مجلة العلوم البحثة والتطبيقية
Journal of Pure & Applied Sciences
www.Suj.sebhau.edu.ly ISSN 2521-9200
Received 27/10/2018 Revised 26/09/2019 Published online 08/10/2019

Steel Corrosion Control in Seawater Using Zinc sacrificial anode

Mohamed A. Khalil[a] , *Elfitouri K. Ahmied[b]
[a] Raslanuf Oil and Gas Processing Company, Libya
[b] Petroleum Engineering Department, Sirte University, Libya
*Corresponding author: e.ahmied@su.edu.ly

Abstract The samples surface preparation has been conducted using electrical machining, well electrical wires have been connected to the upper ends of both test samples, for electrochemical potential measurements. Both samples have been fully immersed in natural seawater environment. Test was conducted according to ASTM G31 immersion corrosion testing. Visual examination (VE), optical photograph on each test sample have been conducted The obtained results have been compared and found to be well correlated. It was found that un cathodically protected test sample has been completely covered by corrosion product, whilst the cathodically protected steel test sample found to be covered with a dense and homogeneous calcareous deposit film and free from any sign of corrosion as expected. According to the obtained results from all used monitoring methods it can be concluded that full cathodic protection has been achieved to the cathodically protected steel test sample in aerated natural seawater, whilst un cathodically protected steel test sample has been severely corroded in the a/m environment and the corrosion rate by means of weight loss coupon method found to be 3 mpy which reduced to only 0.25 mpy this means that the achieved protection efficiency % after application of Cathodic Protection was 91%. The required protection current density of bare mild steel in static natural seawater could be reduced to 82% folds, if a well film of calcareous deposit been maintained.

Keywords: cathodic protection, zinc anodes, corrosion rate.

التحكم في تآكل الفولاذ في مياه البحر باستخدام أنود الزنك المضحي

محمد أحمد خليل[1] و *الفيتوري خليفة أحميد[2]
[1]شركة رأس الأنوف لصناعة النفط والغاز، ليبيا
[2] قسم هندسة النفط– جامعة سرت، ليبيا
*للمراسلة: e.ahmied@su.edu.ly

الملخص تم إجراء تحضير سطح العينات باستخدام الآلات الكهربائية ، وتم توصيل الأسلاك الكهربائية بشكل جيد بالطرف العلوي لعينتي الاختبار ، من أجل قياسات الجهد الكهروكيميائية. تم غمر كلتا العينات بشكل كامل في بيئة مياه البحر الطبيعية. تم إجراء الاختبار وفقاً لاختبار ASTM G31 للتآكل الغمر. تم إجراء الفحص البصري (VE) ، صورة ضوئية على كل عينة اختبار وتمت مقارنة النتائج التي تم الحصول عليها ووجدت أنها مرتبطة بشكل جيد. وقد وجد أن عينة الاختبار غير المحمية بالكاثود تمت تغطيتها بالكامل بواسطة منتج التآكل ، في حين وجدت عينة اختبار الصلب المحمية بالكاثود مغطاة بفيلم رواسب جليدية كثيفة ومتجانسة وخالية من أي علامة للتآكل كما هو متوقع. وفقاً للنتائج التي تم الحصول عليها من جميع طرق المراقبة المستخدمة ، يمكن استنتاج أن الحماية الكاثودية الكاملة قد تحققت لعينة اختبار الصلب المحمي كاثودياً في مياه البحر الطبيعية الخلوية ، بينما تآكلت بشدة عينة اختبار الصلب غير المحمي بالكاثود في بيئة A / m ومعدل التآكل عن طريق طريقة كوبون لفقدان الوزن وجدت أن MPY 3 والتي انخفضت إلى MPy 0.25 فقط وهذا يعني أن كفاءة الحماية التي تحققت ٪ بعد تطبيق الحماية الكاثودية كانت 91 ٪. يمكن تقليل كثافة تيار الحماية المطلوبة للصلب الطري العاري في مياه البحر الطبيعية الثابتة إلى 82٪ من الثنايا ، إذا تمت المحافظة على فيلم جيد من الرواسب الجيرية.

الكلمات المفتاحية: الحماية الكاثودية، أنودات الزنك، معدل التآكل.

Introduction

The rate of corrosion is obviously the most important parameter, and will determine the life of a given metal structure. Whether or not a given rate of corrosion can be tolerated will, of course, depend upon a variety of factors such as the thickness of the metal, the function and anticipated life of the metal structure and the effect of the corrosion products on the environment, etc. Protection potential is the electrode potential at which corrosion may be halted by keeping the electrode potential below a given critical value.

