

Jasper Tamadu Obi^{1,2}, Ihebrodike Maurice Mejeha^{2*},
Kelechukwu Bierechi Okeoma²

¹Isaac Jasper Boro College of Education, Department of Physics, Sagbama, Yenagoa, Nigeria, ²Federal University of Technology, Materials Research Group, Department of Physics, Owerri, Owerri, Nigeria

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The inhibitive effect of magnetic fields on mild steel corrosion in acidic media

ABSTRACT

The inhibitive effect of applied magnetic fields on the corrosion of mild steel in 1.0M HCl and 0.5M H₂SO₄ acid solutions has been investigated at room temperature by using the gravimetric technique. A locally made electromagnet with variable outputs and powered by a direct current source voltage provided the magnetic fields. In a typical experiment, the applied magnetic field was applied perpendicularly onto the surface of a mild steel coupon immersed completely in a chosen acid solution for an exposure time of two hours. It was observed that the corrosion rates of mild steel determined for each case of 1.0M HCl and 0.5M H₂SO₄ test solutions decrease as the applied magnetic field increases. This indicates that the presence of the applied magnetic field inhibits the corrosion of the mild steel in the test solutions. Results also show that the protection efficiency of the magnetic field increases as the applied magnetic field increases. More specifically, as the magnetic field was increased from 118.2 – 764.3mG [or 0.01182 – 0.07643 mT], the protection efficiency increased from 36.34 – 62.67% for mild steel in 1.0M HCl acid solution, while for mild steel in 0.5M H₂SO₄ acid solution, the protection efficiency increased from 12.68 – 46.88%. It was demonstrated that the observed inhibitive effect of the magnetic fields can be attributed partly to the phenomenon of transverse magnetoresistance and partly to the effect of the magnetic fields on the mass transport properties of the constituent ions in the electrochemical system.

Keywords: Mild steel, magnetic field, gravimetric technique, corrosion rate, protection efficiency, magnetoresistance.

1. INTRODUCTION

Wet corrosion of metals and metallic alloys in an acidic, alkaline or indeed any aqueous medium consists in an electrochemical process associated with the flow of electric currents – corrosion currents - between the anodic and cathodic sites on the surfaces of the metal or metallic alloy. This occurs as a result of differences in the electrical potentials of different areas within the metal surface [1,2]. It is a very well - known fact that the motion of electrically charged particles is usually affected by the presence of applied magnetic field in a definite manner. Not surprisingly, corrosion scientists and engineers may have always suspected that the presence of magnetic fields as well as the magnetization state of a metal or metallic alloy do indeed affect the corrosion behaviour of metals or metallic alloys in corrosive environments [3 – 15].

In the above respect, some early research workers on this subject matter have indeed reported that the presence of magnetic field causes a decrease in the corrosion rate of a corroding metal [5,6,11]. Others have focused attention on the effects of magnetic field on the electrodeposition of metals onto metal electrode surfaces, magnetization states of the electrodes, anodic dissolution, electrode kinetics as well as on the electrochemical reactions and processes involved [3,4,7–19]. The main objectives of the such research studies include among others: improvement in electrodeposition quality, enhancement of mass transfer properties of magnetic species (be they ferromagnetic, paramagnetic or diamagnetic) in the electrochemical system, reduction in the microroughness of electrode surfaces, the reduction in the corrosion rates of corroding electrodes [12,20] and the formulation of metal corrosion control mechanisms.

The focus of studies of magnetic field effects on metals or metallic alloys in corroding environments has however been gradually shifting to corrosion control. A number of studies have

*Corresponding author: Ihebrodike Maurice Mejeha

E-mail: micmejeha@gmail.com

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sought to investigate the effect of magnetic fields on the corrosion and adsorption behaviour of metals and metallic alloys in aqueous solutions of acids, alkalis or salts containing various types of corrosion inhibitors [20, 21, 23–25]. These authors have established that magnetic fields inhibit the corrosion of the metals or metallic alloys studied. In all these studies, the investigators used only single fixed values of magnetic fields.

