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Changes On Corrosion Rate After Mechanical Damage

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INTRODUCTION

In the present study, the corrosion rate of ASTM A194 nuts, 2H grade, with different top-coatings, was evaluated before and after mechanical damage of the coating; the damage suffered by this material was originated by two means: grinding the edges of the nut and torqueing the nut to simulate service conditions. The tested electroplated coatings were cadmium, zinc, and Ni-Co; nuts without any damage were used as a reference.

Grinding damage was induce by a rotating abrasive disc and applied to every edge of the nut, torqueing damage was induced by applying a 200 lb-ft torque to every nut, simulating service over-torqueing conditions. The corrosion rate of damaged and intact coatings was measured by two techniques: First, weight loss by total immersion tests according to NACE/ASTM G31-12a were performed; and second, polarization resistance techniques accordingly to ASTM G59-2014 and NFR-194-PEMEX-2013 were also performed; every test was carried out by triplicate in both, intact and damage coatings. The torque selected by these tests represents double the required torque for the normal assembly of nuts.

MATERIALS AND INSTRUMENTATION

The materials and equipment for all tests are listed below:

- Bare 2H ASTM A194 nuts with a nominal diameter of 5/8”.
- Cadmium plated, 2H ASTM A194 nuts with a nominal diameter of 5/8”.
- Zinc-plated, 2H ASTM A194 nuts with a nominal diameter of 5/8”.
- Nickel-Cobalt plated, 2H ASTM A194 nuts with a nominal diameter of 5/8”.
- Plastic, transparent containers of 500 mL.
- A&D GR-200 Analytical balance (sensitivity 0.0001 g).
- Torque wrench in a range 10-500 lb ft.
- Potentiostat-Galvanostat Bio-Logic NS 150.
- Ag/AgCl Reference electrodes.
- Titanium auxiliary electrodes.
- 3 wt.% NaCl solution as electrolyte (5 L).
- Deionized water.

TEST PROCEDURE

3.1 Sample Preparation

The damage caused to the coated materials were carried out by grinding and by torqueing, the former was intended to reveal the base material and expose the couple formed with the coating to the electrolyte in order to evaluate the electrochemical response of the system, the latter was intended for simulating the nut in service conditions. For the grinding, all the edges of the nuts were grinded by hand with a grindstone at 500 rpm until revealing the base material; for the torqueing, a torque exceeding the double of the torque capacity for 2H ASTM A194 nuts (see Table 1) was applied in three cycles of torqueing and loosening by hand. For electrochemical tests, an electrical connection was drilled on one face of each nut and the connection between them isolated with a protective organic coating to avoid introduction of the electrolyte in between connectors and nuts, this is illustrated in Figure 1.

Figure 1 Electrical setting for electrochemical testing

Table 1 Suggested torque for alloy Steel ASTM A193 B7 2H nuts without coating

Diameter (in)	Torque (lbf-ft)
1/2	50
5/8	99
3/4	177
7/8	285

3.2 Total Immersion Tests

- The plastic containers were filled out with the NaCl solution until full.
- The nuts were cleaned with distilled (DI) water and gentle plastic brushing for 30 seconds, immediately after rinsing, the nuts were dried with compressed air and placed in a desiccator for 24 hours.
- Each nut was weighted by triplicate, and the value was recorded.
- The nuts were tied with a non-metallic, inert thread, and hung to the container's lid through a hole, this is to avoid any contact between the nut and the container.
- The nuts were introduced in the containers with the NaCl solution and suspended with the help of the container's lid as it is illustrated in Figure 2.

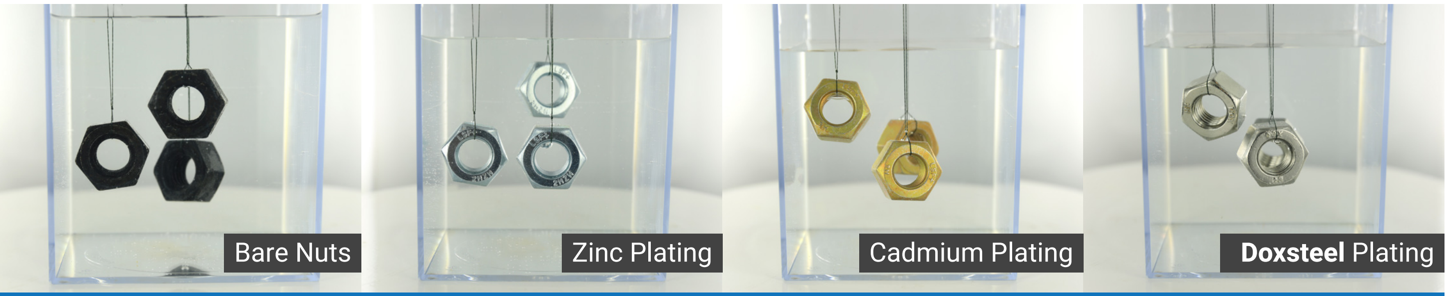

Figure 2 Laboratory immersion test, control group. Immersion solution 3% NaCl

- The containers were located where they could remain static for the duration of the test; solution refilling was slowly added when needed without perturbing the nuts.
- After 7 days, the nuts were removed from the container, cleaned with DI water and gentle plastic brushing to remove corrosion products.
- The nuts were weighted by triplicate and their weights were recorded.
- The average mass loss was calculated by the difference in weight before and after exposure to the solution.

