INVESTIGATION ON CORROSION PROTECTION OF INTERNAL COATED CRUDE OIL PIPELINES

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ABSTRACT

The objective of the current study is to provide data for proper choice of coating material type which will be durable as internal coating for crude oil pipelines. Different types of epoxy resins based paints have been selected for coating steel pipe test samples. The surfaces of these steel samples were pretreated before application of different coatings by blast cleaning. The surfaces profil of treated samples were checked by using the testex tape. The corrosion resistance of the coated samples, to different corroding media, has been determined via two main methodologies. Firstly, through weight loss method and secondly, by potentiodynamic and potentiostatic electrochemical methods. The corroding media have been selected based on the expected environments that a pipeline in the petroleum industry can possibly meet.These environments are mainly restricted into two main types of corrodants, namely, saline water with different concentrations and acidic solution of about 0.1M HCl. The results show that it is possible to rely on the accelerated electrochemical methods in order to predict the durability of the coating material against different corroding media. The study also reveals that some types of epoxy resins are superior in corrosion protection and durability against saline water and acidic corrosive media as compared to the others.

Key words: *corrosion of pipes, polymer coating, oil field corrosion, corrosion protection, epoxy paints.*

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INTRODUCTION

There are several environmental factors which cause corrosion problems of steel used in pipelines [1].The most important factors, are that encountered in actual production formation which, in absence of contamination, are devoid of oxygen [2]. To the initially oxygen-free geologic environment, a variety of oxygen contaminated fluids may be introduced. Additional important environmental aspects are the elevated temperature and turbulence encountered.

The internal coating of pipelines can be achieved with a wide variety of painting materials [3-5]. However, epoxy paints are characterized by their very high resistivity to chemical attack, high mechanical durability, relatively high temperature endurance, and the ability to adhere to a variety of substrates, together with their relatively cost effectiveness.

The aim of the present work is to investigate the effect of various environmental factors, which are the corrosive media (brines and acid), elevated temperature and mechanical stirring, on the durability of five different types of epoxy resins used as internal coating for crude oil pipelines.

EXPERIMENTAL

I- Materials:

a. Steel pipe samples

Twenty six steel samples were taken from oil field pipes (API 5L, Grade X52). All samples had the same chemical composition (0.21%C, 0.9% Mn, 0.26% Si, 0.015% S, 0.09% V and 0.03% Al), according to American Petroleum Institute specification, and were obtained with the same dimensions (42 ×10 × 5 mm).

B. Coating materials

Five different types of epoxy paints were used for coating the tested samples. These types including Penguard Primer (PP), Barrier 77 (B77) and Tankguard Primer (TP) were supplied by JOTUN company, beside PW1020 and PW1011 were supplied by CIBA GEIGY company.

II- Preparation of Sample Surface Prior to Coating:

The samples were cleaned by blast cleaning (using steel balls with size of 250μm and hardness HRc 52) to achieve thorough cleaning and surface profile having a peak to valley within the range 50±20 μm **[6]**. The surface profile was measured by Testex tape (having thickness 50μm) which was sticked to the surface of each sample and rubbed its paste into that surface, using a blunt instrument, until the peaks could be seen butting up to its transparent plastic. The testex tape was removed from the surface and its overall thickness was measured with a dial micrometer. The thickness of the testex tape was deducted from the reading to obtain the surface profile. The measured values of peak, valley and peak to valley of the surfaces of blasted samples were recorded as given in Table(1).

III- Application of Coatings:

The tested samples were coated, after surface preparation, as the mentioned instructions by suppliers.

Blasted steel specimens were painted within a specified period of time depending on the relative humidity of the surrounding atmosphere, as illustrated in Table(2).

The ambient temperature and relative humidity, during coating operation, were 25°C and 60% respectively, which were in the application range mentioned by suppliers.

The visual appearance of coating films indicated that they were free of sagging, flaking or cracking. Also, they were free of softening, wrinkling or blistering after 30 minutes recovery period at room temperature.

The dry film thickness of painted samples was measured by thickness gauge, with range 0-500μm, to be sure that it is within the range given by suppliers.

IV- Corrosion Testing Procedures:

The test specimens were subjected to the following corrosion environments; saline water with different NaCl concentrations of 1, 3 and 5% (which are similar to NaCl concentration of open lakes, sea water and underground water respectively), and acidic solution of about 0.1M HCl. Two classes of experiments were designed to monitor the corrosion of the coated samples compared with the blank (uncoated sample). The first class of experiments was the static bottle test, utilizing the weight loss of hanged coupons in the corrodant. The second was the electrochemical measurements which could be; potential measurements as a function of time (the open circuit corrosion potential), and polarization (anodic and cathodic) measurements.

Potential measurements in combination with weight loss measurements (i.e.,corrosion rate) can provide useful information on film (coat) breakdown.

1- Static bottle test (weight loss measurements)

This procedure was employed as a means of evaluating the rate of deterioration in the coated steel coupons as compared to uncoated coupons, according to TROS analytical procedure TRO-165 [7].

The test samples were dried in an electric oven for 1 hr. at 50°C and then placed in a desiccator till constant weight was reached (to the nearest 0.1mg). The samples were divided into two groups. One group hanged in 1%,3%,5% NaCl solution and the second in 0.1M HCl solution. The coupons were hanged in a 500ml capacity glass bottle with a lid containing the corroding medium for an extended time of 14-24 days. The coupons were taken and pickled with 15% HCl for approximately 10 seconds. Then the coupons were thoroughly rinsed with deionized water, after that the coupons were dipped in and out of water free acetone. The coupons were dried first with fiber free cloth, then in an electric oven for 1 hr. at 50°C and finally were placed in a desiccator till constant weight was achieved (to the nearest 0.1mg).