Quite recently, a group of research workers [26] investigated the inhibitive properties of magnetic fields on the corrosion of aluminium alloys AA3003 and AA8011 in hydrochloric acid solutions. In that study, the aluminium alloy samples were exposed to several different applied magnetic fields while being completely immersed in hydrochloric acid solutions for a period two hours. The study not only established conclusively that the magnetic fields inhibit the corrosion of the aluminium alloys, it further established that an increase in the magnetic field results in an enhanced decrease in the corrosion rates of the alloys and therefore its inhibitive capability.

The trend exhibited by the fractional decrease in the corrosion rate of an aluminium alloy sample relative to the corrosion rate of the unexposed alloy coupons led the investigators to an insightful conclusion that the transverse magnetoresistance property of metallic alloys in the presence of steady magnetic fields may be partly responsible for the observed corrosion rate reductions. This is based on the model that the presence of the applied magnetic field results in an increase in the electrical resistance of the corroding metal or alloy. This in turn limits the corrosion current flow. Once it is recognized that corrosion current [more precisely, corrosion current density], is directly proportional to corrosion rate of the corroding metal or metallic alloy [1], it is easy to appreciate that the reduced corrosion current flow is reflected in the

Table 1. Elemental composition of mild steel

Tabela 1. Elementarni sastav mekog čelika

Element	Mn	C	Si	Cu	Cr	Ni	P	W	Co	S
wt. %	0.49	0.26	0.25	0.24	0.14	0.068	0.063	0.055	0.054	0.031
Element	Sn	Pb	Nb	Mo	As	Al	V	Ti	B	Fe
wt. %	0.027	0.02	0.015	0.011	0.01	0.008	0.008	0.005	0.005	98.3

The sheets of mild steel, were mechanically press-cut into coupons each of dimension 20 x 20 x 1.4 mm³. A hole of diameter 2.00 mm was drilled in the middle of one edge of each coupon. Each mild steel sheet was then wet – polished by using emery clothe of different grades, 200 – 600 in order to obtain shining smooth surfaces. They were

observed reduced corrosion rates of the alloy samples.

The conclusions of these research workers are noteworthy. In the theory of magnetic field effects on electrochemical systems, attention has usually been focused on the magnetohydrodynamic (MHD) and magnetic gradient forces [12,19] that act on ionic and charged magnetic species in the electrochemical system. But the effect of the magnetic field on the electron currents that flow on metallic pathways on surfaces of the corroding metal has always been ignored. Consequently, the theory is considered incomplete [26].

In the present study, the effect of magnetic fields on the corrosion of mild steel in 1.0M HCL and 0.5M H₂SO₄ acid solutions will be investigated. The gravimetric technique will be used in conducting the experiments in the absence and presence of several different applied steady magnetic fields. It is hoped that the outcomes of the investigation will be useful in assessing the reasonableness or otherwise of the ideas earlier deposited by Mejeha and co-worker [26].

2. MATERIALS AND METHODS

2.1. Materials and handling

The mild steel used in this study was obtained in form of sheets from an open market situated along the Federal University of Technology Road, Obinze, Owerri West Local Government Area of Imo State, Nigeria. Three different samples of the mild steel were cut out from different sheets and subjected to compositional analysis using the Burn Method at the Chemical Engineering Laboratory of the Standard Organisation of Nigeria, SON, at Enugu, Nigeria. The elemental composition of each of the samples was determined and the average values of the constituent elements calculated and recorded in weight percent (wt %). These are presented in Table 1.

then degreased in absolute ethanol, washed in double distilled water, rinsed in acetone and allowed to dry in air after which it was weighed and put away in a moisture free desiccator after labelling. An electronic weighing balance of model, S. Mettler FA 2104, with least count of 0.02 mg was used in weighing the mild steel coupons.

The hydrochloric acid, the sulphuric acid and other reagents used in the study were of BDH analytical grade and were supplied by FINLAB Nigeria Limited, Owerri. Double distilled water was used in preparing the 1.0M HCl and 0.5M H₂SO₄ acid solutions.

The magnetic fields used in this study were supplied by a locally made electromagnet with variable output [26] and powered by a direct current source of voltage. It was characterized and calibrated with the aid of a digital gaussmeter with trade mark: Magnetic Field Meter, T.M. 191. The gaussmeter has a measuring scale in units of milligauss, mG. The least count of the device was 0.01 mG (or 1 μ T). When a direct current voltage was applied to the terminals of the electromagnet, a steady magnetic field would be produced and exist in the gap between the poles of the electromagnet.

