Investigation of Corrosion Protection in Oil Mineral Reservoirs by Nanocomposites Used as Coating Layers

Abdulhameed R Al-Sarraf and Samer A Al-Saaidi

Physics Department, College of Education for Pure Science Ibn-Al-Haithm, University of Baghdad

Samerhawk@gmail.com

Abstract. In this study, a number of nanocomposites were prepared by adding magnesium oxide (MgO) with weight percentages (1, 2 & 3)% to cellulose nitrate and sodium silicate as an intermediate layer and other nanocomposites by adding MgO, coal coke and hybrid (MgO & coal coke with ratio 1:1) with weight percentages (1, 2 & 3)% to epoxy resin as final layer. The identity of the used metal is determined by spectrometer OE thermo. The nature and topography of the surface layers were examined by optical microscope and atomic force microscope (AFM). Mechanical properties are indicated by hardness, wear rate, impact strength and adhesion strength. The efficiency of the layers prepared to inhibit corrosion in the oil mineral reservoirs of the oil products distribution company was studied by electrochemical corrosion test in addition to the chemical corrosion test. The used metal is (St-37) according to (ASTM). It was found that the best intermediate layer (cellulose nitrate+3%MgO) and the final layer is the epoxy resin reinforced by 2% hybrid.

Keywords: Corrosion, Electrochemical Corrosion, Chemical Corrosion, Nanocomposites, Cellulose Nitrate, Sodium Silicate, MgO, Hybrid Composite and Epoxy Resin.

1. Introduction

Corrosion is a natural and costly process of destruction like volcanic eruptions, floods, tornados and earthquakes. It's playing an important role in economics and safety, particularly for metals and alloys [1,2]. Corrosion is the destructive attack of a metal by electrochemical or chemical reaction with the environment. Steel has found wide application in a broad spectrum of industries and machinery; in spite of its tendency to corrosion. The corrosion of steel is a fundamental academic and industrial worry that has received a considerable amount of attention [3]. Inhibitors are one of the an important methods used for protecting materials against deterioration due to corrosion [4,5]. Several countries such as (the United Kingdom, China, Germany, the United States, Finland, Australia, India, Japan, Sweden and Kuwait) studied the cost of corrosion and found the annual corrosion costs from the Gross National Product (GNP) of each nation ranged from approximately 1 to 5 percent. The failures in oil and gas production ranged from 25 to 40% are due to corrosion. Consciousness to corrosion, acclimation of timely and appropriate control measures were in the reduction of corrosion failures [6,7].
The research aims to prepare nanocomposite coats in layers form (including sodium silicate and cellulose nitrate composites reinforced by 3 wt.% MgO as intermediate layer and epoxy resin reinforced by 2 wt.% hybrid (MgO & Coal coke) as final layer) in order to inhibit and protect the stainless steel alloy (St-37) from the chemical corrosion resulting from the oil product in the oil products distribution company (Opdc.)

2. Experimental Part

The metal used was analyzed by using spectrometer OE thermo ARL 3460 and has been found the classification of alloy is (St-37) a low Carbon (C = 0.16) and a moderate hardness (130HB = 13HRC) according to ASTM.

The metal piece exposed to corrosion as shown in ‘Figure 1’ and was taken from one of the reservoir in oil product distribution company (OPDC). The thickness was reduced from 6mm to 3mm and cut into two groups (1.5cmX1.5cm & 3cmX3cm) as shown in ‘Figure 2’.

The carbonization process was performed at 950 ºC for 3 hours to eliminate the internal cracks and corrosion microwaves to make the surface of steel stronger and harder (hardness = 589 HB) due to the cohesion of the particles and the formation of surface to coating as shown in ‘Figure 3’.