With metals used as construction materials corrosion control may be regarded as the regulation of the reaction so that the physical and mechanical properties of the metal are preserved during the anticipated life of the structure or the component. In relation to the term 'anticipated life' it should be noted that this cannot be precise, and although the designer might be told on the basis of information available at that time that the plant should last, say, 10 years, it might be scrapped much earlier or be required to give more prolonged service (1-5).

It is also evident that, providing there are no restrictions on costs, it is not difficult to design a plant to last at least 10 years, but quite impossible to design one that will last exactly 10 years. Thus although under design could be catastrophic, over-design could be unnecessarily expensive, and it is the difficult task of the corrosion engineer to avoid either of these two extremes. A further factor that has to be considered is that in the processing of foodstuffs and certain chemicals, contamination of the environment by traces of corrosion products is far more significant than the effect of corrosion on the structural properties of the metal, and under these circumstances the materials selected must be highly resistant to corrosion (5).

Seawater corrosion and biofouling are two natural process existing at the metal-water interface simultaneously, which are important factors endangering the safe operation of offshore facilities. The low alloy steel is one of the most important metals used in marine structures, and has been in service for many years in marine applications. Cathodic protection (CP) is a major technique of improving the durability of marine applications, and it is required for long term anti-corrosion protection of the subsea steel structures [6].

In recent years, zinc alloys have been preferentially selected as sacrificial anode materials for CP of steel due to their high current efficiency, low specific weight and low cost [7]. Many studies investigated the corrosion behaviour of zinc in SRB-containing marine environment [8] and simulated acid environments [9-10].

Cathodic protection works primarily by depressing the natural corrosion potential of the structure to be protected to a value where it does not corrode [11, 12].

Materials and Methods

The steel sample composition is illustrated in table (1).

Table (1): Steel test sample chemical composition and nearest related specifications

Alloy grade	Typical compositions(%) & properties					
	C	Mn	Ph	S	Si	Fe
M 1020	0.2	0.5	0.05 Max	0.05 Max	0.23	Balance

Both samples have been cut and formed in cylindrical shape, with the following dimensions:

Dimensions of sample" A":

Weight = 298 g, length = 30 cm, diameter = 12.12 mm and the surface area=116.4766 cm².

Dimensions of sample "B"

Weight = 294.879 g, length = 30 cm, diameter = 12.08 mm, and the surface area is116.0846 cm².

Both test samples have been polished using silicon carbide grades (200 -400) up to reach clear surface from any other contamination, rust or corrosion.

The test samples have been electrically connected with a suitable electrical well insulated wires in order to avoid any error in the potential measurements which has been confirmed by electrical continuity test method results using the multi-meter device, by measuring the resistance between the electrical wires and the test connected samples.

All obtained electrical continuity test results of all experimental cell components (working, auxiliary and reference electrodes) were within the acceptable ranges (very low resistance)

The chemical composition, of the zinc sacrificial anode are tabulated in tables (2).

Table (2): shows the chemical composition of zinc alloy sacrificial anode

Specification Code	US Mil Spec 118001 K
Cu	0.05% max
Al	0.010 – 0.50%
Fe	0.05% max
Cd	0.025 – 0.07%
Pb	0.006% max
Others (total)	0.10% max
Zn	Remainder

The test electrolyte (corrosive media) was natural seawater in an ambivalent room temperature conducted from Sirte Gulf seawater.

Figure. (2) sacrificial zinc anode.

The electrochemical test sample (working electrode) to electrolyte potential measurements versus (vs.) exposure time was conducted. Daily potential measurements vs. exposure time for time period of more than (3) months a duplicate measurement has to be conducted up reach the acceptable accurate potential reading with respect to Ag/AgCl reference-electrode half-cell).

In order to investigate the mild steel corrosion in natural static seawater environment, weight loss analysis, and corrosion performance were studied by using weight loss method. This method consists of preparing, the test sample, and clean it then weight it before the immersion in the test solution, remove the test sample after the suitable time duration and clean it, according to the corrosion test method standards.

The obtained potential in this experiment will represent the steel protection potential in order to evaluate the mild steel cathodic protection in seawater environment and to be compared with the visual examination and weight lost obtained test results. All parameters such as test sample surface condition, calcareous deposit, electrolyte colour, temperature and pH, have to be monitored evaluated and recorded in a suitable designed forms. The obtained protection potential has to be evaluated

The required protection current has to be measured before and after calcareous deposit build up, and the obtained results has to be compared.