2.2. Experimental procedure.

A 250 ml beaker containing 180 ml of 1.0M HCl acid solutions was placed within the gap between the poles of the electromagnet. A pre-weighed mild steel coupon was completely immersed in the test solution in such a way that it hung vertically with its horizontal sides parallel to the surfaces of the poles of the electromagnet. This arrangement ensured that whenever an applied voltage existed across the terminals of the electromagnet, the magnetic field produced would fall perpendicularly onto the mild steel coupon surface. At the commencement of the experiment, no voltage was applied to the electromagnet. After exposing the mild steel coupon to the test solution for a two – hour duration at room temperature, it was retrieved from the acid solution, dropped into a nitric acid solution to quench further corrosion. It was then washed in double distilled water several times and then degreased in ethanol before being rinsed in acetone and then dried in air. The coupon was reweighed to determine the weight loss resulting from the acid attack.

The experimental procedure was repeated with two other mild steel coupons. With the values of weight loss obtained, the corrosion rate for each of the coupons was determined as explained in sub – section 3.1 and the mean value of the corrosion rate calculated. The result is the mean corrosion rate of the mild steel in 1.0M HCl acid solution for a two – hour duration without an applied magnetic field.

The experiment was repeated, this time, with an applied magnetic field. The repetitions were carried out at each of the different settings of the

source voltage in the range 5.0 – 25.0 volts so that different values of applied magnetic field would be made available.

The entire experimental procedures were again repeated with mild steel in 0.5M H₂SO₄ acid solutions in the absence and presence of various applied magnetic fields, while ensuring that triplicate experiments were carried out at each setting of the direct current voltage source, this way ensuring reproducibility.

3. RESULTS AND DISCUSSION

3.1. Corrosion rates of mild steel immersed in acid solutions in the absence and presence of applied magnetic field

The corrosion rate, ρ , of a mild steel coupon in 1.0M HCl or 0.5M H₂SO₄ acid solutions in the absence and presence of applied magnetic field was determined by using the relation [1, 26 – 28]:

$$\rho = \frac{k\Delta W}{DAT} \quad (1)$$

where:

k = rate constant with a value of 534 in the unit system of mils per year (mpy) with 1 mil = 10⁻³ inch;

ΔW = weight loss in milligrams (mg);

D = density of mild steel coupon in grams per cubic centimeter, gcm^{-3} ;

A = exposed surface area of mild steel coupon, in square inches, in^2 , 1 in^2 = 6.5416 cm^2

T = exposure time in hours.

The corrosion rates, ρ , of mild steel in the 1.0M HCl and 0.5M H₂SO₄ acid solutions in the presence of applied magnetic field are summarized in Table 2. Also recorded in the table are the magnetic field at zero applied direct current voltage and the corresponding corrosion rates in the two acidic media and which shall be called zero – field corrosion rates and designated as ρ_0 . The table shows clearly that when a magnetic field is applied, the corrosion rate decreases below the zero - field value, ρ_0 . This result is consistent with the findings of some previous research workers [5,6,11,20-26]. Furthermore, as the applied magnetic field is increased, the corrosion rate further decreases to lower values. These results clearly indicate that the presence of the magnetic field inhibits the corrosion of mild steel in the two acidic media and that that the strength of the magnetic field determines the extent or degree of reduction of the corrosion rate, a conclusion consistent with the findings of Mejeha and coworkers [26].

Table 2. Variation of corrosion rate and protection efficiency for mild steel in 1.0M HCl and 0.5M H₂SO₄ acid solutions with applied magnetic field for a 2 – hour duration at room temperature

Tabela 2. Varijacije brzine korozije i efikasnosti zaštite za meki čelik u 1.0M HCl i 0.5M H₂SO₄ kiseliniskim rastvorima sa primenjenim magnetnim poljem u trajanju od 2 sata na sobnoj temperaturi

