- VCIs -

A NOVEL APPROACH

TO CORROSION CONTROL

IN THE

PETROCHEMICAL INDUSTRY

BY

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A b s t r a c t

The evaluation of corrosion protection properties of new generation of vapor corrosion inhibitors, specially formulated for application in the petrochemical industry was performed. The paper outlines the protective mechanism of these novel compounds and the technology behind them. The inhibitors provide water displacement, film forming abilities as well as vapor phase protection. When evaluating the protective properties of newly developed inhibitor, the following guidelines were utilized:

Testing for protection against general corrosion
in various types of corrosive mediums,
performed under different patterns of testing,
so as to evaluate to post-action inhibition effect.

Combination of stress accelerated corrosion testing
which includes corrosion-cracking,
induced by dynamic/static stress and corrosion fatigue evaluation.

Hydrogen embrittlement of pipeline steels in the presence of VCIs.

Electrochemical testing of inhibitors,
including studies of electrode kinetics processes
and impedance characteristics.

Introduction

In petroleum operations, corrosion, like taxes and death is inevitable. Therefore, the issue of corrosion protection of oil-wells equipment, pipelines, and storage facilities in the petrochemical industry is very topical today. In the last decade a number of oilfields were discovered in different regions of the world. A common features of these newly discovered deposits are: a high level of water encroachment/ reaching 80% / high concentration of H_2S, CO_2, O_2, high level of brine mineralization - to name just a few. All these factors cause premature wearing of oilfield equipment, corrosion damage of storage tanks and catastrophic failures of pipelines.

Utilization of corrosion inhibitors is currently the major way of protection virtually in all crude oil extracting facilities in the world. Advantages of inhibition protection are high effectiveness of ones, utilization of inhibitors without changing technological procedures of crude extraction and transportation, simplicity of application, and as a consequence substantial savings. The purpose of this work is to evaluate protective properties of new VCIs for petrochemical industry.

Subjects and Methodology of Experiments

1. Materials

Carbon steel was used in this study. Chemical composition of the steel was:

C	-	0.22%
Mn	-	0.48%
Si	-	0.17%
Cr	-	0.30%
Ni	-	0.30%
S	-	0.05%
P	-	0.04%

Inhibitors Cortec VCI-629 wand VCI-365 were used for evaluation of their protection properties. Inhibitors VCI-629 was specially formulated for oil-well equipment protection, and inhibitor VCI-365 for storage tanks protection respectively.

2. Methodology of Testing

- Testing for protection against general corrosion
- Testing for protection against stress corrosion cracking
- Electrochemical testing of the inhibitors
- Testing of technological properties of the inhibitors.

3. Experimental procedures

3.1. Corrosion testings.

Rectangular shaped samples of carbon steel were used for corrosion testings. Dimensions of the sample: 50*20*2 mm. Tests were performed in the following corrosion mediums:

- NACE TM-01-77
  50 q/1 NaCl+5q/l CH_3COOH+H_2S in distilled water.
  pH of solution 3.0-4.0

- Brine water simulation
  17q/1 NaCl+0.6q/l $NaHCO_3$+0.2q/l CaCl+0.2q/l MgCl in distilled water. pH of solution 6.5

- Simulation of brine water/crude oil in ratio 10:l/Heptane was used to simulate crude oil.

Test in NACE TM-01-77 solution was conducted in glass ampoules in which test samples were placed. The corrosive solution was added into the ampoules and the ones were sealed. The ampoules were placed into the oven at 50^o C for 24 hours. After 24 hours ampoules were opened and corrosion products were washed from the metal surface. Corrosion loss was evaluated using gravimetry method.

Special apparatus (Fig. 1) was utilized for testings of steel coupons in brine water and brine/crude mixture. Conditions of the test were: velocity of liquid flow - 1 m/s, temperature - 25^o C. Duration of the test 6 hours. After the test samples were removed from apparatus, corrosion products were washed and weight loss was determined with accuracy to four decimal places.

Effectiveness of inhibition ability was evaluated while using tow schemes of inhibitor application:

- The Cortec VCI-629 was added directly to corrosive medium in a concentration 200 mg/l. - A steel sample was conditioned in the inhibitor for 2 hours in order to allow inhibitor to form protective film on the surface. According to this procedure "post action inhibition effect" was determined. Inhibition coefficient - ϒ and protective action of the inhibitor - Z, was calculated according to the following formulas:

$$\Upsilon = \rho o/\rho I \qquad Z = [(\rho o - \rho I)/\rho o \}] \times 100\ \%$$

where,

ρo - rate of corrosion / q/m^2 hour / in aggressive medium

ρI - rate of corrosion in aggressive medium with inhibitor

3.2. Electrochemistry

Kinetics of electrode processes was studied in the potentiodynamic regime of measurements. Polarization curves were taken utilizing cylindrical carbon steel electrode / 2 mm in diameter, 8 mm in height/ placed in to a glass cell with subdivision on anodic and cathodic areas. As a reference saturated AqCl electrode was used. Potential scan rate 1mV/s, temperature 25^{o} C.
For evaluation of protective properties of Cortec VCI-365, impedance measurements were performed. Active resistivity Ra, differential capacity Cd, and the change of these characteristics with time and frequency were measured. Frequency interval from 0.21 to 50 kHz was used. As a working electrode the steel sample coated with Inhibitor Y was utilized. As a reference platinum electrode was used.

3.3. Complex of stress accelerated corrosion test.

- Corrosion-cracking induced by dynamic/static stress.
- Corrosion fatigue performance evaluation.
- Evaluation of hydrogen diffusion through steel membrane.

Generally, two methods are used in world practice to measure effectiveness of inhibitors in prevention of SCC:

- Determination of a threshold stress, utilizing long term corrosion durability curves σ - log $^{\tau}$F, where σ- stress, $^{\tau}{}_{f}$ - time to failure.

- Determination of relative sensitivity of steel against stress cracking, utilizing tensile stress applied on a steel sample with constant low rate of deformation.

Later method was used in this study. The test was performed using cylindrical steel specimens (Fig 2a) and specially designed experimental cell filled up with corrosive medium. Deformation tension was applied. The rate of deformation was 2*10-6Sl-. After specimen failure relative construction ψ % and relative elongation δ % were measured. Corrosive medium prepared according NACE TM-01-77. The characteristics for evaluation of inhibitor protection action, were coefficient of protection - **K**p, and coefficient of corrosive medium effect - β

$$Kp = \frac{\psi 1 - \psi c}{\psi a - \psi c} \times 100\% \qquad \beta = \frac{\psi a - \psi c}{\psi a}$$

where, ψa - relative contraction in an air medium.
ψc - relative contraction in corrosive medium.
$\psi 1$ - relative contraction in inhibited corrosive medium.

For determination of long-term corrosion strength of steel the static load was applied to cylindrical specimen / Fig 2a / Induced in the sample stress was calculated according the to the following formula: $\beta = 4P/ \pi d^2$**,** where P - load N; D - diameter of the specimen. Duration of the test 720 hours. The test was performed with continuous sparring of H_2S in to corrosive solution. As the characteristics of tendency of steel to be subjected to SCC threshold stress and time to failure were evaluated.

