Effect Of Mixing Speed And Solution Temperature On Cathodic Protection Current Density Of Carbon Steel Using Magnesium As Sacrificial Anode

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Abstract

In present work, The corrosion behavior of carbon steel in sodium chloride (NaCl) solution with different concentrations was studied .Effects of mixing speed (0 to 2220) r.p.m and the solution temperature $(25, 35, 45, 55, 65)^0$c on cathodic protection current density were studied, that would provide a full cathodic protection for tube metal specimen of carbon steel immersed in 3.5% NaCl solution by sacrificial anode method using magnesium (Mg) as sacrificial anode.

The results show that the concentration of sodium chloride in the electrolyte is an important factor in determining corrosion rate, 3.5 % concentration of sodium chloride gives maximum rate of corrosion. In addition, it has been found that the cathodic protection current density showed sharp increasing with mixing speed. The results have showed also that the cathodic protection current density increased with increasing the solution temperature and shifts the protection potential to high negative value.

تأثيرسرعة الخلط ودرجة حرارة المحلول على قيمة كثافة تيار الحماية الكاثودية لحديد الفولاذ بأستخدام المغنيسيوم كأنود مضحي

الخلاصة

يتضمن البحث دراسة سلوكية تاكل حديد الفولاذ في وسط ملحي بتراكيز مختلفة لكلوريد الصوديوم. أثبتت النتائج أن معدل التاكل يزداد بازدياد تركيز الملح(كلوريد الصوديوم) الى أن يصل الى حالــة الأشـباع وذلك عند تركيز يساوي تقريبا (3.5 %) ثم يبدأ بالتناقص وذلك بسبب تضاؤل كمية الأوكسجين المذاب في المحلـول ومــن ثــم دراســة تأثيرســرعة الخلــط(صـفر -2220)دورة/دقيقــة و درجــة حــرارة المحلول(25و35و45و 55و 65)^{0}م ، على قيمة كثافة تيار الحماية الكاثوديــة (بطريقةالأنودالمــضحي) الــذي يعطي حماية كاثودية كاملة لعينة انبوب معدني من حديد الفولاذ مغمور بمحلول كلوريد الــصوديوم بتركيـز 3.5% وذلك باستخدام المغنيسيوم كأنود مضحي, أوضحت النتائج أن كثافة تيار الحماية يزداد زيادة حــادة عند الانتقال من الحالة الساكنة الى حالة الخلط ويستمر بالزيـادة عنـد الاسـتمرار بزيـادة ســرعة الخلــط (المزج) وتبين زيادة تيار الحماية الكاثودية عند زيادة درجة الحرارة ومن الواضح ان تاثير سرعة المزج كان اوضح من تاثير درجة الحرارة ,وتمت دراسة تاثير درجة الحرارة على الفولتية المجهـزة مــن قبــل انــود المغنيسيوم,حيث تبين ان زيادة درجة الحرارة تؤدي الى زيادة الفولتية المجهزة من قبــل انــود المغنيــسيوم بالاتجاه السالب.

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Eng. &Tech. Journal. Vol. 27, No. 8, 2009

**Theoretical Aspects of some
Mechanical Properties of Composites**

Nomenclature

A: area (cm^2)
Am: ampere
CP: cathodic protection
CS: carbon steel
E: difference in potential between the anode and cathode in volts
I: current flow in amps
K: constant
Mpy: mils penetration per year
SCE: standard calomel electrode
SHE: standard hydrogen electrode
T: temperature (^{o}C)
t: time of exposure in (hour)
R: total circuit resistance in ohms
V: volts
ρ: density :(gm /cm^3)
ΔW: weight loss (gm)

1. Introduction

Corrosion in aqueous solutions is an electrochemical reaction that involves charge transfer oxidation (loss of electrons) and reduction (gain of electrons) so corrosion is a metal dissolution process with the metal ions going into solution [1]

Humphrey Davy,s work on cathodic protection the copper sheathing on wooden hulls in the British Navy by sacrificial anode[2]. Metals (including alloys) can be arranged in a galvanic series representing the potential they develop in a given electrolyte against a standard reference electrode. The relative position of two metals on such a series gives a good indication of which metal is more likely to corrode more quickly. However, other factors such as water aeration and flow rate can influence the process markedly.