Applied voltage, V (volts)	Magnetic field B (mT)	Corrosion rate ρ (mpy)		Protection efficiency η %	
		HCl	H ₂ SO ₄	HCl	H ₂ SO ₄
0	0.003786	1117.96	2764.48	-	-
5	0.01182	711.26	2413.85	36.34	12.68
10	0.025429	611.64	2013.5	45.29	27.17
15	0.044286	500.43	1779.97	55.24	35.61
20	0.059129	450.72	1668.76	59.68	39.64
25	0.076429	417.35	1468.59	62.67	46.88

3.2. Magnetic field protection efficiency for mild steel in 1.0M HCl and 0.5M H₂SO₄ acid solutions

The implication of the finding that the presence of applied magnetic field inhibits the corrosion of mild steel in the 1.0M HCl and 0.5M H₂SO₄ acid solutions is that the applied magnetic field offers some degree of protection against the corrosion of the mild steel in the acidic solutions. The protection efficiency of the magnetic field can be defined in analogy to the inhibition efficiency of additive corrosion inhibitors as when a corrosion inhibitor is added to a corrodent in which a metal or metallic alloy coupon is immersed [27, 28]. Therefore, the protection efficiency of the magnetic field can be defined as [26]:

$$\eta\% = \frac{\rho_0 - \rho_B}{\rho_0} \times 100\% \quad (2a)$$

$$= \frac{\Delta\rho}{\rho_0} \times 100\% \quad (2b)$$

where:

ρ_0 = zero – field corrosion rate

ρ_B = corrosion rate in the presence of an applied magnetic field

$\Delta\rho = \rho_0 - \rho_B$ = decrease in corrosion rate.

In columns 5 and 6 of Table 2 are given the magnetic field protection efficiencies for mild steel magnesteel in 1.0M HCl and 0.5M H₂SO₄ acid solutions respectively at room temperature. They were obtained for mild steel samples completely immersed in the acid solutions for two – hour durations. It can be noticed that as the applied magnetic field is increased, the magnetic field protection efficiency also increases. In the case of mild steel in 1.0 M HCl acid solutions, the magnetic field protection efficiencies observed varied from 36.34 % to 62.67 %, while for mild steel in 0.5M

H₂SO₄ acid solution, they varied from 12.68 % to 46.88 % for the same magnetic field range. This result suggests that the nature of the corrodent (the corroding solution) is a factor affecting the degree of protection offered against corrosion by the applied magnetic field.

3.3. Corrosion protection mechanism for mild steel in acid solutions in the presence of applied magnetic field.

It is pertinent at this point to seek a possible scientific model that can explain the observed large reductions in the corrosion rates of mild steel in the acidic media in the presence of applied magnetic field. One then calls to mind the two components of the corrosion current. The first to mention is the electrical current that arises in the electrochemical system due to the movement of charged reactants, electrons and corrosion products. The second component consists of the movement of electrons released during the corrosion process and which move along metallic pathways from the anodic to the cathodic sites [2, 22]. The effect of the applied magnetic field on the first component of the corrosion current has been extensively studied and the theories of magnetohydrodynamics (MHD) and gradient magnetic forces have been adequately applied in the studies [12,19]. But the effect of applied magnetic field on the second component of the corrosion current has previously been ignored. Only recently, Mejeha and co-workers [26] pointed out that the effect of the magnetic field on the electron current along metallic pathways within the corroding metal may indeed largely account for the observed large reductions of the corrosion rates of aluminium alloys AA3003 and AA8011 in hydrochloric acid solutions.

It is well-known that when a piece of metal, metallic alloy or semiconductor carrying electrical current is placed in a steady magnetic field, its electrical resistance changes [29-31]. For most materials, the change is an increase. This property

of the materials is known as magnetoresistance. When the direction of electric current flowing in the material is perpendicular to the direction of the applied magnetic field, the increase in the electrical resistance of the material is referred to as transverse magnetoresistance [29, 31].

Experimental and theoretical studies of the phenomenon of transverse magnetoresistance have shown that an increase in applied magnetic field would lead to further increase in the electrical resistance of the metal, metallic alloy or semiconductor sample. But the pattern of increase depends on the type and nature of the material. Three categories of metals have been identified. If one denotes the fractional increase in the electrical resistance as $R(B)/R(0)$ where $R(B)$ is the electrical resistance of the sample material in the presence of magnetic field, B , and $R(0)$ is the electrical resistance in the absence of magnetic field, that is, the zero – field resistance, then:

For Category I materials: $R(B)/R(0)$ varies quadratically initially with increase in magnetic field, B , then varies more slowly as B before saturating, that is, becoming independent of B [29, 31].