Interpretation of all obtained data during both performed experiments at the end of each experiment, each test sample has to be removed visually inspected, optically photographed, before and after cleaning then weighed in order to calculate the corrosion rate in each.

Results and Discussion

Investigation of Mild steel corrosion in seawater environment without application of any corrosion control method. The electrochemical measurement of corrosion potential versus time, conducted during full immersion condition of bare (without any applied protective coating) mild steel test sample (working electrode) (WE), in seawater environment, in order to simulate steel jetty and/ or platform piles submersed zoon corrosion.

The test electrolyte (seawater) pH at first immersion of the test sample (0 exposure time) was 8.045 and remained constant and /or minor change up to the 18th day which indicate gradually increases (from 8.102 to 8.19) with time at 30th day than showed quite fluctuation by mine increases or decreases up to the 64th day and back to the gradual increases with time with noticed drop in on 63rd day and back to the same gradual increases with time with noticed flocculation by small increases or decreases with time up to the 83rd day and back to the gradual visible increases with time from 84th day up to 95th day ranged from 8.205 to 8.28, it is noticed that the corresponding steel test sample corrosion potential readings during this period were shifted to the positive direction and attained the steady state corrosion potential(-388 mV). The electrolyte temperature the time duration of 95 days were ranged from 16°C to 29 °C (the room temperature) as a minimum and maximum obtained readings and no significant clear trend can be noticed for the relationship can be detected.

Fig.(2) shows corrosion potential (mV) represented by Y axis, whilst the X axis represents the exposure time (in days), as seen the mild steel corrosion potential increases gradually toward positive direction with increasing of exposure time and attained the steady state condition at day 63 and continuous with minor changes up to the end.

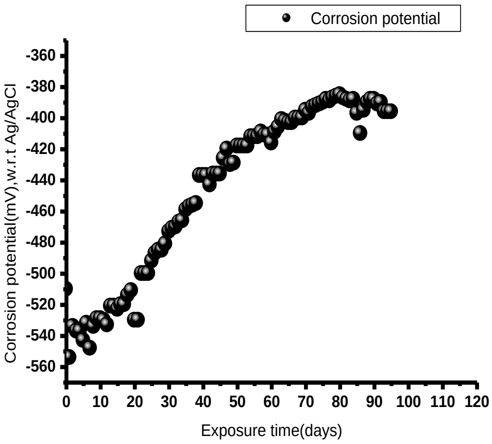

Figure. (2) Mild steel corrosion potential vs. time in natural seawater environment.

As seen from Equation (1), the percentage of weight loss of mild steel in seawater increases with respect to time.

CR(mpy) = $\frac{534W}{DAT}$ (1)

Where:-

mpy: corrosion rate(CR) in mils inch per year

W: weight loss in mg

D: density of mild steel in g/cm^3

T: exposure time in hours

A: test sample area in in^2

Initial weight (W1) of steel is 294.87g after 95 day of full immersion in natural seawater, the weight its becomes after a period of exposure time (W2) = 293.11g

Weight lost(W) = W1-W2 =294.87-293.11=1.76g= 1760 mg

D=7.85 g/cm^3

T =95*24=2280 hr

A=πdL+ $\frac{2\pi d^2}{4}$

Test sample diameter (d)

d =1.208cm

Test sample length (L) =30cm

A=2.292+113.85=116.142 cm^2=18.0023 in^2

CR=2.93 mpy = 0.074mm/y, this corrosion rate value, is met the corrosion rate reported in a corrosion protection guide for steel bearing piles in temperature climates, These are broadly in line with the rates given in BS 8004. Considerably higher corrosion rates have been experienced in situations where there is a roughly constant water level and in these cases appropriate methods of protection are recommended.

After 95 days of immersion the test sample has been removed and cleaned for evaluation of corrosion type and rate. Visual examination has been performed on the mild steel test sample and general corrosion (uniform corrosion) were noted on whole test sample surface and no any significant appearance of any localized corrosion as can be clearly confirmed by the optical photo graphs indicated in figure (3).

Figure. (3) The general corrosion on the test sample after immersion of 95 days in natural seawater environment and after removing all existing corrosion product and well surface cleaning.

