Bar Steel Corrosion Control in Seawater Using Cathodic Protection Technique

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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. Natural potential has been recorded at zero time using high impedance potentiometer device. Visual examination(VE), optical photograph on each test sample have been conducted, in order to monitor the corrosion products and the calcareous deposit film on both freely corroded and cathodically protected mild steel test samples respectively. 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. The required protection current densities, have been measured on cathodically protected steel test sample before and after calcareous deposit build-up. Corrosion rate have been measured and calculated on both catholically and un- cathodically protected steel test samples and presented. 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, 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 CP 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.

Key words— cathodic protection, corrosion, corrosion rate, seaware, current density, potential.

I.INTRODUCTION

Corrosion is the reaction of a metal with its environment, and it was emphasized that this term embraces a number of concepts of which the rate of attack per unit area of the metal surface, the extent of attack in relation to the thickness of the metal and its form (uniform, localized, intergranular , cracking, etc.) are the most significant. 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

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metal structure and the effect of the corrosion products on the environment, etc. 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).

Corrosion protection is guaranteed only if good adhesion properties are attained between the metallic substrates and the coating. Enhanced adhesion can be achieved by the use of an appropriate surface preparation prior to coating (etching, polishing, etc.) or with a good pretreatment which can also provide additional corrosion protection and adherence (6, 7). So an appropriate combination of surface preparation, pretreatment and coating provides increased durability of the protective system.

Xia *et al* (8) proposed a new parameter of coating degradation coefficient by analyzing the changing rate of impedance which correlates well with the protective performance of organic coating. The advantage of above methods is that the parameters are mainly obtained in middle and high frequency domains of EIS, as a result, the measurements in low frequency domains and complicated fitting and calculation for EIS data can be avoided.

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				
M 1020	C	Mn	Ph	S	Si	Fe
	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 cleaned 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 avoided any error in the potential measurements as illustrated in figure (1), 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 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.

The electrochemical test sample (working electrode) to electrolyte potential measurements versus (vs.) exposure time was conducted, in accordance to NACE Standard TMO497- 2002 sections 4, 5 and 6. 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. 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 color, temperature and pH, have to be monitored evaluated and recorded in a suitable designed forms. The obtained protection potential has to be evaluated in accordance to NACE standard TM0497-2002 section 8.

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 bare 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 as a minimum and maximum obtained readings and no significant clear trend can be noticed for the relationship can be detected.

Fig. (1) 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.

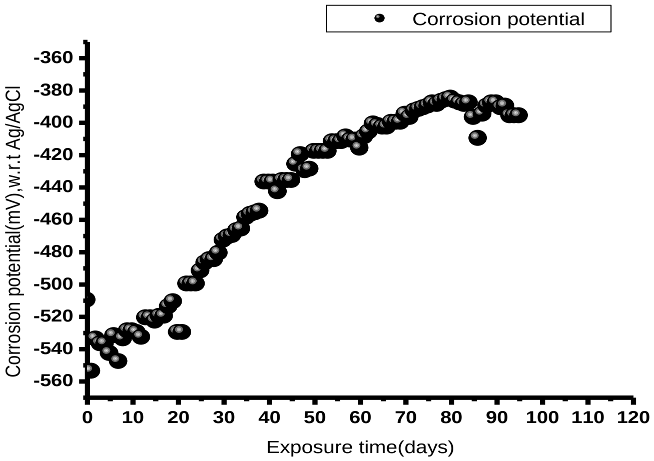

Figure**. (1) Mild steel corrosion potential vs. time in natural seawater environment.**

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

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

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 cm²=18.0023 in²

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 (5).

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 (2).

Figure. (2) 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. Remedy action has been taken and 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.(3)

Fig. (3): 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.

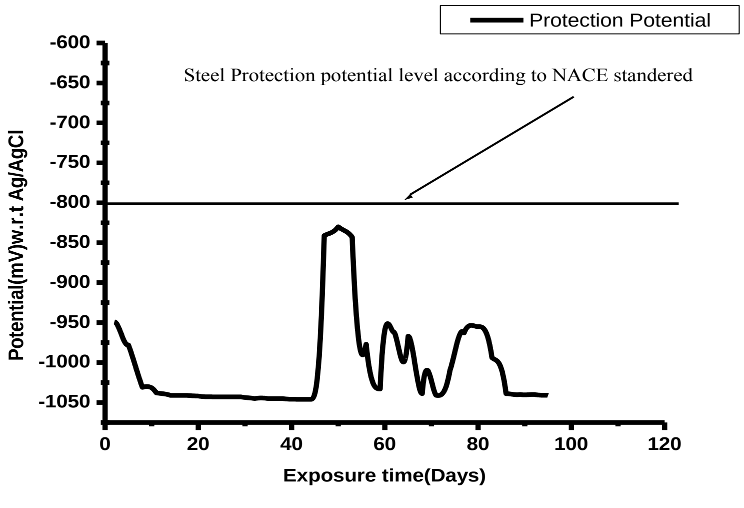

Figure (3): Mild steel corrosion potential vs. exposure time in natural seawater environment

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 in fig. (4).