The weights of coupons were determined before and after test. The corrosion inhibition percentage of the coated steel coupon was calculated using the following equation:

$$\textbf{Corrosion inhibition \%} = (W_1 - W_2)/W_1 \cdot 100$$

W_1 = average wt. loss of blank, W_2 = wt. loss of coated coupon

The corrosion rate of the coupon in mils per year (mpy) was calculated according to the following equation:

$$\textbf{mpy} = 534\ W\ (\text{mg})\ /\ \rho(\text{g/cm}^3).A(\text{in}^2).t(\text{hr})$$

Where W = weight loss, ρ = specimen density, A = specimen area and t = exposure time.

2- Electrochemical measurements

The tested samples were dried in oven for 1 hr. at 50°C and then placed in a desiccator till constant weight was reached (to the nearest 0.1mg). The samples were divided into two groups. The first group for potential measurements in all electrolyte solutions (1, 3 and 5% NaCl) and the second group for polarization measurements, i.e., accelerated corrosion condition in (mixture of acid and electrolyte).

i. Corrosion potential measurements

The test coupon was placed as a specimen electrode in a cell containing the test electrolyte (NaCl solution or acid solution). A reference electrode (Calomel electrode “CE”) was dipped in a beaker containing 0.1M KCl and bridge via a salt bridge.

A laboratory high-precision potentiostate Model Bank LB 81 (West Germany) was used for measuring the resulting corrosion potential with respect to CE. Corrosion potential in mV was recorded with time.

ii. Polarization measurements

In these experiments the test coupon was subjected to accelerated corrosion conditions by electrochemical method. The electrochemical cell was constructed as explained by ASTM recommended practice G5. It was the same previous explained cell used for measuring corrosion potential but with addition of a Platinum electrode as a counter electrode which was dipped into the test electrolyte remote from the specimen electrode (Working electrode).

The potential was polarized at a fixed rate of about 100 mV/min and the corresponding current was registered. The current density in mV/cm^2 was plotted against potential in mV for both cathodic and anodic range of potential.

Tafel extrapolation method was used to calculate the corrosion current ($I_{corr.}$) in $mA/\ cm^2$ from the plotted anodic and cathodic curves [7-9].

iii. Effect of temperature and mechanical stirring on corrosion protection of coating materials

The effect of temperature on the corrosion potential of the tested samples has been investigated in the 5% NaCl corroding medium. The corrosion media were heated up to 60°C using submersible automatic heater (Akva-Stabil, COMBI). The combined effect of temperature and mechanical stirring has been studied also in the 5% NaCl corroding medium by using a mechanical stirrer at 1200 rpm.

RESULTS AND DISCUSSION

I- Effect of The Corroding Media on The Coating Material:

The present study deals with the effect of corroding media on the durability (corrosion resistance) of different epoxy coatings as anti-corrosion protecting agents for steel. In all experiments, it has been crucial to compare the obtained results with that of the blank (uncoated) steel samples at the same conditions. This will give an idea about the fate of the bare steel surface when it is subjected to these corroding media. The effect of corrodant has been divided into three main categories, which are:

i. Effect of acid corrodants (0.1M HCl)

The inhibitive efficiency of the investigated coats in acidic media has been determined by means of static bottle test and electrochemical test. It has been already mentioned that the static bottle test is planed for giving an idea about the durability of the paint against corrosion in natural conditions. However, the electrochemical technique is primarily designed for accelerated corrosion studies.

The experimental results of these series of tests are given in Table(3) and represented graphically in Figures(1 and 2).

The corrosion resistance of the studied paints, represented as %corrosion inhibition and corrosion rate (mpy), which was measured by the static bottle test (wt. loss) is illustrated in Table(3).

It is clear from the data given in Table(3) that, the paints PW1020, PW1011, TP and PP have higher corrosion inhibition and lower corrosion rate than that of the paint B77.

Figure (1) shows a plot of the natural electrode potential against time of the coated metal samples by PW1020, PW1011, TP, PP and B77 dipped in 0.1M HCl. In this set of experiments, the potential was held constant until it shifts to less noble potentials. The more the time taken for the specimen to shift to a less noble potential, the more is its resistance to corrosion. It is clearly demonstrated by this curve that the paints TP, PW1020, PW1011 and PP are superior to the paint B77 in protecting the steel surface against corrosion and also that the five tested paints are more efficient in corrosion protection compared to the bare steel surface (blank).

These results were confirmed by the values of corrosion rate (mpy) of the five paints given in Tables(3), which are:

PW1011 = 35, PW1020 = 38, TP = 68, PP = 230 and B77 =1290

Thus, it is worth to mention that the shift of the specimen potential to less noble indicates the collapse of the paint **[10]**.

Figure (2) shows the measured current density as a function of potential in 0.1M HCl solution for the different tested coated steel samples in comparison with the uncoated sample (blank). The potential was polarized at fixed rate of about 100mV/min and corresponding current was recorded.

The corrosion current density (mA/cm^2) was determined from these plots as the point of intersection of the tangent lines for the more noble part and the less noble part of the specimen open circuit potential, i.e., according to Tafel extrapolation method [7-9]. A high corrosion current value is an indication of a high corrosion rate and vice versa. It is clear that, the coated steel samples with PW1020, PW1011, TP and PP have corrosion current which is almost equal to zero, which means that they are very resistant to HCl media.