Coating samples includes three stages:

2.1. First stage

After cleaning samples from impurities they were painted by red iron oxide as an initial layer as shown in ‘Figure 4’.
2.2. Second stage

Samples were coated by pure cellulose nitrate, pure sodium silicate, cellulose nitrate reinforced by MgO with different percentages (1, 2 & 3 wt.%) and sodium silicate reinforced for the same percentage as intermediate layer as shown in ‘Figure 5’, ‘Figure 6’, ‘Figure 7’ and ‘Figure 8’, respectively.

The following tests were performed (adhesion force, electrochemical corrosion and chemical corrosion) by the samples coated with sodium silicate and cellulose nitrate reinforced by 3% MgO immersing in three types of oil products (gasoline, gasoil and kerosine) for 24, 48, 72 and 96 hours.

2.3. Third stage

Composite material was prepared from epoxy resin reinforced by nano magnesium oxide, coal coke and hybrid MgO & coal coke (1:1) all of them were with different percentages (1, 2 & 3 wt.%) as final layer.

The following tests were performed (adhesion force, electrochemical corrosion and chemical corrosion) by the samples (hybrid composite with 2 wt.% ) immersing in three types of oil products (gasoline, gasoil and kerosine) for 24, 48, 72 and 96 hours. Table 1, shows the specifications of used oil products.
3. Results and discussion

Based on the following tests: hardness and wear rate, the samples coated with sodium silicate and cellulose nitrate reinforced by 3% MgO were chosen as intermediate layer because they gave the best results compared to the other reinforcement ratios.

Based on the following tests: impact, hardness and wear rate, the hybrid composite with 2 wt.% was chosen as final layer because it gave best results compared with other composites.

Table 1. Specifications of oil products

| Oil product | pH at 25°C | Density gm/cm³ at 15°C | Sulfur content ppm |
|-------------|------------|------------------------|-------------------|
| gasoline    | 6.78       | 0.710                  | 10                |
| gasoil      | 6.6        | 0.850                  | 10                |
| kerosine    | 7.16       | 0.801                  | 10                |

The hardness and wear rate tests were carried out for the intermediate layer, their results were shown in table 2 and table 3.

Table 2. Values of surface hardness for prepared coatings with reinforcement ratios

| Reinforcement ratio % | Surface Hardness |   |   |
|-----------------------|------------------|---|---|
|                       | Sodium Silicate  |   |   |
|                       | Cellulose Nitrate|   |   |
| 0                     | 58.3             | 76.8 |
| 1                     | 61.7             | 78.3 |
| 2                     | 63.7             | 82.4 |
| 3                     | 65.6             | 85.2 |

Table 3. Values of wear rate for prepared coatings with reinforcement ratios of intermediate layer

| Reinforcement ratio % | Wear Rate (Intermediate layer) |   |   |
|-----------------------|---------------------------------|---|---|
|                       | Sodium Silicate*10⁻⁵ |   |   |
|                       | Cellulose Nitrate*10⁻⁵ |   |   |
| 0                     | 9.031                         | 7.0032 |
| 1                     | 7.092                         | 6.0018 |
| 2                     | 5.38                          | 2.0072 |
| 3                     | 3.009                         | 1.484 |

From table 2, we noticed that the increase in hardness with the increase of the reinforcement ratios is due to the nanoparticle penetrates inside the base material and works to fill and reduce the gaps that formed during the molding process, which gave better mechanical properties.

The increase in the reinforcement ratio leads to the decrease in the wear rate because of the increase in the rates of slippery communication between the touching surfaces as shown in table 3. From this, we conclude that the reinforcement ratio 3% gave the best results compared to the other reinforcement ratios.

The topography surface of the intermediate layer was studied by AFM microscope and its results are shown in ‘Figure 9’ and ‘Figure 10’. The nature and homogeneity of the surface of the coat were studied by the optical microscope and their results are shown in ‘Figure 11’ and ‘Figure 12’.
Figure 9. Topography intermediate layer (cellulose nitrate)

Figure 10. Topography intermediate layer (sodium silicate)

Figure 11. Nature surface of intermediate layer (cellulose nitrate)

Figure 12. Nature surface of intermediate layer (sodium silicate)

Microscopic images showed that the reinforce by nano magnesium oxide increases the homogenization process thus obtaining better mechanical properties.