For Category II materials, $R(B)/R(0)$ varies quadratically as B , that is:

$$R(B)/R(0) = \kappa B^2 \quad (3)$$

where κ is a constant parameter. For category II materials therefore, $R(B)/R(0)$ increases without limit as B increases [29].

For Category III materials, $R(B)/R(0)$ exhibits some anisotropy. Its value and pattern of variation with the magnetic field depends on the crystallographic direction along which the magnetic field is applied. In some crystallographic directions, $R(B)/R(0)$ will increase without limit as the applied magnetic field increases as for Category II materials. In some other crystallographic directions, as the applied magnetic field increases, $R(B)/R(0)$ increases quadratically initially, then more slowly before attaining saturation as for Category I materials [29].

As already pointed out, a corroding metal sample carries corrosion current on its surface.

This consists of the flow of electrons from anodic to cathodic sites along metallic pathways [2, 22]. In the presence of a magnetic field applied perpendicularly to the sample surface, the electrical resistance of the metal sample increases leading to a further limiting of the corrosion currents. As a result, the corrosion rate of the metal sample decreases. This is predicated on the known fact that corrosion current (or more precisely corrosion current density) is directly proportional to corrosion rate [1]. Therefore, any reduction in the corrosion current is observed as a reduction in the corrosion rate of the sample.

The insight provided by the above exposition has prompted Mejeha and co-workers [26] to conclude that the observed large reductions of the corrosion rates of some aluminium alloys in acidic solutions in the presence of applied magnetic field can largely be attributed to the phenomenon of transverse magnetoresistance and secondarily to the mass transfer of the charged reactants and corrosion products present in the electrochemical system. The authors showed that in the presence of applied magnetic field, the fractional decrease in the corrosion rates, $\Delta\rho/\rho_0$, over the zero – field corrosion rate, ρ_0 , conforms, all – be – it, qualitatively, to a polynomial function of the form [26]:

$$\frac{\Delta\rho}{\rho_0} = aB^2 + bB + c \quad (4)$$

where a , b and c are constant parameters while B is the applied magnetic field.

Fig. 1 shows how the fractional decrease in the corrosion rates of mild steel in 1.0M HCl and 0.5M H₂SO₄ acid solutions determined in this study vary with applied magnetic field. Both curves depicted for mild steel corrosion mimic very closely the fractional increase of resistance of a Category I materials described in the preceding paragraphs when exposed to applied magnetic fields. The curves represent polynomial equations of order 2. The parameters a , b and c as well as the squares of the coefficients of correlation R^2 which give the degree of fit between the corrosion data and the polynomial equation are also displayed in Table 3.

Table 3: Values of squares of correlation coefficients, R^2 , and coefficients a , b and constant parameter, c , appearing in Eq. 4 for mild steel in 1.0M HCl and 0.5M H₂SO₄ acid solutions in the presence of applied magnetic fields

Tabela 3: Vrednosti kvadrata koeficijenata korelacije, R^2 , i koeficijenata a , b i konstantnog parametra, c , koji se pojavljuju u jednačini 4 za meki čelik u 1.0M HCl i 0.5M H₂SO₄ kiselinim rastvorima u prisustvu primenjenih magnetnih polja

Parameter of fit	a	b	c	R2		c	R2
Mild steel in HCl	- 5.0 x 10 ⁷	8.696 x 10 ³	0.2673	0.9997		.70E+03	0.9997
Mild steel in H ₂ SO ₄	- 5.0 x 10 ⁷	9.658 x 10 ³	0.0348	0.9789		0.0348	0.9789