4. Results and Discussion

4.1. Effectiveness of VCI-629 protection of carbon steel immersed into corrosive medium.

Table 1 presented the results of the test for carbon steel coupons submerged into corrosive medium. Coupons were preconditioned in the VCI-629 for two hours before the test. As it can be seen VCI-629 shows the protection action of approximately 97%. It is also interesting to mention that VCI-629 is more effective in low concentrations. This feature of the inhibitor can be of great interest, because of economical side of it's application.

The data show in Table 2 reflected effectiveness of protection offered by VCI-629 for steel coupon, which was not conditioned in the inhibitor before the test. Concentration of the inhibitor added to corrosive solution was 200 gm/1. As it can be concluded the effectiveness of VCI-629 decreased but not significantly from 97% to 92%. VCI-629 protects steel effectively because it forms dense absorbed layer on the metal surface and also provides protection in a vapor phase. This conclusion can be drawn from comparison of the results obtained in the tests with preconditioned coupons and coupons without pretreatment. It is also relevant to mention that after the tests corrosion found on a metal surface appeared to be uniform without pittings or local corrosion. This type of performance is especially important in petrochemical industry where majority of failures occur due to various types of local corrosion.

Table 1.

Inhibitor	Concentration of inhibitor in test solution, mg/1	Rate of corrosion ρ **g/m²** Inhibition coefficient Protection action - **Z%**		
-		ρ	γ	**Z**
Without inhibitor	50	0.033	36.1	97.2
	100	0.027	44.07	97.7
VCI-629	200	0.039	30.5	96.5

Table 2.

Inhibitor	ρ	γ	Z
Without inhibitor	1.19		
VCI-629	0.09	13.2	92.4

Table 3 presented result of effectiveness of inhibitor protection in simulated brine water. Apparently, corrosivity of both aggressive mediums / simulated brine and TM-01-77 / is comparable / rate of corrosion 1.09 g/m^2 hour and 1.19 g/m^2 hour respectively /. However, effectiveness of VCI-629 in brine water was somewhat less. It may be explained by the fact that presence of H_2S in TM-01-77 corrosive medium causes synergistic effect coincided with inhibition protection. Without preconditioning of steel, effectiveness of protection action did not exceed 50%. However, if protection film already exist on the metal surface / after condition in the inhibitor / the effectiveness of protection action significantly increases. Protection action for VCI-629 in this case reaches 85%.

The test data on protection action of the inhibitor additive to the medium of brine/crude mixture were presented in Table 4. As it can be seen this medium is the most aggressive one.

The presence of hydrocarbons in brine system accelerates corrosion process. The same tendency, namely, increase in inhibition protection action with pretreatment of metal in the VCI-629 can be seen. On the bases of presented results of conclusion can be drawn that VCI-629 provides up to 97% of corrosion protection action in the most aggressive crude/brine solutions.

Table 3.

Inhibitor concentration 200 mg/1
Velocity of liquid flow 1 m/s, at 25^o C.

Inhibitor	Pretreatment in the VCI-629	ρ	γ	Z
Without inhibitor		1.09		

VCI-629	Yes	0.165	6.6	84.9
	No	0.84	1.3	42.1

Table 4.

Inhibitor	Pretreatment in the VCI-629	ρ	γ	Z
Without inhibitor		1.40		
VCI-629	Yes	0.045	31.1	96.8
	No	0.99	1.41	46.2

4.2 Effect of VCI-629 on SCC, Corrosion Fatigue, and Hydrogen Embrittlement of Carbon Steel.

In Table 5 the results of SCC test for carbon steel coupons are presented. Data for relative elongation - δ, and relative contraction - ψ were shown in table. Steel coupons had the following characteristics of durability: σ_1 = 440 Mpa, σ_2 =331 Mpa. As it can be seen from the data / 3-5 measurements mean / carbon steel is very susceptible to H_2S induced brittlnes - coefficient of medium effect is 0.94; time to failure decreased by 3.7 times. The inhibitor significantly increased durability of steel and its resistance to SCC. Presence of VCI-629 in solution boosted protected more than 30%.

According to the world standards inhibitors that offer this degree of protection can be recommended for industrial application.
Under static loading carbon steel in the corrosive environment is also susceptible to failure / see Table 6.
Time to failure of the specimens applied with a stress of (0.9-0.5) was less than 720 hours. According to the NACE TM-01-77 standard this steel can be characterized as very susceptible to SCC.
Pattern of failure is brittle crack. Presence of VCI-629 allowed significant increase of steel durability under the same conditions of the test. After 720 hours no signs of failure were observed on the steel specimen.

Comparative analysis of SCC data for the steel under static and dynamic stress allows to suggest application of VCI-629 in corrosive mediums containing H_2S.

The results in the Table 7 represented data reflecting inhibition effect of VCI-629 on low-cycle fatigue. Low-circle fatigue test of steel specimens in the atmosphere of air did not show any signs of failure after 50,000 cycles of applied stress. However, from the results of the test performed in corrosive medium it can be seen that VCI-629 significantly improve performance of carbon steel by increasing number of cycles till failure.

Addition of VCI-629 allows to increase this important characteristic by more than 2 times. Figure (7) represents the data of hydrogen diffusion rate through steel membrane immersed in corrosive solution. As it can be seen clearly, in 35-40 minutes after immersion intensive diffusion of hydrogen through steel membrane was observed in uninhibited solution.

As a result potential of passivated side of membrane dropped to significantly less noble values. In comparison, in the inhibited solution, practically, no hydrogen diffusion was observed after 12 hours of the test.

Table 5.

SCC of Steel. NACE TM-01-77. Rate of deformation 2*10(-6) s(-1).
Inhibitor concentration 200 mg/1.

Inhibitor/ medium	τ_F	ψ%	δ%	K_P	β
Air	52	58.3	16.6		
Control	14	3.3	2.8		0.94
VCI-629	28	22.5	8.1	35.3	0.61

where,
- τ_F - time to failure
- ψ - relative contraction of the specimen
- δ - relative elongation of the specimen
- K_P - coefficient of protection
- β - coefficient of medium effect

Table 6.

SCC of the steel subjected to static stress
Inhibitor concentration 200 mg/1.

Inhibitor/ medium	Stress δ Mpa	Time to failure τ_Fh	Pattern of Failure
TM-01-77	298 (0.9 δ)	85	Brittle
	231 (0.7 δ)	197	Brittle
	166 (0.5 δ)	350	Brittle
VCI-629	298	>720	No failure
		>720	No failure
		>720	No failure

Table 7.

Low-cycle fatigue of steel. Inhibitor concentration 200 mg/1.
Load frequency 0.17 Hz.