Table 4, shows the values of adhesion force of the intermediate layer. It was found adhesion force of the cellulose nitrate is better than of sodium silicate because the mechanical bonding of the cellulose nitrate with the steel surface is better than that of sodium silicate and the locations of sodium silicate at the surface are working as a store of adhesive material that used in the adhesive force measuring device.

| Intermediate layer               | Adhesion (Pa) |
|----------------------------------|---------------|
| Sodium Silicate + 3% MgO         | 171           |
| Cellulose Nitrate + 3% MgO       | 232           |

The lowest corrosion rate is the intermediate layer (Cellulose Nitrate + 3% MgO) works as a dielectric (inhibitory layer) oxidizes with the steel surface and union with oxygen prevents the corrosion metal, this reduces or stops the reaction. This is reported in table 5, ‘Figure 13’ and ‘Figure 14’.

Table 5. Values of electrochemical corrosion of intermediate layer

| Intermediate layer               | Current density μA/cm² | Weight lose gm/m² | Penetration lose mm/a |
|----------------------------------|-------------------------|-------------------|-----------------------|
| Sodium Silicate + 3% MgO         | 117.22                  | 29.3              | 1.36                  |
| Cellulose Nitrate + 3% MgO       | 2.75                    | 0.687             | 0.0319                |
‘Figure 15’ show the values of the chemical corrosion. The reason for the raise of the curve at (1&3) hours of immersion time for sodium silicate, this area is considered a polymer grout area which has an increase in weight and directly proportional to the density because the penetration of water is rapid through polymer chains which lead to increase the chemical bond between them. When the density of bonding increases the susceptibility to absorption of polymer decrease, the difference in concentration between the liquid and the area in which will penetrate during increase. The speed of diffusion is higher according to Fick's law of diffusion. The increased density leads to weight gain (bulge of the intermediate layer) and therefore the weight loss is greater, this means more corrosion and this is clear when samples immersion in gasoil product.
From the three tests above, the intermediate layer (cellulose nitrate +3% MgO) gave the mechanical and chemical protection of the surface sample better than the intermediate layer (sodium silicate +3% MgO) because the ratio of sand to soda 2:3 is called aquatic glass and it is considered a brittle material.

Impact strength, Hardness and wear rate tests were carried out for the final layer showing their results in table 6, table 7 and table 8, respectively.
Table 6. Relation between reinforcement ratio and impact strength for final layer

| Reinforcement ratio% | Pure | MgO | Coal coke | Mix |
|----------------------|------|-----|-----------|-----|
| 0                    | 3.918| -   | -         | -   |
| 1                    | 2.989| -   | 3.785     | 4.625|
| 2                    | 3.761| -   | 3.035     | 4.712|
| 3                    | 4.589| -   | 3.94      | 4.283|

Table 7. Relation between reinforcement ratio and hardness for final layer

| Reinforcement ratio % | Pure | MgO | Coal coke | Mix |
|-----------------------|------|-----|-----------|-----|
| 0                     | 67.5 | -   | -         | -   |
| 1                     | -    | 70  | 79        | 80.2|
| 2                     | -    | 77.6| 79        | 84.1|
| 3                     | -    | 79  | 76.4      | 79  |

Table 8. Relation between reinforcement ratio and weight loss for final layer

| Reinforcement ratio % | Pure | MgO | Coal coke | Mix |
|-----------------------|------|-----|-----------|-----|
| 0                     | 1.009| -   | -         | -   |
| 1                     | -    | 3.009| 5.027     | 3.0063|
| 2                     | -    | 1.081| 2.036     | 1.009|
| 3                     | -    | 5.69 | 1.027     | 2.018|

The hybrid material (2 wt.%) has the highest value of hardness due to the reinforcement particles that carry a large part from the loads applied on the composite material and works to prevent the spread of the cracks in order to increase the bond between the touching surfaces (matrix and reinforcement) as shown in ‘Figure 16’ and ‘Figure 17’, this leads to prevent the dislocation motion and the particles share the matrix phase in the carrying of forces and stresses, which leads to increase the impact strength. The hybrid composite with 2 wt.% was chosen because it gave best results according to the three tests above.