TEST PROCEDURE

3.3 Polarization Resistance Tests

- The plastic containers were filled out with 500 mL of NaCl solution.
- The nuts were cleaned with DI water and acetone to clean all organic residuals.
- The nut with the electrical connections was totally immersed into the solution, ensuring that nothing remained out.
- The reference and auxiliary electrodes were also introduced in the solution in the proximity of the nut.
- The connections of the potentiostat were carried out taking care of connecting the nut to the Working Electrode, the titanium to the Counter Electrode, and the Ag/AgCl electrode to the Reference Electrode in the potentiostat configuration. No connection was immersed into the solution.
- The rest potential was measured for 55 minutes to warranty the stability of the system.
- A DC potential of ±20 mV was applied to the nut at a sweep rate of 10mV/min.
- After finishing the test, the polarization resistance was measured and the corrosion rate calculated.

RESULTS

The corrosion rate for the immersion tests was calculated from the average mass loss, and according to Equation 1. Table 2 shows the corrosion rate results from immersion tests, and Figure 3 shows these values in a histogram for a visual comparison.

1 *Corrosion rate (μm/year) = A x mass loss (g)*

In Equation 1, the constant A considers the exposure time, the exposed area, and the physical properties of the different materials.

Table 3 Laboratory immersion test results of 5/8” nuts with and without plating.

	Initial Weight (g)	Final Weight (g)	Mass Loss (g)	Corrosion Rate (μm/year)
Without plating/Control	48.3916	48.3356	0.0560	34.04
Without plating/Torque 200%	48.6192	48.5599	0.0593	36.05
Without plating/Grinding	42.8845	42.8154	0.0691	42.01
Cadmium/Control	48.7384	48.7037	0.0347	19.00
Cadmium/Torque 200%	49.3698	49.326	0.0438	24.00
Cadmium/grinding	49.3192	49.2681	0.0511	28.00
Zinc/Control	48.2475	48.1497	0.0978	65.00
Zinc/Torque 200%	48.4812	48.3669	0.1143	76.00
Zinc/grinding	49.3971	49.3189	0.0782	52.00
DOX-Steel/Control	50.9501	50.9459	0.0042	2.25
DOX-Steel/Torque 200%	50.7269	50.7201	0.0068	3.62
DOX-Steel/grinding	50.6907	50.6776	0.0131	7.00