On the other hand, coating steel samples with paint B77, show that, the current was approximately equal to half that of the blank (uncoated sample). This means that, the ability of paint B77 to resist acidic conditions is much inferior as compared to the other tested coating materials. This inferior resistance of the B77 coating material against acidic corrodant can be attributed to the presence of zinc in its formulation only (as mentioned by suppliers of different types of used epoxy paints), which is attacked by HCl to form $ZnCl_2$. As a result of this act, Cl^- penetration of the coating film occurs possibly without apparent destruction of the coated layer leading to an increase in the corrosion rate [2]. The resistance against acid corrodant by coating materials based on epoxy resin can be explained by the fact that these epoxy resins are hardened by cross linking mechanism which forms a relatively high impermeable layer to acids and other corroding environments.

It is obvious that the different testing procedures of accelerated electrochemical corrosion as compared to the natural corrosion techniques show a consistency between both results. This will give us the opportunity to rely on the methods of electrochemical corrosion as a means of accelerated corrosion technique.

ii. Effect of saline water as a corroding medium

The resistance of the investigated coating materials against saline water corroding media containing various concentrations of NaCl has been investigated by means of the static bottle test and the electrochemical test. The salinity of the water co-produced with the crude oil could very greatly differ from one production site to another. This is the reason for the current study to investigate the effect of different NaCl concentrations present in the saline water (i.e., 1, 3 and 5% NaCl) and the ability of the studied five paints to protect the steel surface. The experimental results of this series of tests are represented graphically in Figures (3-5).

The corrosion resistance of the investigated five paints, represented as %corrosion inhibition, which was measured by the static bottle test (wt. loss) is illustrated in Table (4).

Corrosion rate (mpy) of the investigated paints in water containing 5% NaCl was estimated by the loss in weight and the results are illustrated in Table (5). It is clear from the data given in Tables (4 and 5) that, the paints PW1020, PW1011 and TP have slightly higher corrosion resistance (i.e., higher % inhibition and lower corrosion rate) than that of the paint PP, however, the paint B77 has markedly lower corrosion resistance than the mentioned for paints.

Thus, three types of the investigated paint; PW1020, PP and B77 were selected to study the effect of salt concentration on the natural elrctrode potential of the coated steel samples as a function of time.

Figures (3-5) show the effect of salt concentration on the natural electrode potential of steel samples, coated with PP, B77 and PW1020, respectively, as a function of time. In addition, the same effect was studied on the blank (uncoated sample) at salt concentration of 5% NaCl and plotted on the same figures for comparison. In this set of experiments, the potential was held constant until it shifted to less noble potential. The more time taken for the specimen to shift to a less noble potential, the higher its resistance to corrosion. Accordingly, Figure (3) illustrates that, the corrosion resistance of the paint PP decreases with the higher salt concentrations, i.e., 3 and 5% NaCl, and seems to be unaffected with the lower salt concentration, i.e., 1% NaCl, while Figure(4) shows that, the corrosion resistance of the paint B77 is affected by all salt concentrations under test, and markedly decreases with increasing NaCl concentration. On the other hand, as illustrated in Figure (5), the corrosion resistance of the paint PW1020 seems to be slightly unaffected by saline water with different NaCl concentration. In addition, it is clear that, the corrosion resistance of the three paints is superior to the blank (uncoated sample) in 5% NaCl solution.

Therefore, it can be concluded that, the paints PW1020, PW1011 and TP are very resistant to the saline water corrosion at different salt concentrations, while the paint PP is resistant to the saline water with low salt concentration and it could be affected by the higher salt concentration. On the other hand, the paint B77 is affected by saline water with different salt concentrations and this effect is markedly increased with increasing salt concentration.

Salt solutions can cause corrosion by accumulating at the water-line (cathodic zone), where alkali may accumulate and creep up between paint and metal, and cause softening and loosening of the paint [2]. This process may also occur where the metal is completely immersed, particularly below the paint films pigmented with zinc or aluminum. Caustic soda is formed at the steel surface (which is made cathodic by the zinc) resulting in the softening of oil-base paint and consequent loss of adhesion. In sea-water, at the local cathodes the total concentration of ions will exceed that in the surrounding sea-water, and water may be drawn in by osmosis, with resultant alkaline blistering. This is usually the first sign of electrochemical corrosion; alkaline peeling and corrosion of the metal become apparent only later.

II- Effect of Temperature and Mechanical Stirring on Corrosion Protection of the Coated Materials:

From the previous results and discussions, it is clear that the paints PW1020, PW1011 and TP are superior in protection against different corroding mediums as compared to the other investigated paints, i.e., PP and B77. Thus, the paint PW1020 was selected to find out its durability (corrosion resistance) against temperature and mechanical stirring, which are considered as important environmental factors encountered during the production of crude oil.

Therefore, these series of tests were carried out to study the effect of temperature (60°C) and mechanical stirring (1200rpm) on the natural electrode potential for the painted sample with PW1020 in 5% NaCl solution, functional with time. In addition, the same effect was studied also on the blank (uncoated sample) for comparison. The experimental results of this series of tests are represented graphically in Figure (6).

As illustrated in Figure (6) it is clear that the paint PW1020 is markedly resistant to elevated temperature (60°C) and mechanical stirring in comparison with the results obtained at room temperature without movement (static solution). However, for the uncoated samples, there exist a large decrease in the corrosion resistance as a result of using mechanical stirring at elevated temperature and a slight decrease as a result of increasing temperature from about 25 to 60°C without movements.

In case of the uncoated steel samples, the effect of temperature in decreasing the corrosion resistance is attributed to the increase in corrosion rates as a result of increasing the kinetic energy required for the electrochemical process, in which the steel is dissoluted into the oxide form. The mechanical stresses resulted with stirring also contribute largely in increasing the rate of the anodic dissolution of the steel surface subjected to the corrodant medium and hence increase the rate of corrosion. The stirring helps in removing the newly dissolute oxide metal away from the metal surface and hence disrupting the equilibrium concentration existing between the metal (steel) in the reduced form at the surface of the specimen and the metal in the oxide form dissolute in the solution.