Table 9. Values of adhesion force

| Sample                                                                 | Adhesion (Pa) |
|-----------------------------------------------------------------------|---------------|
| Intermediate layer) +(Final layer) (Sodium Silicate +3%MgO) +(2%hybride)(Cellulose Nitrate +3%MgO) +(2%hybride) | 137           |
| (Cellulose Nitrate +3%MgO) +(2%hybride)                                | 196           |

Figure 16. Nature surface of final layer  
Figure 17. Topography surface of final layer (a) two direction (b) three direction
The relationship between the current density (current of the corrosion) and the potential shown in ‘Figure 18’ and ‘Figure 19’ is linear, this means that the increase of the current shall be with constant potential and any change in potential proof is that the corrosion occurred. The tangents represent the cathode and anodic behavior and the intersection point of these tangents represents the corrosion current.

**Figure 18.** Electrochemical corrosion of (Cellulose Nitrate + 3% MgO) and final layer  
**Figure 19.** Electrochemical corrosion of (Sodium Silicate + 3% MgO) and final layer
Figure 20. Relation between weight loss and reinforcement ratio of final layer

‘Figure 20’, the lowest corrosion rate is (final layer + cellulose nitrate + 3%MgO) because of the reduced potential of (cellulose nitrate +3%MgO) lies under the reduced potential of the steel in the chemical chain and works as a protective layer. Cellulose nitrate is a saturated and stable compound (inert) that does not dissolve in water so it gives chemical protection from corrosion by preventing moisture from reaching the steel surface and it is a good base for the cohesion of the final layer.

4. Conclusion

Mechanical properties increase with the increase of carbonation temperature and the reinforcement ratios of nanoparticles for sodium silicate and cellulose nitrates due to the elimination of internal cracks and the nanoparticles penetration within the polymer chain. The adhesion force of the (final layer + cellulose nitrates + 3%MgO) is greater than the (final layer + sodium silicate + 3%MgO) because of slippery communication between the two layers. Inhibitor coat reduce or stop corrosion metal in order to be united with oxygen and oxidizes with the steel surface.

The particles can be shared the matrix phase in the standing for of forces and stresses applied, which leads to increase the mechanical properties. The Resistance to chemical and electrochemical corrosion of the (final layer +cellulose nitrates + 3%MgO) is greater than the (final layer + sodium silicate + 3%MgO).The hybrid composite (2%) is better than the other hybrid composites according to the mechanical tests. The oil products (gasoline, gasoil and kerosion) are natural according to pH meter.
References

[1] Ahmad Z 2006 Principles of corrosion engineering and corrosion control *butterworth heinemann*

[2] Bentiss F, Traisnel M and Lagrene M 2000 Substituted 1,3,4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media *Corros. Sci.* 42 p 127–146

[3] Khadom A 2010 Mathematical and quantum chemical studies for the corrosion inhibition of steel in HCl acid *Diyala journal of engineering sciences* Vol 03 No 01

[4] Trabanelli G 1991 Inhibitors an old remedy for a new challenge *Corrosion* 47 p 410–419

[5] Khadom A, Yaro S, AlTaie S and Kadum A 2009 Electrochemical, activations and adsorption studies for the corrosion inhibition of low carbon steel in acidic media *Port. Electrochim. Acta* 27 p 699-712

[6] Hantoosh A 2010 Study of the effect of polymer inhibitors on the (Al-Cu) galvanic corrosion in hydrochloric acid *University of Technology*

[7] Sastri S, Hoey R and Revie W 1994 Corrosion in the mining industry *CIM Bulletin* Vol 87 No 976