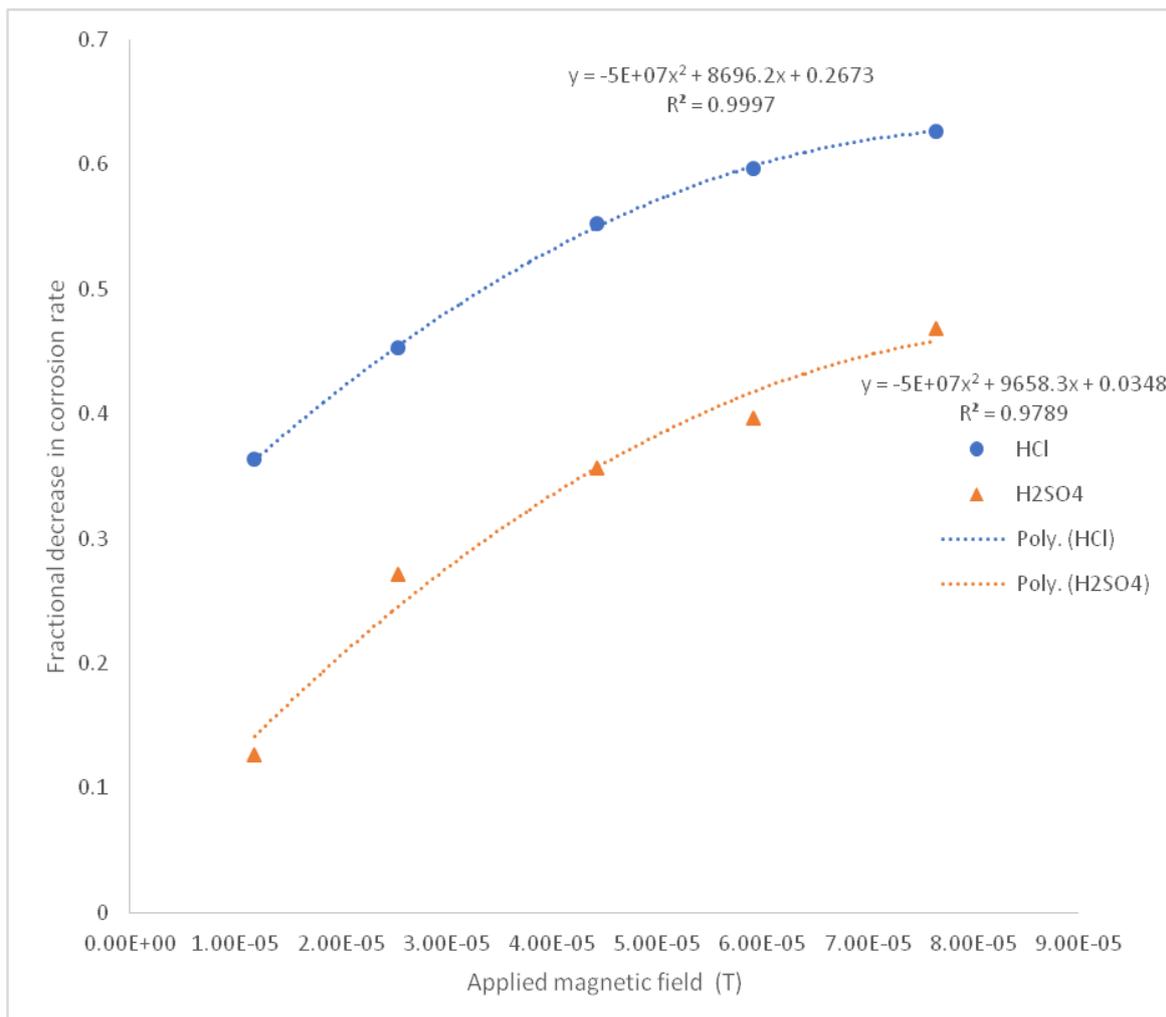


Figure 1. Variation of the fractional decrease in the corrosion rates of mild in 1.0M HCl and 0.5M H₂SO₄ acid solutions with applied magnetic field for a duration of 2 hours at room temperature

Slika 1. Varijacija frakcionog smanjenja brzine korozije u 1.0M HCl i 0.5M H₂SO₄ kiselinskim rastvorima uz primenjeno magnetno polje u trajanju od 2 sata na sobnoj temperaturi