The effect of temperature on accelerating the corrosion rate in case of the coated metal specimens is only pronounced in presence of small holes on the surface of the coated metal. Temperature increasing causes an increasing of water diffusion under the coated layer resulting in pealing and deterioration of the coating material and hence in increasing of the corrosion rate. The application of mechanical stirring on the surface of coated material with elevated temperature, surely lead to an increase in the rate of pealing and deterioration of the coated material. However, the epoxy resins show outstanding durability against temperature and mechanical stirring **[3]**.

CONCLUSION

From the experimental data, it can be concluded that:

1- Corrosion resistance of the coated pipes with the investigated epoxy paints namely Penguard Primer (PP), Barrier 77 (B77), Tankguard Primer (TP), PW1020 and PW1011 is much superior compared to the uncoated pipes at different corrosive environmental factors.

2- Corrosion resistance of the coated pipes with PW1011, PW1020 and TP epoxy paints in acidic solution and brines is superior to that coated with PP and B77 paints.

3- The ability of B77 paint to resist acidic solution and brines is much inferior as compared to PP paint. The corrosion resistance of both paints markedly impairs with increasing the salinity (NaCl concentration) of water.

4- Corrosion resistance of the coated pipes with the epoxy resins in brines is unaffected by elevated temperature (60°C) and motion (mechanical stirring), however, uncoated steel is much corrodible at these conditions in comparison with that at room temperature and without motion.

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Table 1- Peak , Valley, and Peak to Valley Average Values

Specimen No.	Peak (µm)	Valley (µm)	Peak to Valley (µm)
1	30	30	60
2	35	30	65
3	34	36	70
4	35	35	70
5	32	33	65
6	31	33	64
7	30	28	58
8	32	30	62
9	34	33	67
10	30	30	60
11	30	31	61
12	34	34	68
13	33	32	65
14	32	31	63
15	30	32	62
16	30	30	60
17	33	35	68
18	35	35	70
19	32	33	65
20	33	34	67
21	33	35	68
22	32	32	64
23	31	30	61
24	35	35	70
25	32	32	64

*Above reading values were substrated by 50µm (thickness of paper)

Table 2- Maximum Time Required For Painting of Blasted Metal Specimen

%Relative Humidity	Time (hr)
>75-85	2
60-75	3
<60	4

Table 3- %Corrosion Inhibition and Corrosion Rate of The Investigated Coating Materials Against Acidic Corrodant "0.1M HCl" (Wt. Loss Method)

Type of paint	%Corrosion inhibition after 14 days	Corrosion rate µmpy
B77	76.3%	1290
PP	98.7%	230
TP	100	68
PW1020	100	38
PW1011	100	35

Table 4- %Corrosion Inhibition of The Investigated Coating Materials Against Different NaCl Concentrations (Wt. Loss Method)

Type of paint	%Corrosion inhibition after 24 days		
	1%NaCl	3%NaCl	5%NaCl
PP	100%	94.6%	89.3%
B77	91.2%	86.1%	70.2%
TP	100%	100%	100%
PW1020	100%	100%	100%
PW1011	100%	100%	100%

Table 5- Corrosion Rate of Investigated Coating Materials Against Water Containing 5% NaCl (Wt. Loss Method)

Type of paint	%Corrosion inhibition after 24 days	Corrosion rate (µmpy)
B77	70.2	1760
PP	89.3	389
TP	100	55
PW1020	100	59
PW1011	100	52