Inhibitor/ pattern medium	δ, Mpa	N	Failure
Air	198 (0.6 δ)	>5*104	Failure
	168 (0.5 δ)	>5*104	was not
	135 (0.4 δ)	>5*104	observed
TM-01-77	198	9370	
	166	12750	
	135	26050	
VCI-629	198	22750	
	166	28300	
	135	36550	

4.3. Electrochemical behavior of carbon steel in test solutions.

On Figures 8, 9, 10 potentiostatic / potentiodynamic polarization curves for carbon steel in TM-01-77 and brine solutions were presented respectively. It can be concluded from the test data that VCI-629 has tendency to change steel potential, in the inhibited solution, to more noble values if compare to non inhibited once. In other words VCI-629 mostly affects anodic process.
High effectiveness of the inhibitor, evidently, can be connected to absorption of inhibitor molecules and formation of protective layer on the metal surface.

Protective action can be also, partially, attributed to the presence of inhibitor in vapor phase. It is interesting to mention that in the presence of VCI-629 polarization resistivity Rp, that is a functional characteristic of chemisorbed film, had highest value. This respectively reflects superior protective properties of this chemisorbed layer. The data reflecting electrochemical behavior of steel in inhibited corrosive solutions summarized in Table 9.

Table 9

Inhibitor	Concentr. mg/1	Tm-01-77 E. mV	Tm-01-77 Rp kOm/Cm^2	Tm-01-77 z	Brine/Crude E	Brine/Crude Rp	Brine/Crude z
Without Inhibitor		-428	0.25		-510	0.92	
VCI-629	50	-303	5.5	99	-190	13.0	99
	100	-364	3.4	99	- 90	25.0	99
	200	-286	6.5	99	- 58	70.0	99

4.4 Protective lining Cortec VCI-365. Electrode impedance and environmental test results.

After 30 days of humidity chamber test VCI-365 did not change its visual appearance. Film maintained excellent adhesion to the metal surface and could not be stripped even after application of significant mechanical stress. After final removal of the VCI-365 film no corrosion was observed on the steel surface. The test in TM-01-77 medium revealed no losses of metal, corrosion rate was equal to zero.
It should also be mentioned that steel surface was covered with dense sulfide film under VCI-365. Evidently, sulfide/hydrosulfide ions still had ability to migrate through with subsequent formation of additional protective layer. VCI-365 slightly changed its color from creamy to light brown, however, adhesion properties remained unchanged.

The results of impedance measurements of steel electrode coated with VCI-365 was represented on Fig. 11. It can be seen that VCI-365 provided continuous protection for steel during two months test in brine water environment. Effective resistivity Ra initially had high value / 10 Om/cm^2/, which did not change during test period.

Frequency interrelation Ra=F(w), as it can be concluded from Fig. 12a. had high slope, which indicated excellent protective properties of the film. In the 0.1 M solution of HCI VCI-365 provided sufficient protection for 18 days.

On the 18th day of the test sharp decease /10^2/ of effective resistivity was observed Fig. 12b. Complete absence of Ra and frequency dependency indicated loss of protected properties.

CONCLUSIONS

A comprehensive series of environmental and electrochemical tests of new corrosion inhibitors for protection of oil-well equipment, pipelines and storage tanks has been completed in this work. The results lead to the following conclusions:

- VCI-629 provides excellent protection properties for steel subjected to different types of corrosive petrochemical environments due to it's surface absorption, film forming, and vapor phase action.

- VCI-629 protective characteristics can be increased if using pretreatment of steel surface.

- VCI-629 provides uniform protection without pitting and localized corrosion attack. Protective action of the inhibitor is 85-97%.

- VCI-629 effectively protects steel, subjected to brine and crude/brine medium, against SCC. It boots protection action by more than 30%.

- VCI-629 provide sufficient protection against hydrogen embrittlement. No diffusion of hydrogen into steel was observed in inhibited solutions.

- VCI-365 provides excellent protection for storage facilities subjected to crude brine environment. VCI-365 protective film provides sufficient mechanical / anti- abrasion / properties, and provides temporary protection even in HCL solutions.

Figure 1. Apparatus for test of the inhibitors in Samotlorskoye corrosive medium.

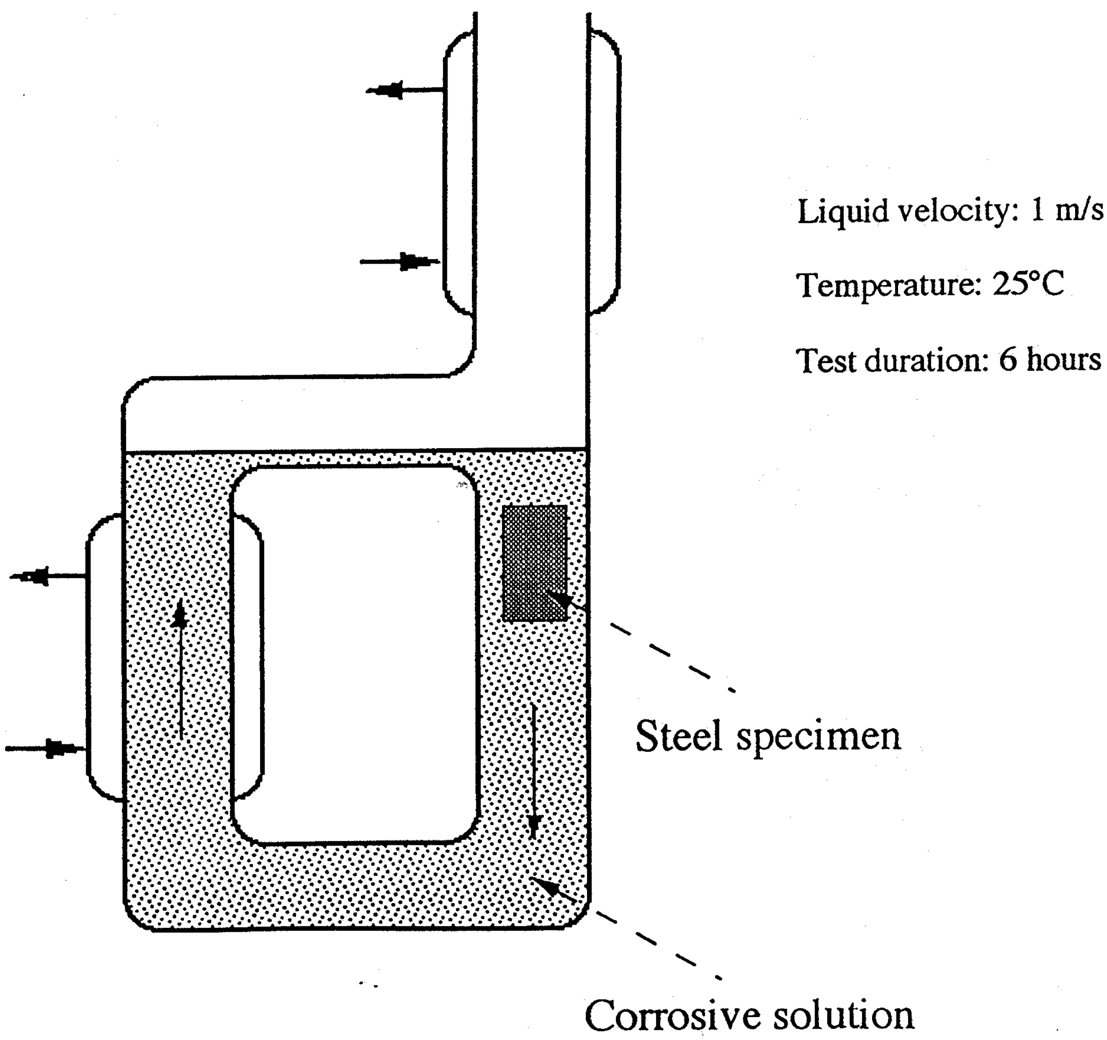
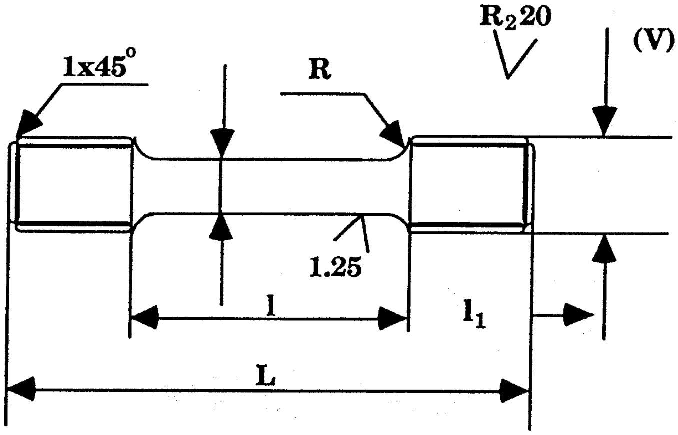