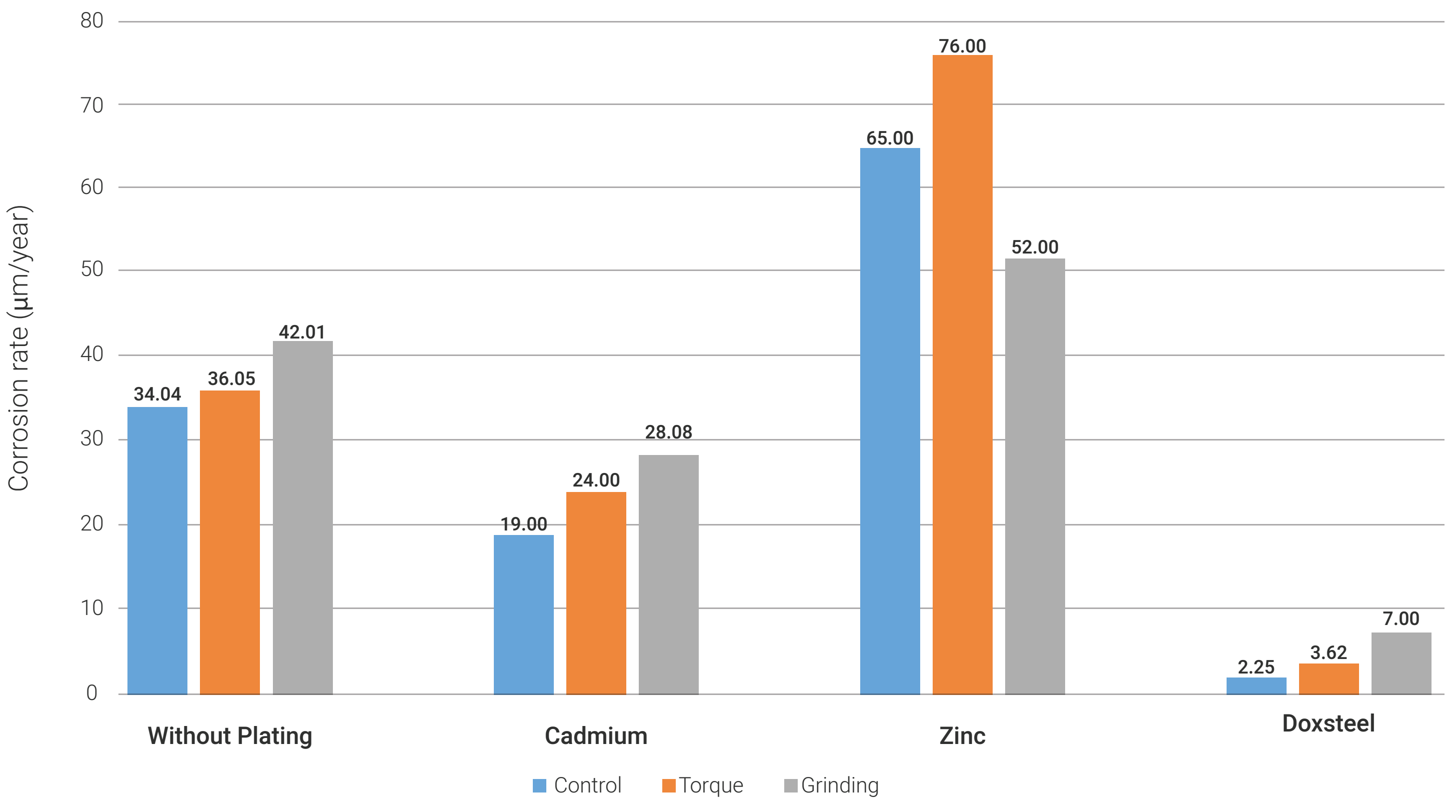

Figure 3 Corrosion rate expressed in µm/year obtained by laboratory immersion testing

The corrosion rate for the polarization resistance technique was calculated from the corrosion current obtained by Tafel analysis in equation 2:

2 *I (A) = B/Rp*

Where the constant B considers the Tafel slopes from potentiodynamic plots. The corrosion rate was calculated from the corrosion current as it is shown in Equation 3.

3 *Corrosion rate (µm/year) = C x corrosion current (A)*

Table 3 Results for the polarization resistance measurements in 5/8” nuts with and without plating.

Plating/Mechanical stress	Rp(ohm)	Icorr (µm)	Rp (ohm*cm²)	Corrosion Rate (µm/year)
Without plating/Control	89	293	4913	61
Without plating/Torque 200%	77	341	4230	71
Without plating/Grinding	43	602	2365	124
Cadmium/Control	245	144	13475	55
Cadmium/Torque 200%	122	239	6710	91
Cadmium/grinding	75	350	4110	133
Zinc/Control	48	531	2640	142
Zinc/Torque 200%	46	594	2555	159
Zinc/grinding	56	484	3080	129
DOX-Steel/Control	17339	5	953645	0.970
DOX-Steel/Torque 200%	7004	36	385220	6.930
DOX-Steel/grinding	171	142	9603	18