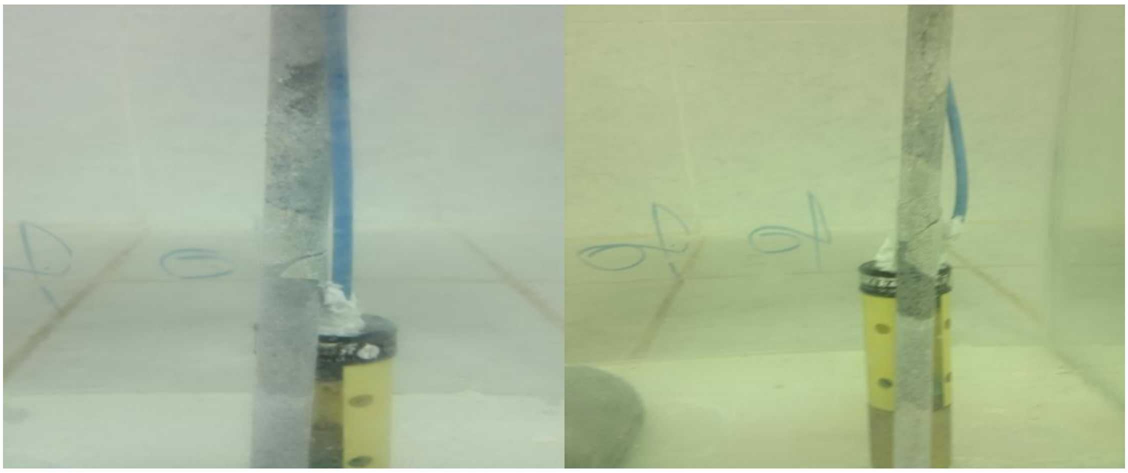

Figure. (4): Restoration of the damaged calcareous deposit at localized areas after fixing the bad connection problem

Fig. (5) Shows a comparison between mild steel freely corroding (A) and cathodically protected (B) test samples surface condition, after 53 days of fully immersion in natural seawater environment. As seen the mild steel without applied cathode protection subjected, to heavy corrosion product appeared on the surface as a thick and dense layer of corrosion product, thick corrosion product accumulated layer on the glass container bottom and visible changes in the seawater cooler, on the other hand the mild steel cathodically protected test sample shows thick and dense layer of calcareous deposit a papered as a white barrier covered the whole surface, without any brown changes in the seawater color and thick accumulated layer of calcareous deposit on the glass container bottom, which reviled well correlation between the electrochemical and physical examination obtained results.

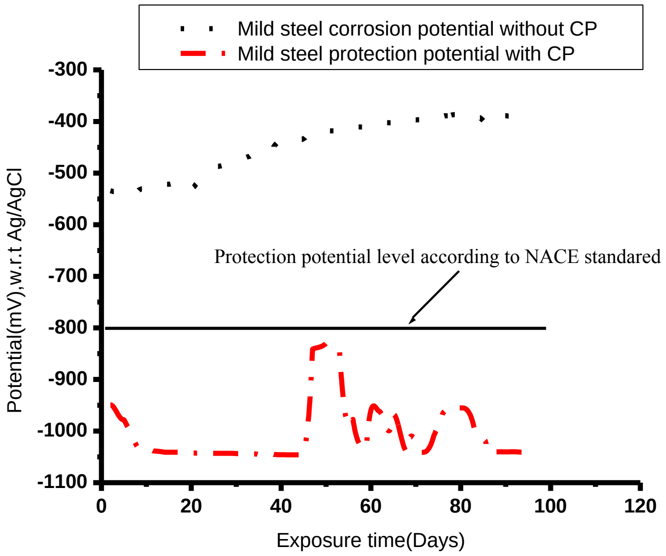

Figure. (5): Comparison between Mild steel corrosion potential and protection potentials vs. time in natural seawater environment

Thus brucite (Mg $(OH)_2$) is also commonly found on surfaces under cathodic protection in seawater. 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 (6).

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. (6) 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.