Figure 2. Specimens for evaluation SCC (a) and corrosion fatigue (b)

A)



L= 70 mm; l= 40 mm; l_1= 15 mm; M8

B)

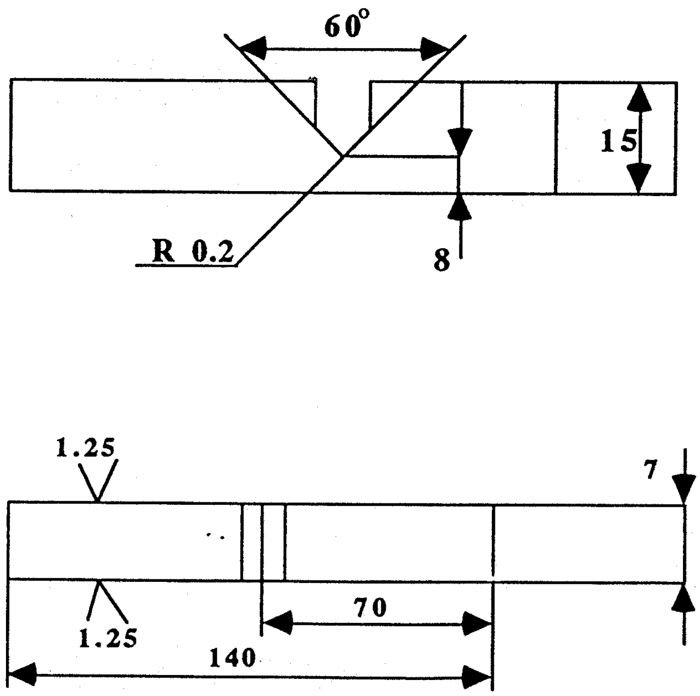


Figure 3. Apparatus (cell) for testing of SCC.

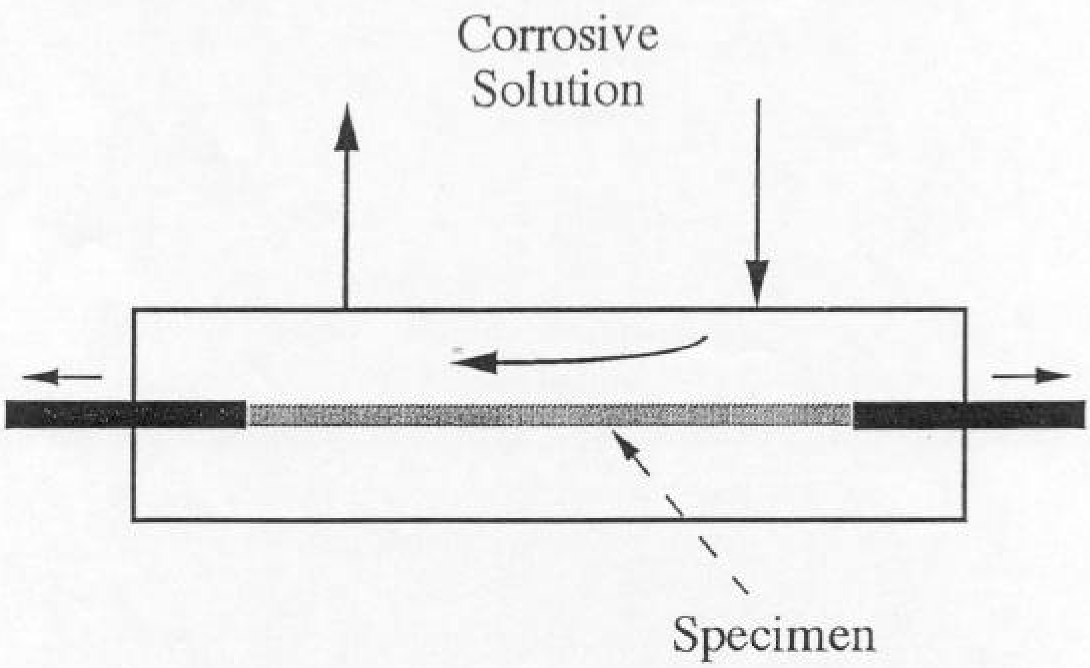


Figure 4. Diagram of testion of carbon steel under rate of deformation $2x10^{-6}$ s^{-1}. 1-air; 2-corrosive medium; 3-inhibited corrosive medium.