From 46th day up to 53rd day, the sudden jump to the positive potential, was due to the bad contact between the tests samples (WE) mechanically connected electrical wire, leading to high increase in circuit resistance (between the test sample and the wire), decreasing the zinc anode current output and the test sample (WE) protection potential consequently, fortunately the obtained protection potential during this period(7 days), dose not reached the limit of NACE standard TM0497-2000,which stated that the minimum protection potential criterion should not be less than (-800 mV with respect to Ag/AgCl reference-electrode half-cell), this has been confirmed by visual monitoring results which does not reviled any changes in the water cooler and /or any visible appeared spot of rust on the steel test sample surface, during this time period, as will be discussed in detailed in the visual examination section. The bad contact problem has been eliminated and good contact has been insured which can be noticed by high negative increases in the protection potential readings from 54th day with 140 mV in magnitude and continued fluctuated between negative and positive protection potentials range (-910 mV to -1041 mV) during the duration of exposure time from 55th day to 85th day than back to steady state condition on 86th day up to the end of the experiment. All protection potential obtained result have been plotted in graph indicated in fig. (4)

Fig. (4): Demonstrates the mild steel protection potential represented by Y -axis vs. immersion time reprinted by X- axis in natural seawater environment as can be seen that the test sample received full protection potential from the zero time of immersion up to the end of the experiment.

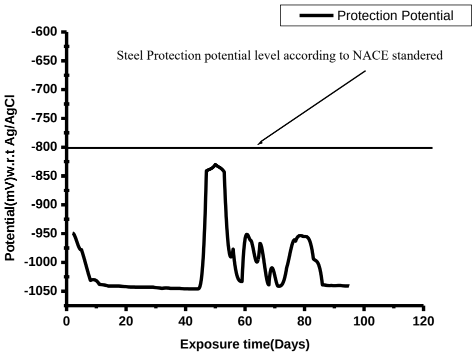

Figure (4): Mild steel corrosion potential vs. exposure time in natural seawater environment.

After completion of 93 days, despite of the high recorded positive shift and the fluctuation in protection potential the limit of steel protection level (line indicated in the graph) was not attained as a/m, protection potential re-back to the steady state condition as can be confirmed by the a visible restoration of calcareous deposit clearly appeared on optical microscopic graph in fig. (5).

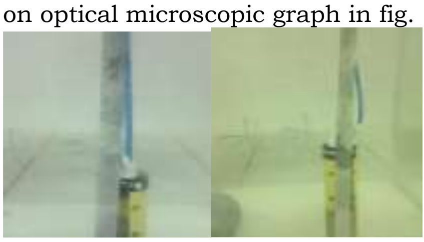

Figure. (5): Restoration of the damaged calcareous deposit at localized areas after fixing the bad connection problem

Figure (6) Illustrate the Comparison between Mild steel corrosion potential and protection potentials vs. time in natural seawater environment .as seen all corrosion potential obtained readings were above the line of steel accepted protection level, whist all obtained protection potential readings were below protection limit line i.e. within the accepted steel protection potential level, as already experimentally confirmed, by the visual evaluation of both un cathodically (freely corroded) and cathodically protected steel test samples see figure (5).

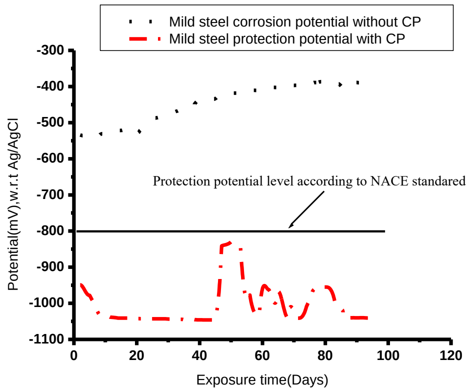

Figure. (6): Comparison between Mild steel corrosion potential and protection potentials vs. time in natural seawater environment

Because more hydroxyl ions (higher pH) are required to cause magnesium hydroxide to precipitate, the magnesium is virtually always found in the calcareous deposits associated with calcium and its presence is an indicator of a high interfacial pH and thus either high cathodic current densities or relatively poor seawater refreshment. The practical consequences of these events are that once the calcareous film has formed, a cathodic current density at least an order of magnitude lower than that required to protect bare steel is needed to maintain protection. Although temporary damage to the film (for example, storm action) may create a temporarily increased current demand, the film soon repairs and the lower current demand is restored.

Visual examination as a second method used to investigate and evaluate the mild steel corrosion protection effectiveness. It is very easy to monitor the steel corrosion in very high classified corrosive environment such as natural seawater. It is well known that four hours are enough to see the rust, on the steel cleaned surfaces in corrosive environment, as can be seen no any change appeared in the seawater cooler, and/or on fully immersed test sample during the whole period of test sample exposure time. Fig. (7) shows the comparison between zero day exposure time and the 2nd day cathodically protected steel surface conditions. As seen calcareous deposit, start to precipitate on the test sample surface on the 2nd day of immersion correspond to protection potential -949 mV.

