 5.

Compared with exposure to normal tap water, the rate of loss here is more than that of normal tap water, which can be attributed to the increase in charge carriers resulting from the ionization of salt.
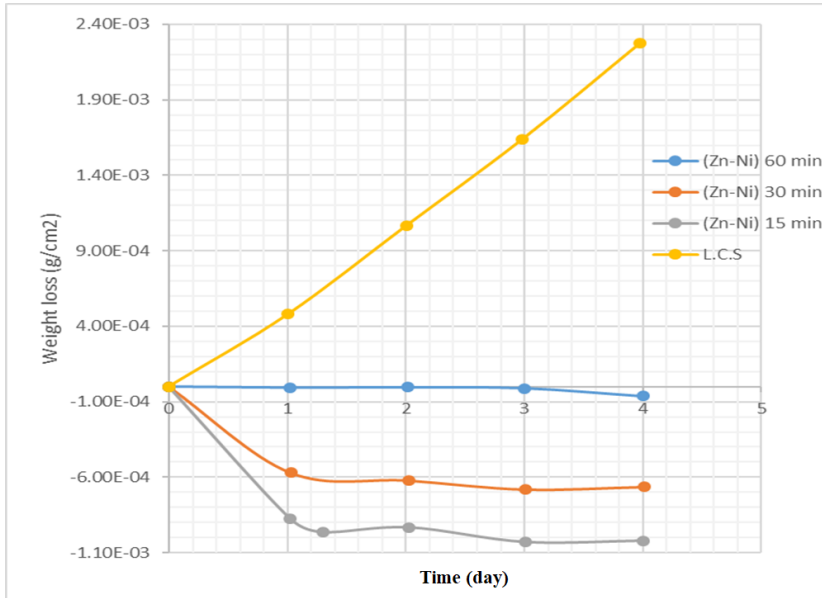
Fig. 4. Effect of tap water exposure time on the lost weight of uncoated carbon steel and Zn-Ni coated samples.
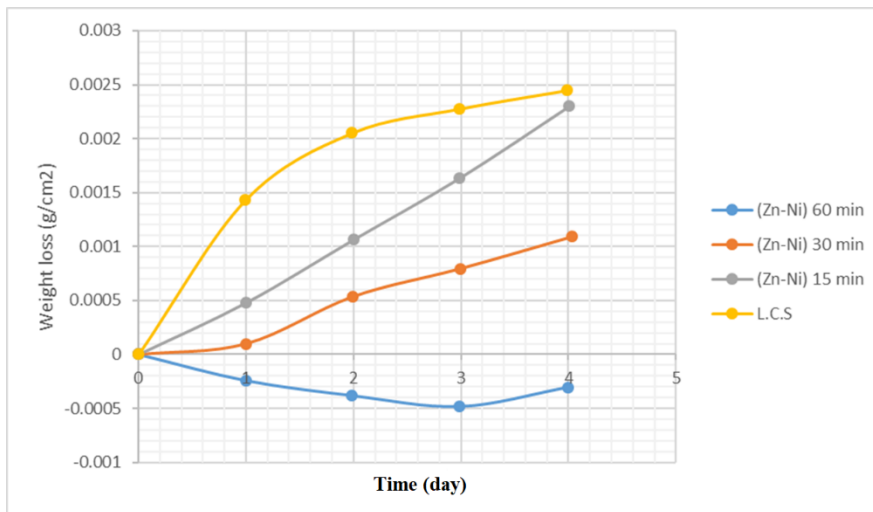
Fig. 5. The effect of the exposure period of (3% NaCl) solution by weight on the lost weight of uncoated carbon steel samples and samples coated with (Zn-Ni) alloy.

The corrosion test was conducted at room temperature and in a (3%HCl) solution by volume. The change in the sample weight was calculated for different exposure periods, and the lost weight per unit area was obtained as shown in Table 7. Figure 6 shows the effect of the exposure period for (3%HCl) solution by volume on the lost weight of carbon steel samples with an alloy (Zn-Ni) coated with different coating thicknesses and uncoated steel samples.