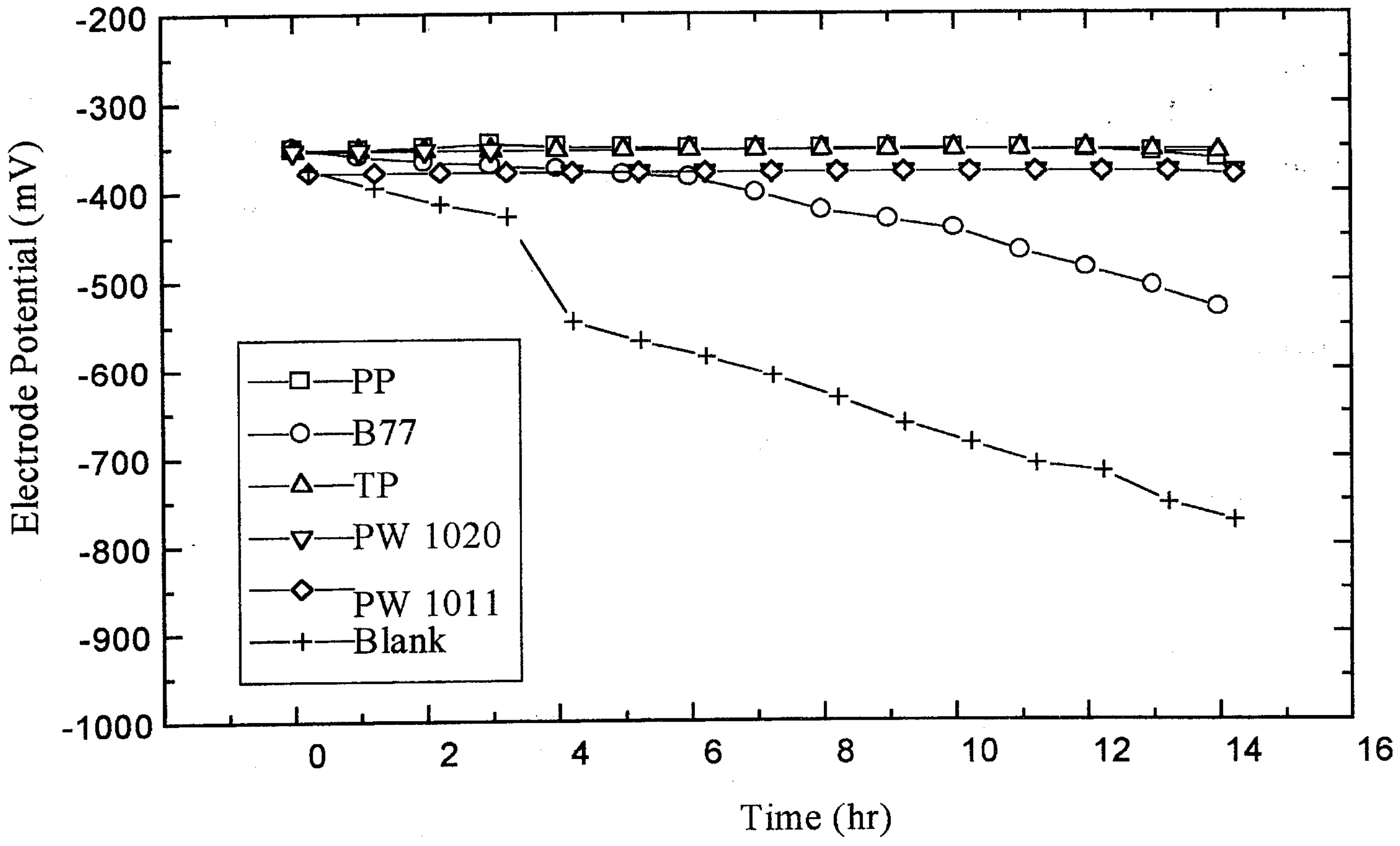

Fig.1.Natural electrode potential in HCl corrodant as a function of time for different coated steel samples

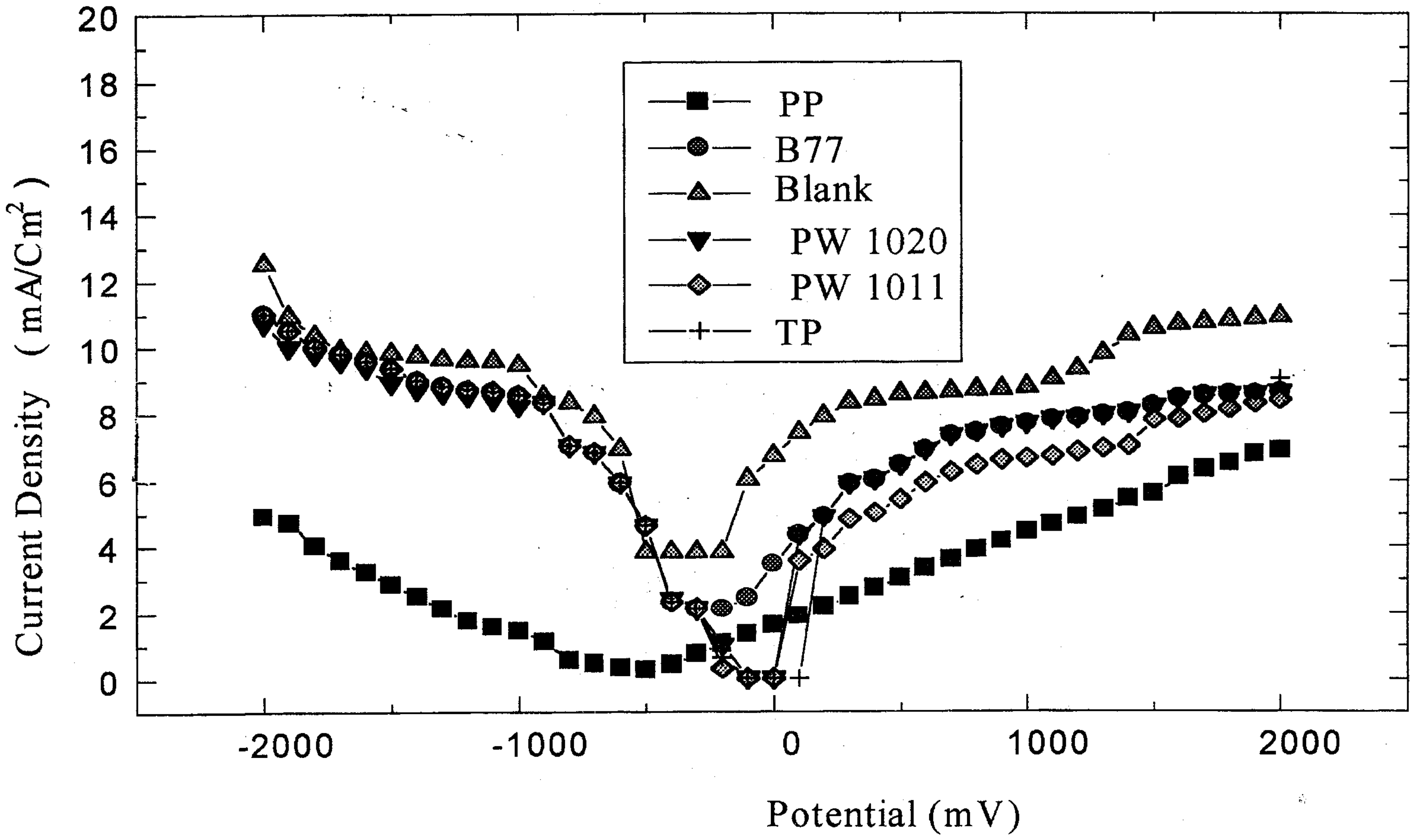

Fig.2. Current density as a function of potential 0.1 mHCl corrosion different coated steel samples