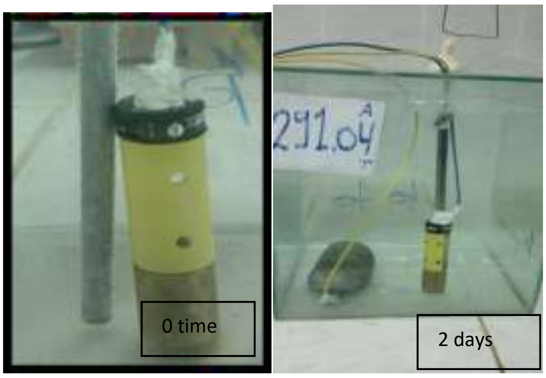

Figure. (7): Test sample at 0 exposure time a), Calcareous deposit precipitation after 2 days immersion in seawater environment

Fig. (8) shows the optical photographic photos of calcareous deposit precipitation on cathodically protected bare steel test sample vs. immersion time, as seen the calcareous deposit layer precipitated on the surface at 9th day corresponding to the protection potential (-1029 mV), figure(5-20).a, is less dense and thick compared, with that precipitated on at 38th day with corresponding protection potential (-1045 mV)

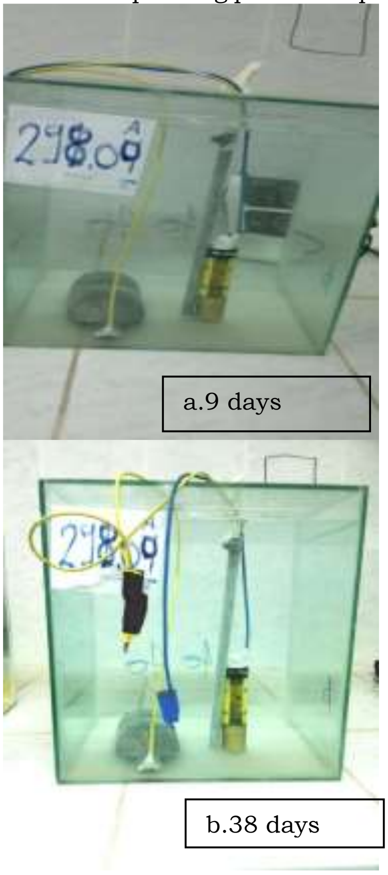

Figure. (8) Calcareous deposit complete layer built up after 9 days (a), and more dense and homogenous

Conclusions

From the results of this study, we can conclude that:

1. Mild steel in static seawater immersion test for duration time of 95 days showed only general corrosion and no any visible pitting corrosion and the obtained corrosion rate by means of weight loss method found to be 2.93 mpy.
2. Mild steel corrosion potential in static seawater environment increases toward the positive direction with increasing the immersion time.

Acknowledgment

The authors wish to thank Raslanouf Oil Company and The University of Sirte for their support and encouragement.

References

[1]- L L Shreir, R A Jarman. (1994), "corrosion 1 metal / Environment Reaction ", Oxford Auckland , Boston ,p p p 1:6-1:12-2:135
[2]- L L Shreir, R A Jarman. (1994), "corrosion 2 Corrosion Control ", Oxford Auckland , Boston
[3]- Donald L. Basham, P.E. et la James W Wright, P.E, Kathleen I. Ferguson, P.E., Get W. Moy, P.E.(2003), Unified Facilities Criteria (UFC)
[4]- Mars G. Fontana.(1987),"Corrosion Engineering", New York.
[5]- Pierre R. Roberge.(2000)," Handbook of Corrosion Engineering", New York San Francisco Washington, London.
[6]- W. Li, Y. Yan, G. Chen, Proc. Eng., 12(2011) 27.
[7]- R. Song, Z. Guo, A. Fan, Corros. Sci. Prot.Technol., 16(2004) 25.
[8]- F. Liu, S. Zhang, J. Zhang, Chin. J. Mater. Res., 24(2010) 411.
[9]- X. Li, D. Chen, J. Chen, Corros. Sci. Prot. Technol., 22(2010) 14.
[10]- B. An, X. Zhang, E. Han, Acta Metall. Sinica.,40(2004) 202.
[11]- I. Gurrappa, "Cathodic protection of cooling water systems and selection of appropriate materials," Journal of Materials Processing Technology, vol. 166, no. 2, pp. 256–267, 2005.
[12]- C. A. Loto and A. P. I. Popoola, "Effect of anode and size variations on the cathodic protection of mild steel in sea water and sulphuric acid," International Journal of Physical Sciences, vol. 6, no. 12, pp. 2861–2868, 2011.