All layers of coating again showed a continuous decrease in weight with the increase in the exposure period to the acidic solution, as shown in Fig. 6. Furthermore, compared to the value of the loss in the saline solution shown in Fig. 5, what these specimens lose in minutes is more than what they lose in days in normal tap water or saline solution. The significant increase in the weight loss of the acidic solution compared to the rest of the media is mainly due to the presence of positive hydrogen ions (H+) that work to discharge electrons and accelerate the reaction.
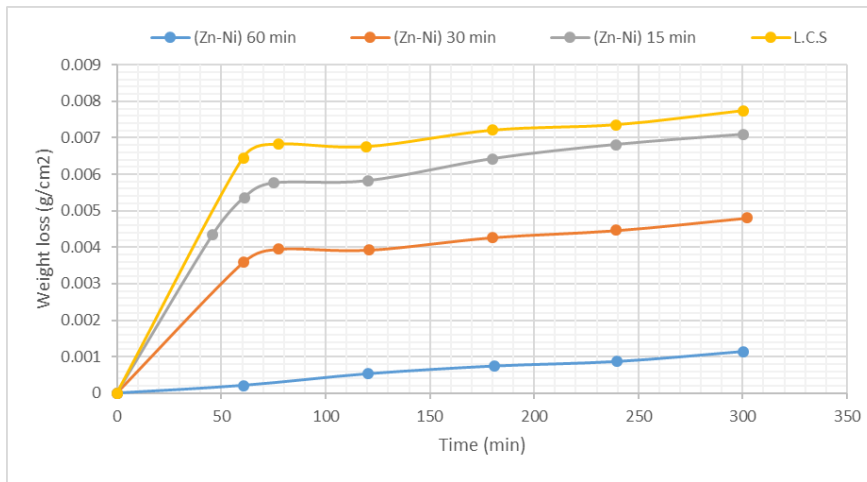

Fig. 6. shows the effect of the exposure period of (3%HCl) solution by weight on the lost weight of uncoated carbon steel samples and samples coated with (Zn-Ni) alloy.

Table 7. Summary of corrosion results.

Corrosion Environment	Coating Layer	Weight loss (g/cm²)	Corrosion time (Hours)
Tap water	Low carbon steel	0.00230	96
	(Zn-Ni)15min.	-0.00010	96
	(Zn-Ni) 30min.	-0.00061	96
	(Zn-Ni) 60min.	-0.00110	96
(3%NaCl)	Low carbon steel	0.00225	96
	(Zn-Ni)15min.	0.00223	96
	(Zn-Ni) 30min.	0.00012	96
	(Zn-Ni) 60min.	-0.00031	96
(3%HCl)	Low carbon steel	0.00775	5
	(Zn-Ni)15min.	0.00700	5
	(Zn-Ni) 30min.	0.00510	5
	(Zn-Ni) 60min.	0.00112	5

The covering layer (Zn-Ni) provides protection against corrosion for the steel model coated with it due to the resistance of this layer to various corrosive media, as the coating layer (Zn-Ni) is a sacrificial anode layer for the base metal. This resistance comes from The single phase (δ), which, as mentioned above, contains a percentage of nickel ranging up to 10% [35]. This percentage of nickel gives anti-corrosion resistance six times better than if zinc was deposited alone [35]. The nickel in the precipitated alloy increases the resistance of the alloy because nickel, as it is known, is a ductile element, so it renders the (Zn-Ni) layer resistant to corrosion in most corrosive media [39].

5. Conclusion

The current research showed a relationship between the properties of the coating layer in general and its thickness, as the corrosion resistance reached good values in all corrosive media for the (Zn-Ni) 60min coating layer.

- The crystallization nature of the three deposited coating layers were in the following order: (Zn-Ni)60 min>(Zn-Ni)30 min>(Zn-Ni)15 min.
- The size of the coating particles deposited for the three layers of the coating was in the following order: (Zn-Ni)15 min>(Zn-Ni)30 min>(Zn-Ni) 60 min
- The corrosion resistance of the coating layer (Zn-Ni) in normal tap water, in a brine solution of sodium chloride (3%NaCl) by weight, and an acidic solution of hydrochloric acid (3%HCl) by volume was in the following order: (Zn-Ni)60 min>(Zn-Ni)30 min>(Zn-Ni)15 min> (LCS).

Acknowledgments

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