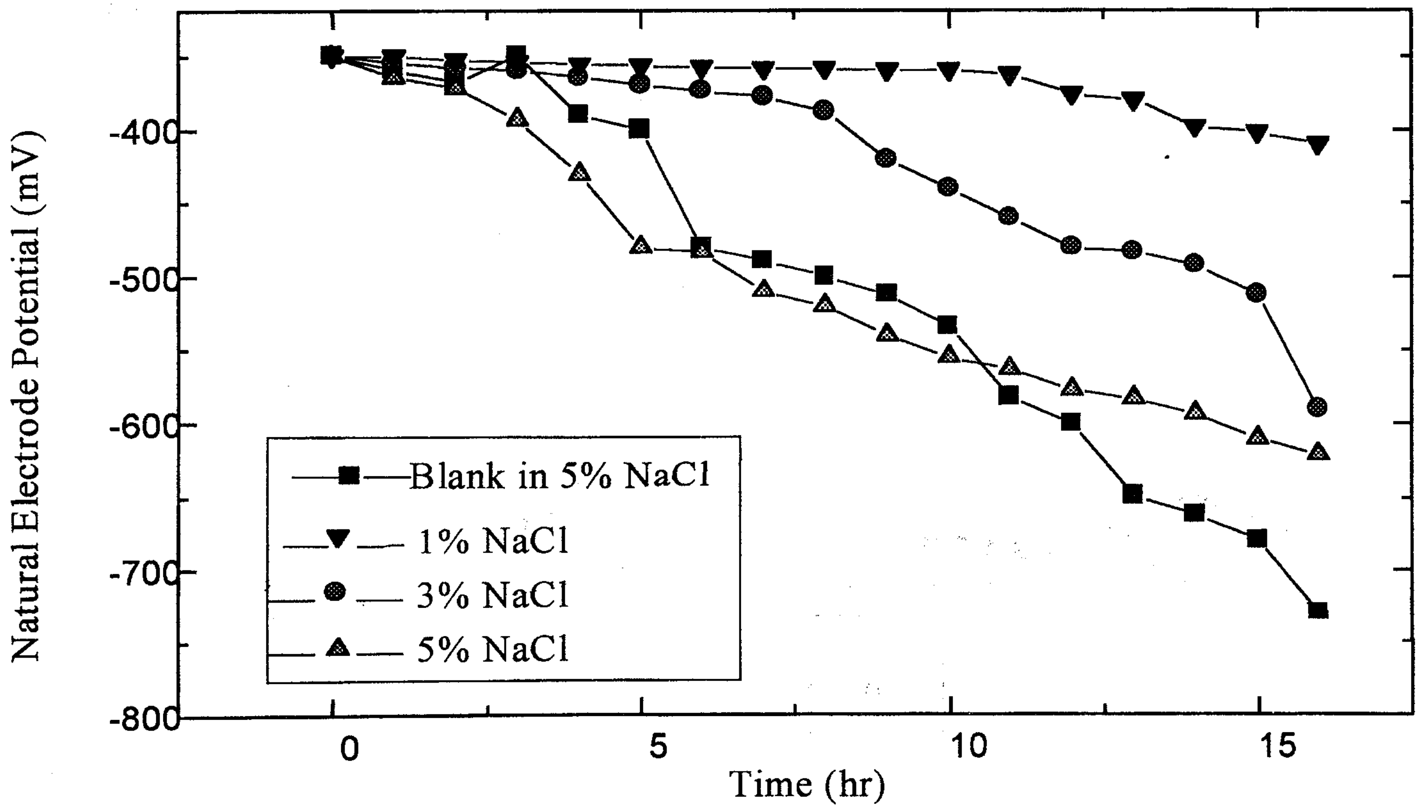

Fig.3. Natural electrode potential as a function of time at different NaCl concentrations for the Sample PP