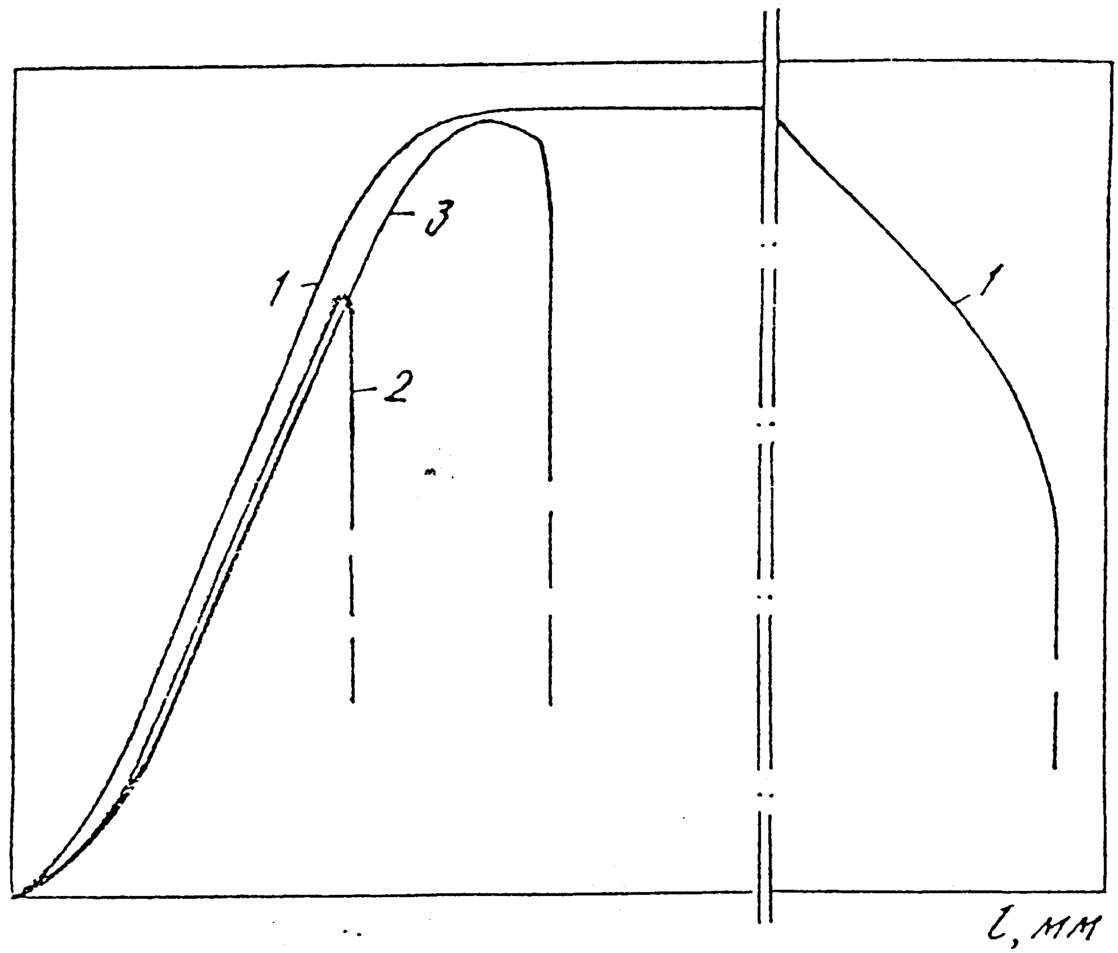


Figure 5. Apparatus for low-cycle fatigue testing

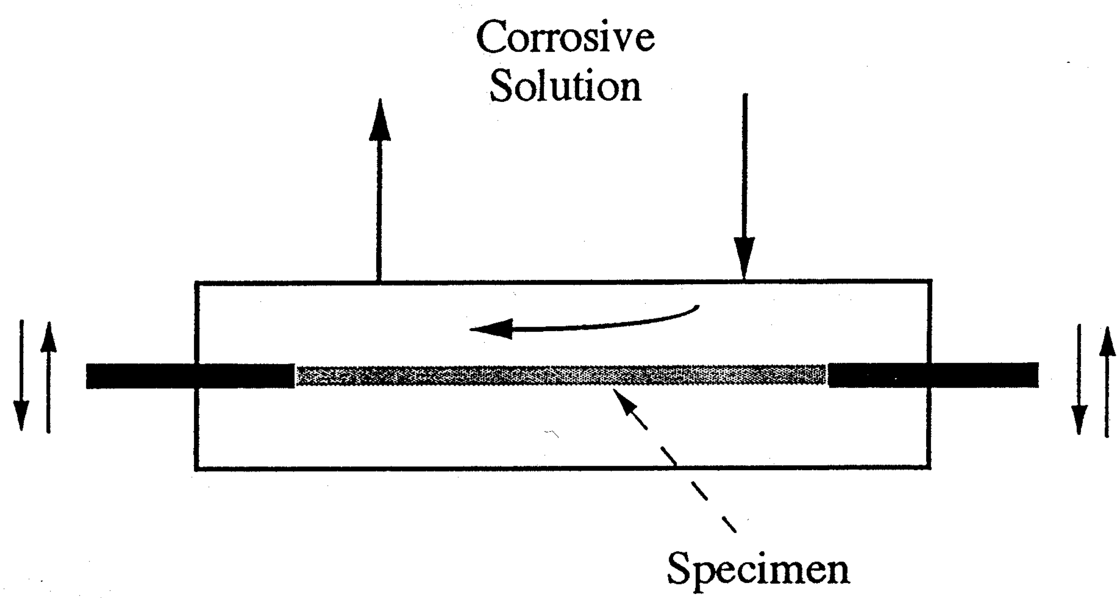
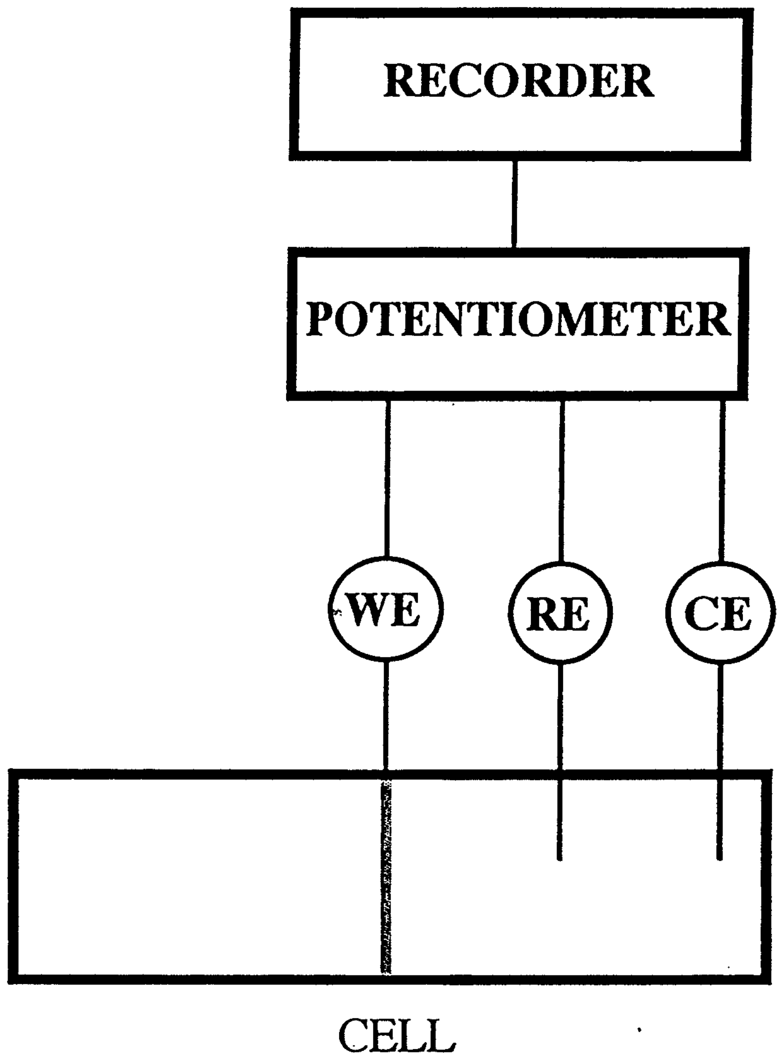


Figure 6. Testing cell for evaluation of hydrogen diffusion through steel membrane.