It is evident from Fig. 1 and Table 3 that the experimental data fit very well with the empirical equation, Eq. 4, since the high R^2 values of 0.9997 and 0.9789 were obtained for mild steel in 1.0M HCl and 0.5M H₂SO₄ acid solutions respectively. An intriguing finding is that the constant parameter a , which is the coefficient of the quadratic term in the polynomial equations, Eq. 4, obtained in this study has the same value for mild steel in the two acidic media. This suggests that the quadratic term in the empirical equations, Eq. 4 may be the contribution of the transverse magnetoresistance effect to the corrosion rate reduction in the mild steel corrosion while the linear term may largely be the contribution due to the effect of the induced mass transport of the charged reactants and corrosion products in the electrochemical system in the presence of applied magnetic field. That the

values of the constant parameter b , the coefficient of the linear term in Eq. 4, are different for mild steel in the two acid solutions may be due to the fact that the two corrodents are indeed different in nature. The conclusions in this paragraph are however tentative since more research work is urgently needed to confirm or repudiate them.

4. CONCLUSION.

It has been established in this study that the presence of an applied magnetic field causes a decrease in the corrosion rate of mild steel 1.0M HCl and 0.5M H₂SO₄ acid solutions. This implies that applied magnetic field inhibits corrosion of mild steel in the test solutions. It further means that the presence of applied magnetic field offers some degree of protection against acid corrosion.

Results also show that an increase in the applied magnetic field leads to further decrease in the corrosion rate of mild steel in the acidic solutions. This implies that the protection efficiency of the magnetic field against mild steel corrosion increases with increase in the applied magnetic field.

It was also demonstrated that the fractional decrease in the corrosion rate of mild steel in the acidic solutions varies with applied magnetic field in almost the same way as the fractional increase in the electrical resistance of Category I materials varies with increase in perpendicularly applied magnetic field. This strongly suggests that the corrosion protection mechanism is largely attributable to the phenomenon of transverse magnetoresistance.

Preliminary findings suggest that the quadratic part of the empirical formula (Eq. 4) representing the dependence of the fractional decrease of the corrosion rate, $\Delta\rho/\rho_0$, on the applied magnetic field may be due to the contribution of transverse magnetoresistance effect on the mild steel corrosion in the acidic media in the presence of the applied magnetic fields. The linear term of the empirical formula may be largely due to magnetic field effects on the mass transport of the charged reactants and corrosion products in the electrochemical system due to the presence of applied magnetic fields. However, more research work is needed for this conclusion to be firmly established.

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IZVOD

INHIBITIVNI EFEKAT MAGNETNOG POLJA NA KOROZIJU MEKOG ČELIKA U KISELOM MEDIJU

Inhibitivni efekat primenjenih magnetnih polja na koroziju mekog čelika u 1.0 M HCl i 0.5 M H₂SO₄ kiselinskim rastvorima ispitan je na sobnoj temperaturi gravimetrijskom tehnikom. Lokalno napravljen elektromagnet sa promenljivim izlazima i napajan iz izvora jednosmerne struje obezbeđivao je magnetna polja. U tipičnom eksperimentu, korišćeno magnetno polje je primenjeno okomito na površinu kupona od mekog čelika koji je u potpunosti uronjen u izabrani rastvor kiseline tokom vremena izlaganja od dva sata. Uočeno je da se brzine korozije mekog čelika određene za svaki slučaj testnih rastvora od 1.0 M HCl i 0.5 M H₂SO₄ smanjuju kako se primenjeno magnetno polje povećava. Ovo ukazuje da prisustvo primenjenog magnetnog polja inhibira koroziju mekog čelika u ispitivanim rastvorima. Rezultati, takođe, pokazuju da se efikasnost zaštite magnetnog polja povećava kako se primenjeno magnetno polje povećava. Tačnije, kako je magnetno polje povećano sa 118,2 – 764,3 mG [ili 0,01182 – 0,07643 mT], efikasnost zaštite je porasla sa 36,34 – 62,67% za meki čelik u 1.0 M rastvoru HCl kiseline, dok je za meki čelik u kiselini 0.5M H₂SO₄ efikasnost zaštite povećana sa 12,68 – 46,88%. Pokazano je da se uočeni inhibicioni efekat magnetnih polja može delom pripisati fenomenu poprečne magnetootpornosti, a delom uticaju magnetnih polja na svojstva transporta mase konstitutivnih jona u elektrohemijском sistemu.

Ključne reči: meki čelik, magnetno polje, gravimetrijska tehnika, brzina korozije, efikasnost zaštite, magnetootpornost.

Naučni rad

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