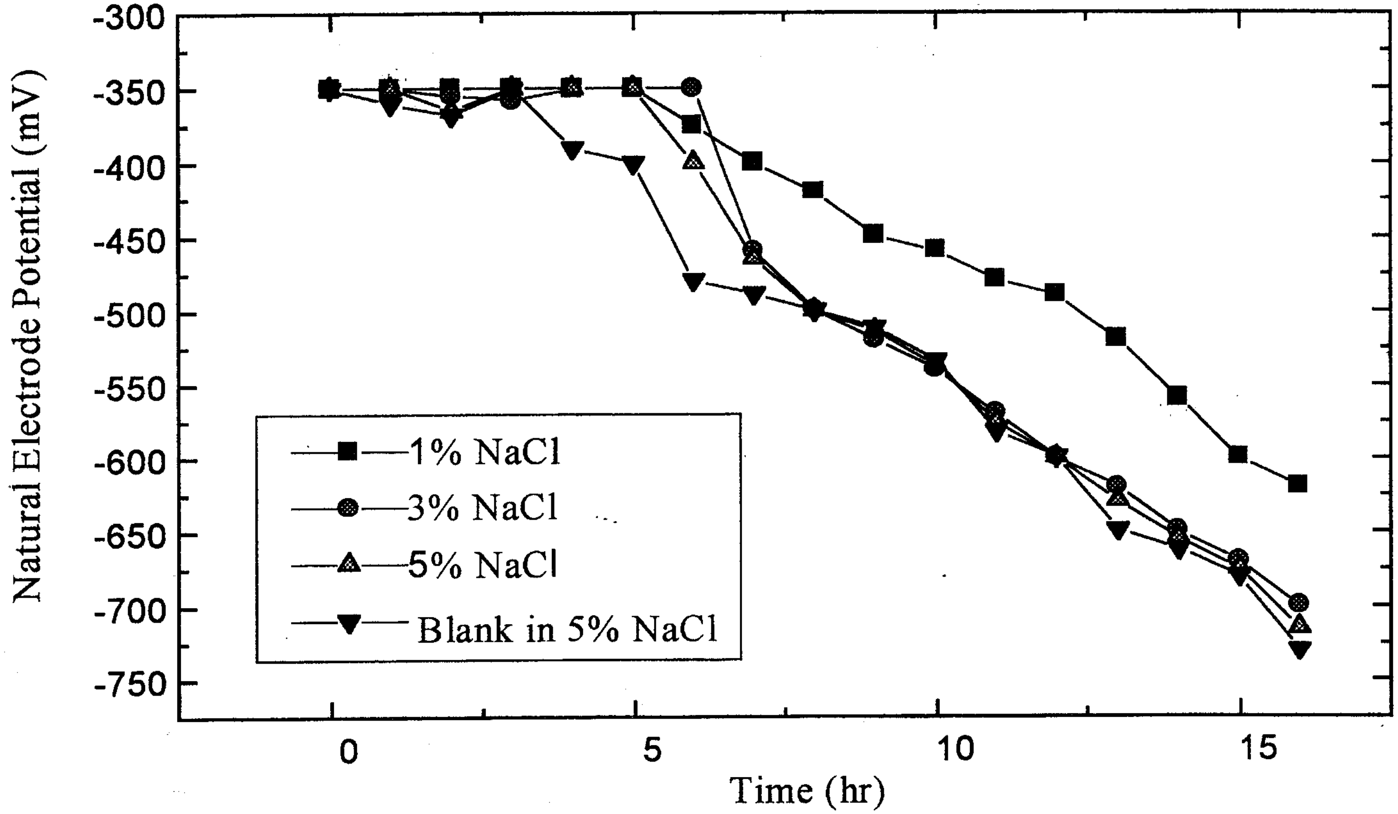

Fig. 4. Natural electrode potential as a function of time at different NaCl concentrations for the sample B77

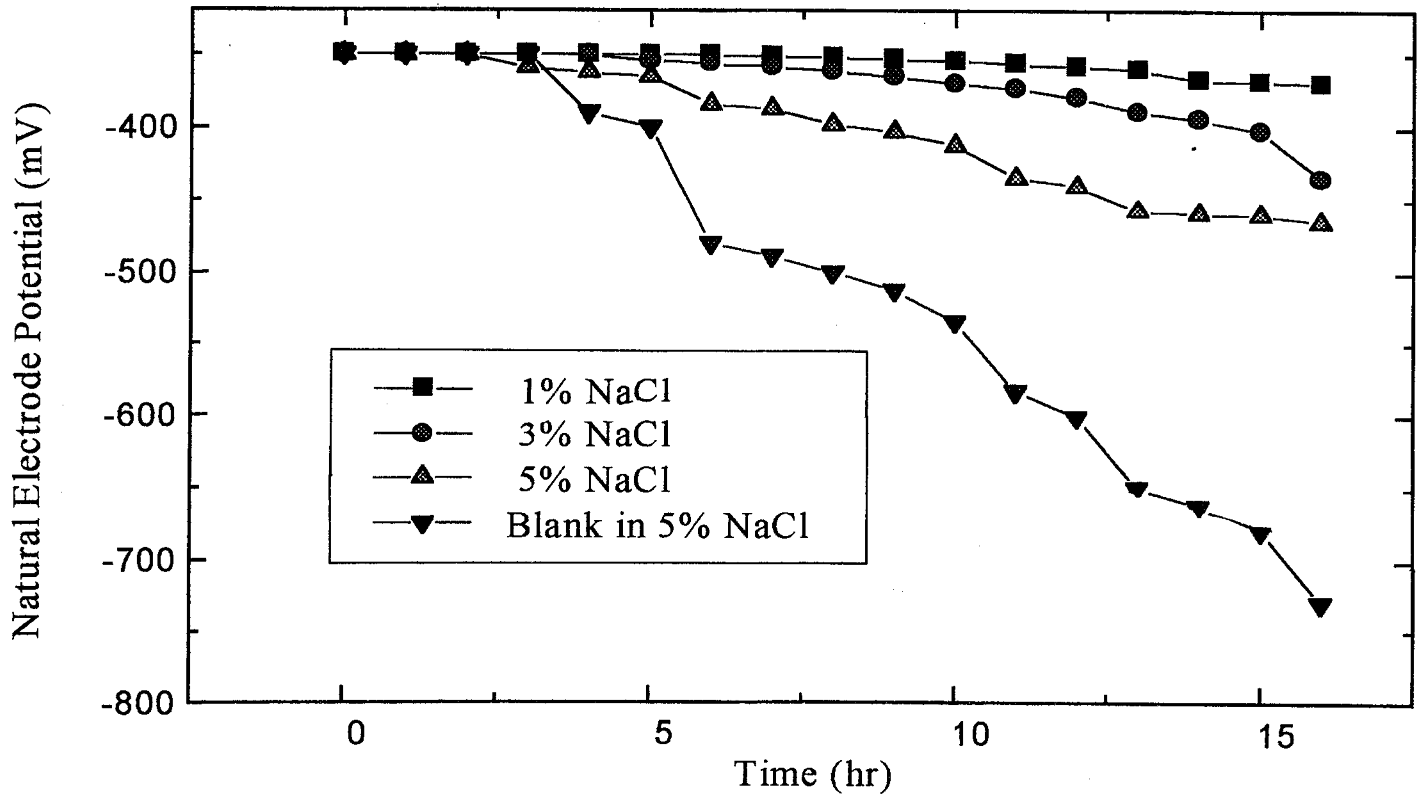

Fig.5. Natural electrode potential as a fuction of time at different NaCl concentrations for the sample PW1020