WE: Steel Membrane
RE: Saturated AgCl Electrode
CE: Platinum Electrode

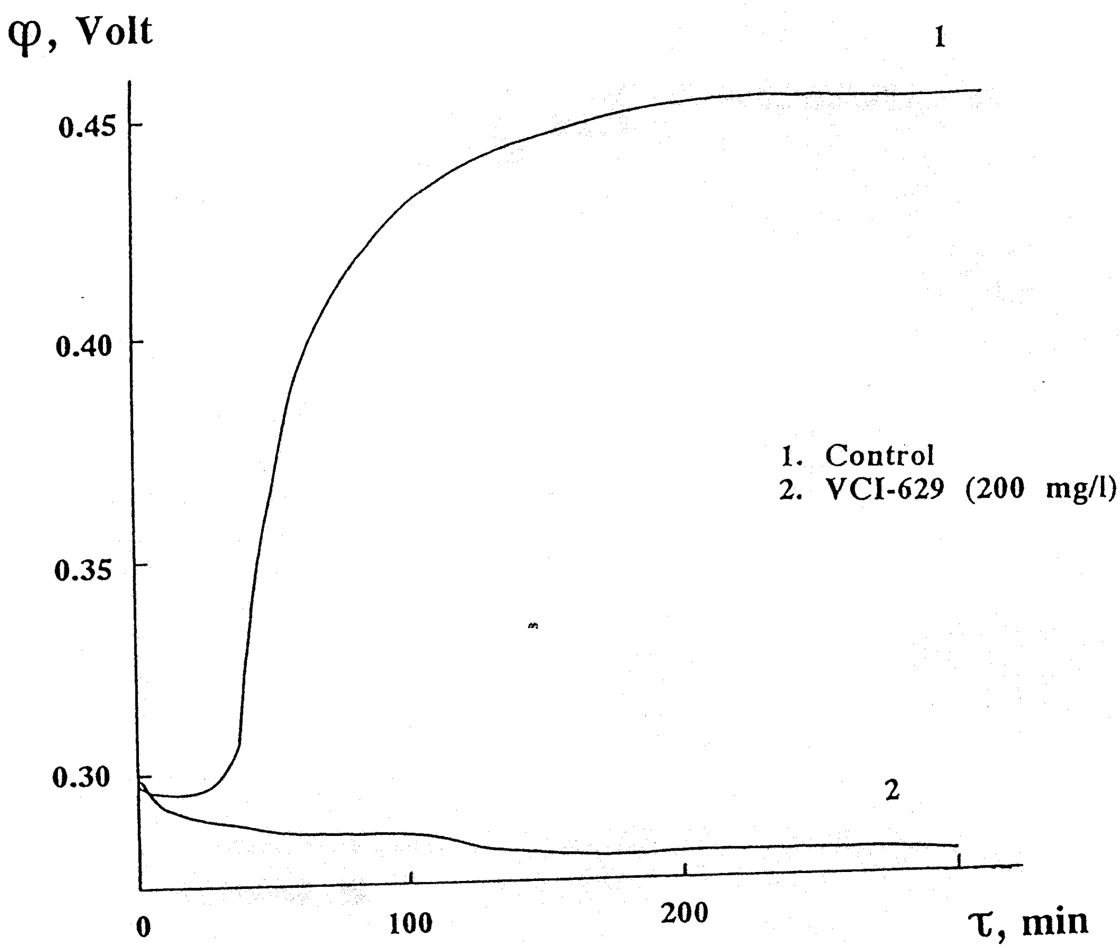


Fig. 7 - Change in potential of the passivated side of the steel membrane

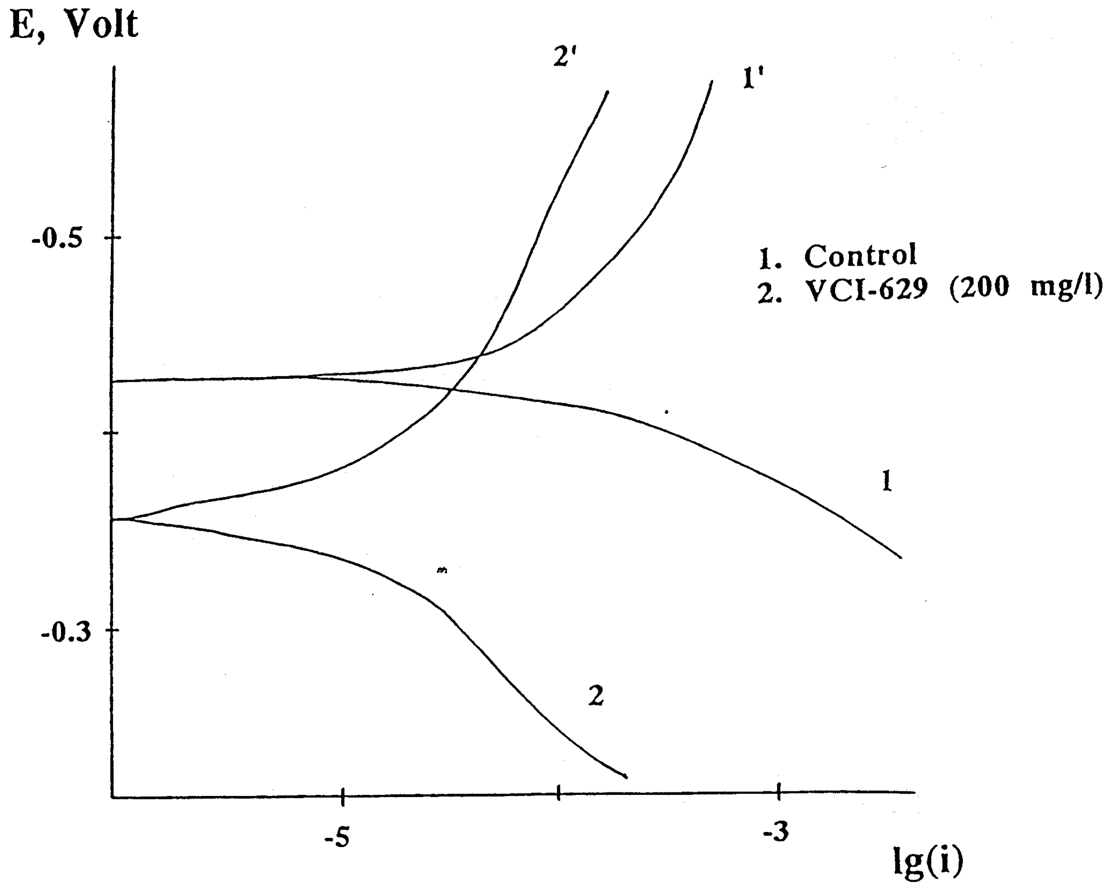


Fig. 8 - Potentiostatic polarization curves for a steel electrode immersed in NACE TM-01-77 corrosive medium.