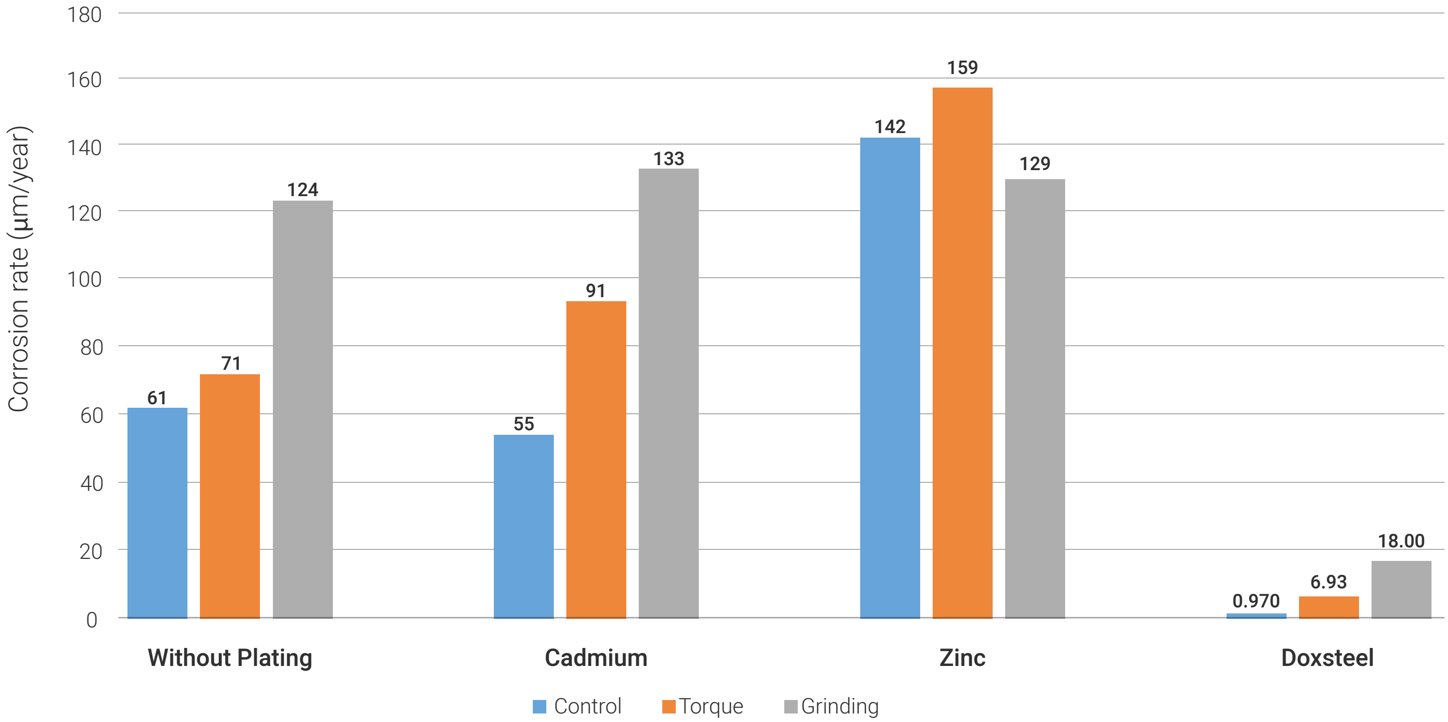

Figure 4 Corrosion rate through polarization resistance measurements

COMMENTS

For the control groups, with no induced damage, the corrosion rate results obtained by the two methods, mass loss and polarization resistance tests, showed that Ni-Co plating has the lowest corrosion rate, approximately one order of magnitude lower than the rest of the coatings used in this project.

For the damaged coatings, the tendency was the same than with intact coatings, the Ni-Co plating had the lowest corrosion rate in both tests, mass loss and polarization resistance, compared to the other coatings, however, the behavior was slightly different. In general, Cd and Ni-Co showed an increasing corrosion rate as further damage was induced, this is happening because the base material is revealed, and the system becomes more active. For the case of zinc, the corrosion rate decreased with further damage, the reason why this happens is due to the galvanic sacrificial effect of zinc when steel starts corroding, despite this decrement in corrosion rate, such decrease is not significant. Although the nuts with Ni-Co plating showed an increase in corrosion rate with respect to the surface damage, the increment in corrosion rate was not significant, and it stopped after certain time; despite the cathodic character of Ni-Co with respect to steel, the slow kinetics (negligible corrosion rate) of Ni-Co does not provide the driving force to steel for further corrosion, the galvanic couple effect is significantly decreased despite the differences in electrochemical potential.

CONCLUSIONS

Ni-Co plating on ASTM A194 nuts have the lowest corrosion rate compared to zinc and cadmium coating on the same material. Despite the induced damage caused by grinding and torqueing, Ni-Co showed the best performance of all these materials. In a hypothetical case that nuts in a flange are tightened with an incorrect torque, or mechanically damaged for manipulation and installation, Ni-Co plating will help to decrease the corrosion rate on these nuts and the little corrosion happening on this material will not compromise the whole flange system. The galvanic couple formed by Ni-Co and steel, is not highly active, and the corrosion rate won't compromise the plated material.

RECOMMENDATIONS

To strengthen the findings in this report, it is recommended to perform a study of galvanic couple, in which, by measuring the output current that produces a galvanic couple, so an assessment on the contribution of the less active material to the corrosion rate of the more active material can be done.

REFERENCES

- NRF-194-PEMEX-2013 Testigos y probetas corrosimétricas.
- ASTM A193 / A193M - 14 Standard Specification for Alloy-Steel and Stainless-Steel Bolting for High Temperature or High Pressure Service and Other Special Purpose Applications.
- ASTM A194/A194M-14 Standard Specification for Carbon and Alloy Steel Nuts for Bolts for High Pressure or High Temperature Service, or Both.
- ASTM G59-97(2014) Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements.
- ASTM G1-03(2011) Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.
- ASTM G102-89(2010) Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements.
- ASTM NACE/ASTMG31-12a Standard Guide for Laboratory Immersion Corrosion Testing of Metals

decreased despite the differences in electrochemical potential.