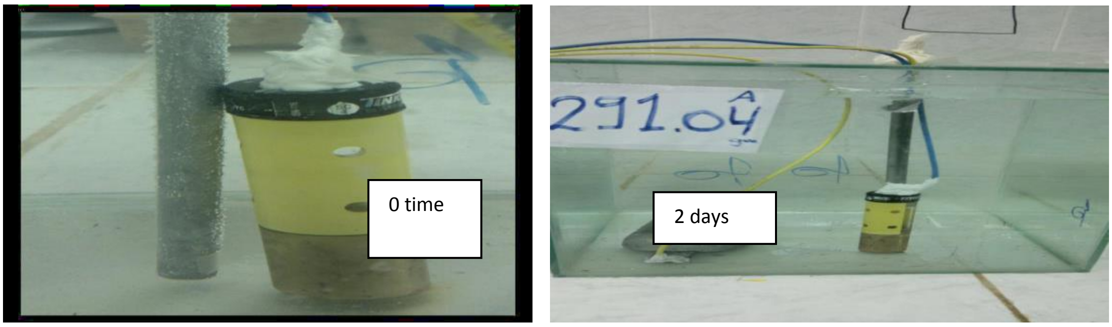

Figure. (6): Test sample at 0 exposure time a), Calcareous deposit precipitation after 2 days immersion in seawater environment

Fig. (7) shows the 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 7.a, is less dense and thick compared, with that precipitated on at 38th day with corresponding protection potential (-1045 mV)

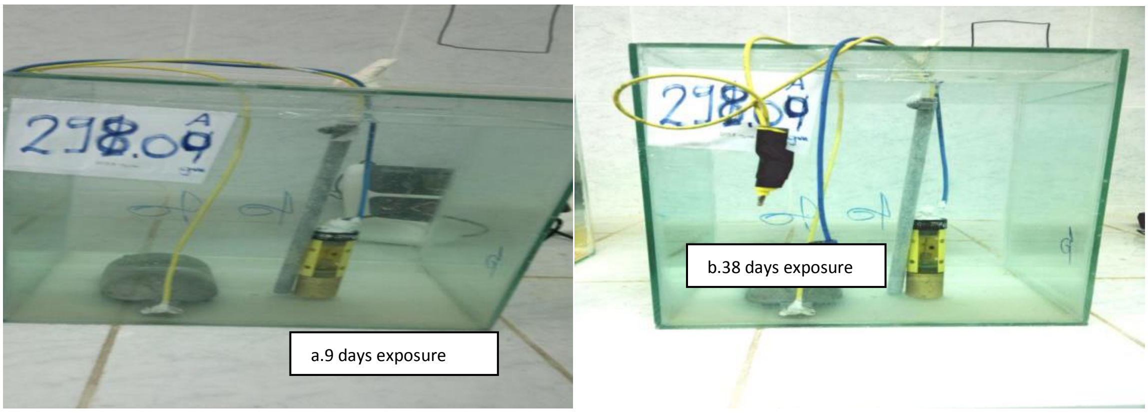

Figure. (7) Calcareous deposit built up after 9 days (a), and more dense and homogenous.

Conclusions

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.

Mild steel corrosion potential in static seawater environment increases toward the positive direction with increases the immersion time.

Zinc Sacrificial anode cathodic protection SACP, is an effective corrosion control method, for fully immersed bare mild steel, in static seawater environment.

SACP can reduce corrosion rates up to 91 folds of fully immersed bare mild steel in natural static seawater environment.

The calcareous deposit layer can reduce the required protection current/current density 82 /82.1 folds respectively of fully immersed bare mild steel in natural static seawater environment.

Well correlation between the electrochemical (potential measurement) test method and visual examination obtained results.

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التحكم في تآكل الحديد باستخدام تقنية الحماية المهبطية

الملخص: تم إجراء تحضير سطح العينات باستخدام الآلات الكهربائية، وتم توصيل الأسلاك الكهربائية بشكل جيد بالطرف العلوي لكلتا عينتي الاختبار، من أجل قياسات الجهد الكهروكيميائي. تم غمر كلتا العينات بشكل كامل في بيئة مياه البحر الطبيعية. تم إجراء الاختبار وفقًا لاختبار ASTM G31 للتآكل الغمر. تم تسجيل الإمكانات الطبيعية في وقت صفر باستخدام جهاز الجهد العالي المقاومة. تم إجراء الفحص البصري (VE)، صورة ضوئية على كل عينة اختبار، من أجل مراقبة منتجات التآكل وفيلم الودائع الجيرية على كل من عينات اختبار الفولاذ الطري المتآكل والمحمي بشكل كاثودي على التوالي. تمت 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. تم قياس كثافة تيار الحماية المطلوبة، على عينة اختبار الصلب المحمي كاثوديًا قبل وبعد تراكم الودائع الجيرية. تم قياس معدل التآكل وحسابه على كل من عينات اختبار الصلب المحمية بالكاثول وغير الكاثودي وعرضها. وفقًا للنتائج التي تم الحصول عليها من جميع طرق المراقبة المستخدمة، يمكن استنتاج أن الحماية الكاثودية الكاملة قد تحققت لعينة اختبار الصلب المحمي كاثوديًا في مياه البحر الطبيعية الخلوية، ومعدل التآكل عن طريق طريقة قسيمة فقدان الوزن التي تم العثور عليها 3 mpy انخفض إلى 0.25 ميغابايت فقط وهذا يعني أن كفاءة الحماية المحققة ٪ بعد تطبيق CP 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.

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