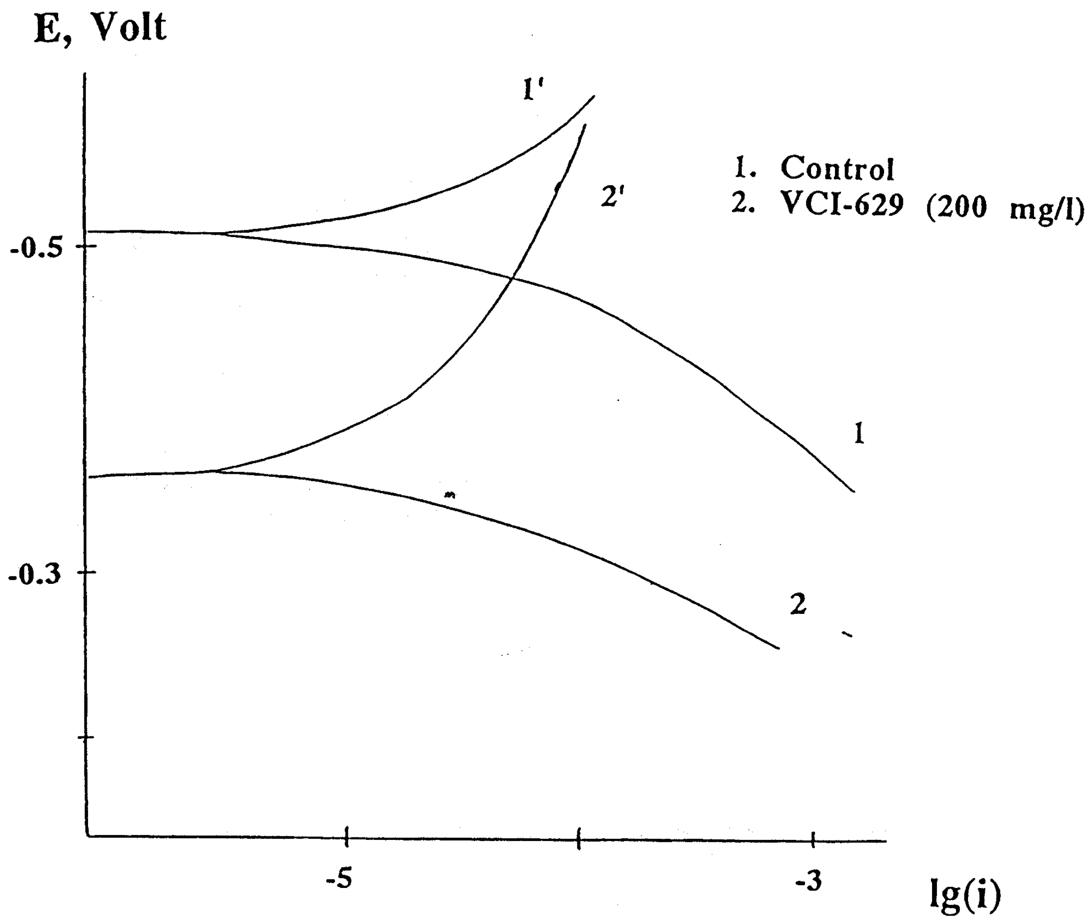


Fig. 9 - Potentiodynamic polarization curves of a steel electrode in a brine solution.

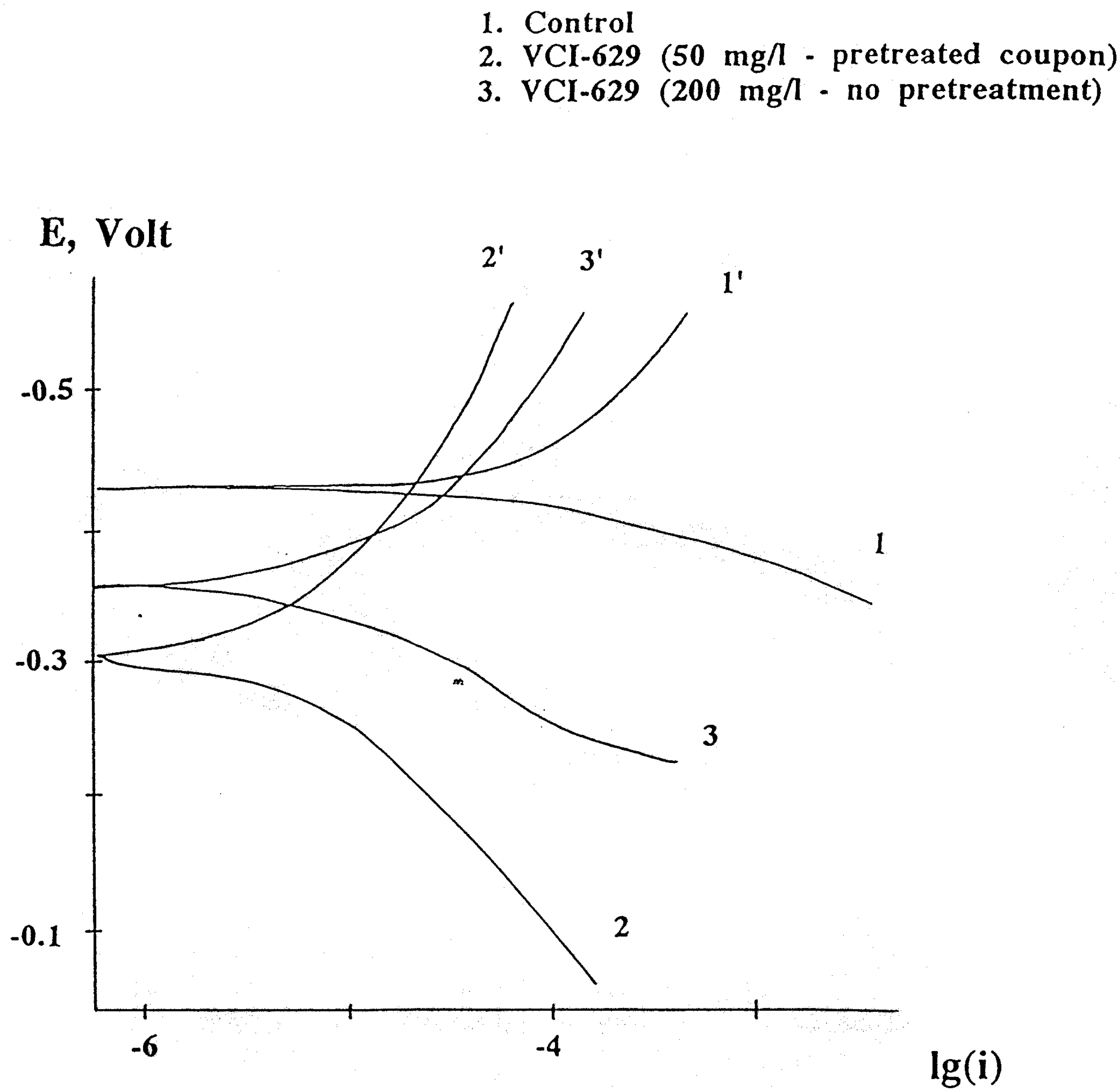


Fig. 10 - Potentiodynamic polarization curves of a steel electrode immersed in NACE TM-01-77 corrosive medium.