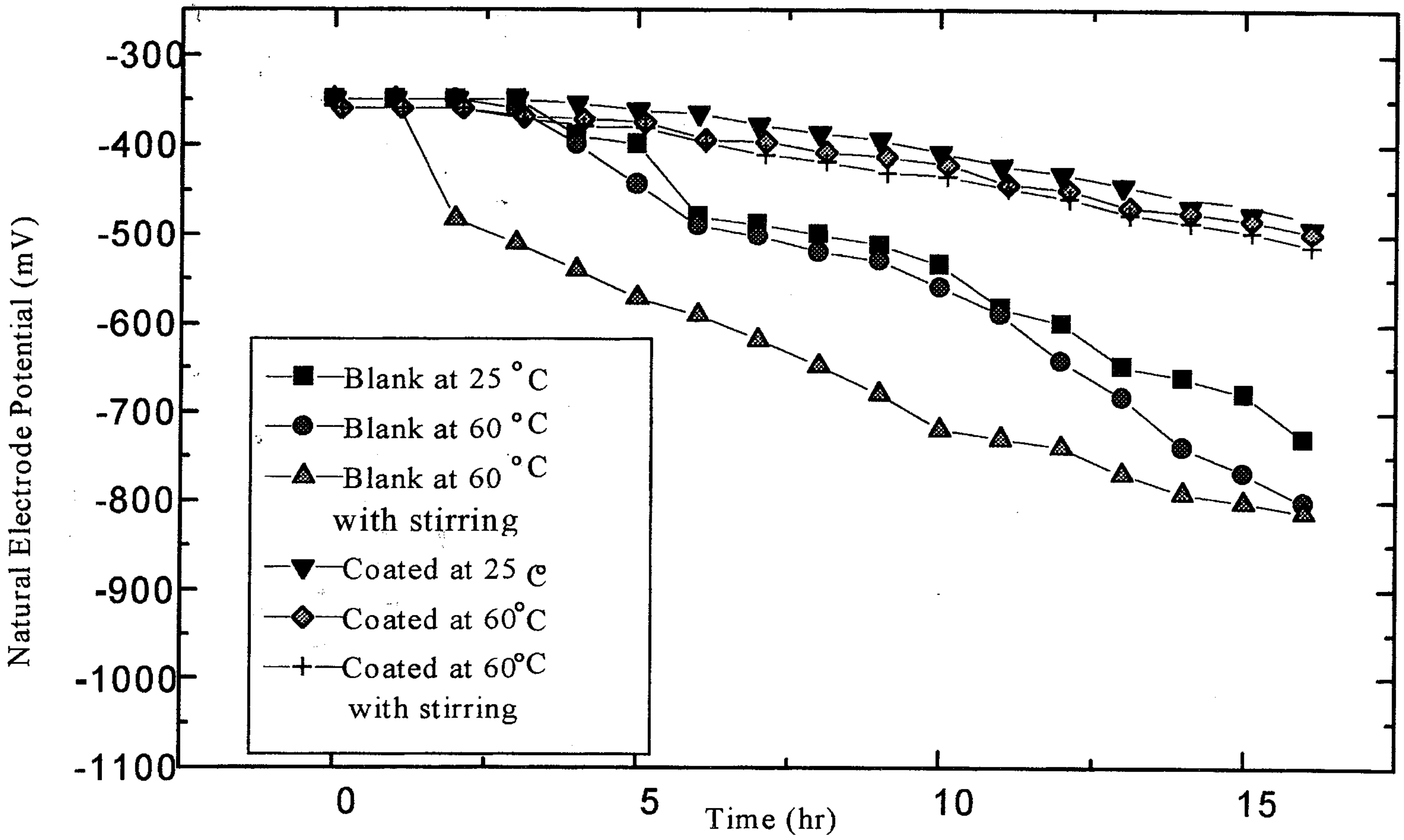

Fig.6. Effect of temperature and mechanical stirring on the natural electrode potential as a function of the sample coated PW.1020 in 5% NaCl solution as a function of time

دراسة كفاءة الدهانات الواقية المستخدمة داخل أنابيب البترول الخام

ملخص

إن الهدف من هذه الدراسة هو الإمداد بالبيانات اللازمة للاختيار الأمثل لمواد الطلاء المستخدمة للحماية الداخلية لأنابيب البترول الخام، حيث تم اختيار أنواع مختلفة من طلاء الايبوكس لتغطية عينات من صلب الأنابيب، بعد تجهيز أسطحها قبل الطلاء بواسطة السفح والحصول على خشونة سطح مناسبة.

وقد تم اختبار كفاءة الأنواع المختلفة من طلاء الايبوكس، فى حماية سطح عينات الصلب من التآكل عند تعرضها للعوامل البيئة المختلفة، باستخدام نوعين من الاختبارات المعملية، الأول عن طريق الفقد فى الوزن، والثانى عن طريق استخدام الطرق الكهروكيميائية.

هذا وقد تم اختيار ظروف الاختبارات لتكون محاكاة للظروف الطبيعية الناتجة أثناء نقل البترول الخام داخل الأنابيب من حيث وجود أوساط ملحية وحامضية (0.1 MHCl).

وقد بينت النتائج أنه يمكن الاعتماد على الطرق الكهروكيميائية للتنبؤ بمدى كفاءة الأنواع المختلفة لمواد الطلاء فى حماية سطح الصلب عند تعرضه للعوامل البيئية المختلفة وقد أظهرت الدراسة أن بعض هذه الدهانات أفضل فى حماية سطح الصلب، فى الأوساط الملحية والحامضية، مقارنة ببعضها الآخر.