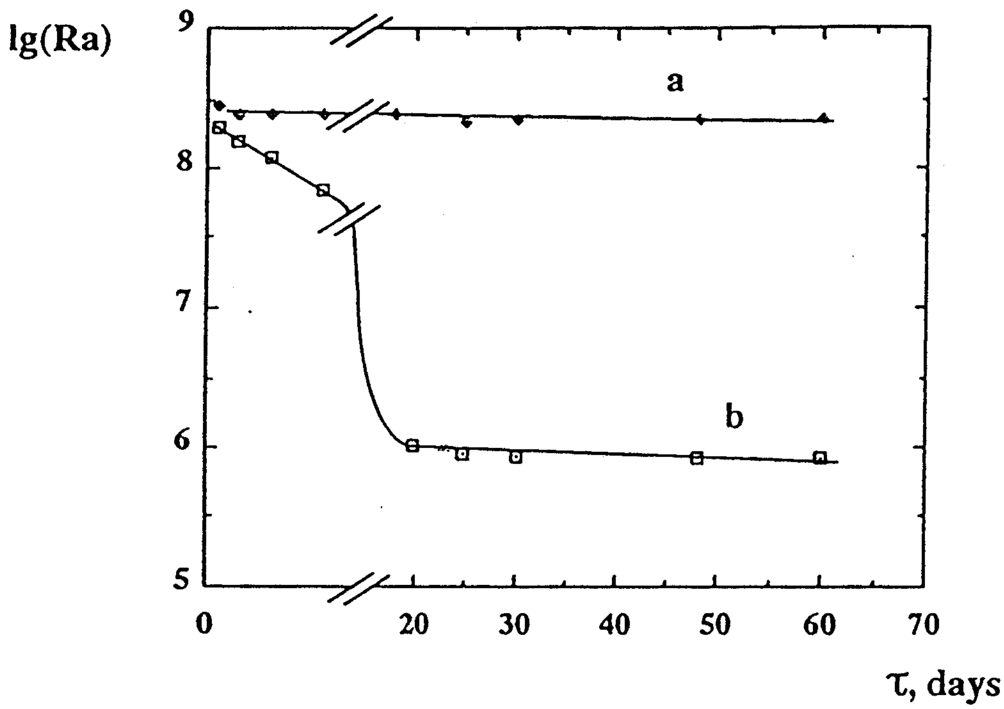
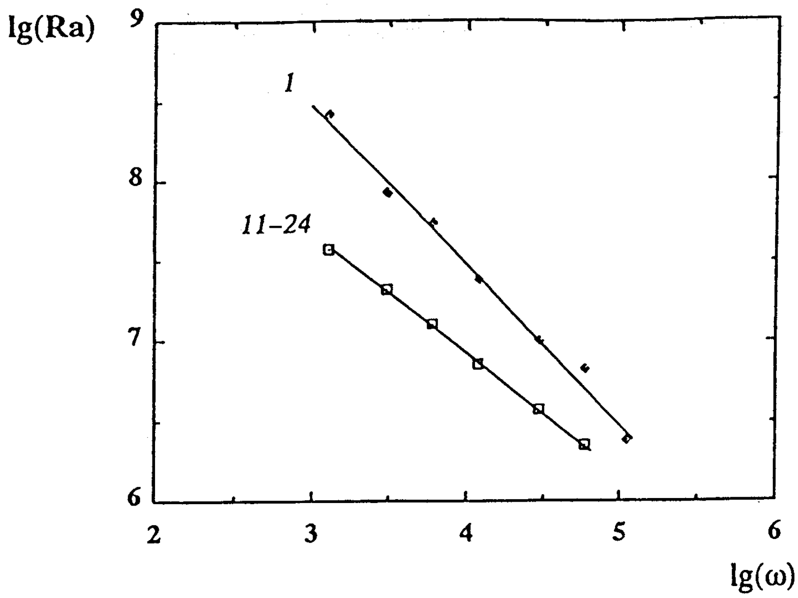
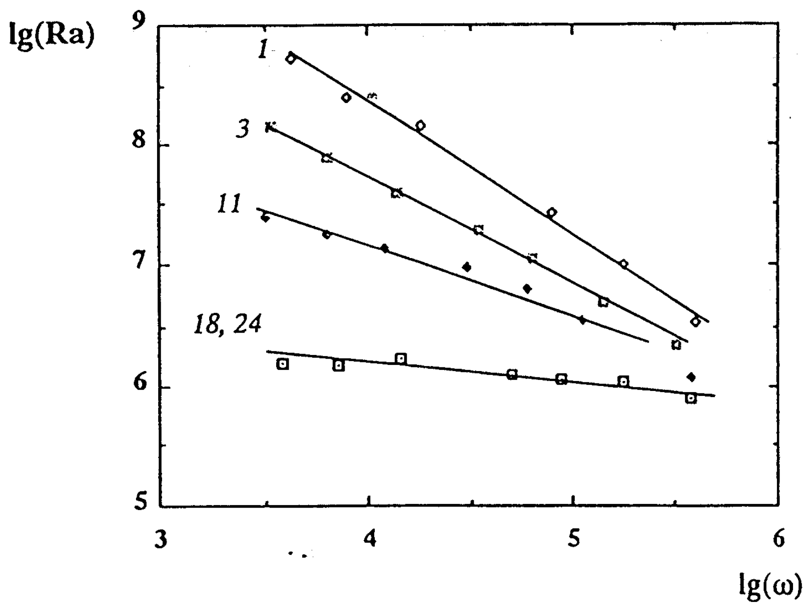


Fig. 11 - Active resistivity (Ra) of an electrode coated with VCI-365
(film thickness = 200 μm) vs. Test duration (τ)
a - Brine water
b - 0.1 M HCl



a - Brine water



b - 0.1 M HCl

Fig. 12 - Active resistivity (Ra) of an electrode coated with VCI-365 (film thickness = 200 μm) vs. Frequency (ω) for electrodes immersed in:
a - Brine water
b - 0.1 M HCl