Galvanic corrosion is of major interest to the marine industry. Galvanic series tables for seawater are commonplace due to the extensive use of metal in shipbuilding. It is possible that corrosion of silver brazing in a salt water pipe might

have caused a failure [3]. Galvanic corrosion is the most frequent cause of unexpected corrosion failures in seawater. It has caused failures of ship fittings and deckhouse structures, fasteners, hull plating, propellers, shafts, valves, condensers, and piping. In sea atmospheres, galvanic corrosion causes failures of roofing, gutters, and car trim. The reason that galvanic corrosion causes so many failures is that it can occur any time that two different metals are in electrical contact in seawater. Since most structures and devices are made of more than one kind of metal, this diversity of materials is common [4].

The principle of cathodic protection is in connecting an external anode to the material to be protected from corrosion and passing of an electrical DC current. So that all area of the metal surface become cathodic and therefore do not corrode. The external anode may be a galvanic (sacrificial) anode or it may be an impressed current anode where the current is impressed from external dc source.

The well known protection criterion for steel in soil was reportedly pioneered by Robert J. Kuhn [5].

There are two systems for cathodic protection: Impressed Current cathodic protection system , and sacrificial (galvanic) cathodic protection system. Sacrificial (galvanic) cathodic protection anodes are lower cost than impressed current cathodic protection anode. These anodes are otherwise known as galvanic cathodic protection anodes [6].

A potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution figure (1). When these two metals are electrically connected to each other in a electrolyte e.g. seawater, electrons will flow from the more active metal to the other, due to the difference in the electrical potential, the so called "driving force". When the most active metal (anode) supplies current, it will gradually dissolve into ions in the electrolyte, and at the same time produce electrons, which the least active (cathode) will receive through the metallic connection with the anode. The result is that the cathode will be negatively polarized and hence be protected against corrosion. To calculate the rates at which these processes occur, one has to understand the electrochemical kinetics associated with the complex sets of reactions that can all happen simultaneously on these metals [7].

Corrosion of the less corrosion – resistant metal is usually increased, as compared with the behavior of these metals when they are not contact. The less resistant metal becomes anodic and the more resistant metal cathode.
Usually the cathode or cathodic metal corrodes very little or not at all in this type of couple. In sea water and marine environment carbon steel needs corrosion protection. The most common methods are cathodic protection, organic or metallic coating and chemical treatment .Cathodic protection has grown to have many uses in marine and underground structures, oil pipelines, water storage tank ,oil platform supports ,and many other facilities exposed to a corrosion environment [8].

In this type of cathodic protection a metal anode that is more reactive to the corrosive environment of the system to be protected is electrically linked to the protected system, and partially corrodes or dissolves which protects the metal of the system it is connected to .As example an pipelines may be protected by magnesium sacrificial anode which will dissolve into sea water or soil and prevent pipelines from being corroded. The flow of electrons is always from anode that it will gradually dissolved into ions in the electrolyte, and the same time produce electrons towards cathode outside of the cell or device .The chosen of anode and cathode depends on different factors one of these important is the location of these metals in table of standard electrode potentials it must be a suitable differences between these metals such as magnesium that has a much more negative electrode potential than iron (-2.37)V for magnesium ,versus (-0.44)V for iron Vs (SHE) [9].

The galvanic series shows that magnesium heads the list as the most anodic metal and is widely separated from iron in the galvanic series. Magnesium coupled to iron provides sufficient galvanic potential to provide positive protection.

Magnesium sacrificial anodes may have a protective coating of a very dense oxide film on their surface (which usually has a charcoal-gray appearance). This condition usually occurs in freshwater, but it can also happen in saltwater areas.

A sacrificial anode, or sacrificial rod, is a metallic anode used in cathodic protection where it is intended to be

Eng. &Tech. Journal. Vol. 27, No. 8, 2009

Theoretical Aspects of some
Mechanical Properties of Composites

dissolved to protect other metallic components [10].

In laymen's terms, it is a piece of more readily-corrodible metal attached by a conductive solid to a less readily-corrodible metal, with both metals immersed in a conductive liquid, typically fresh or salt water. The more active metal corrodes first and generally must oxidize nearly completely (hence the term "sacrificial") before the less active metal will corrode, thus acting as a barrier against corrosion for the protected metal [11]

More scientifically, a sacrificial anode can be defined as a metal that is more easily oxidized than the protected metal. Electrons are stripped from the anode and conducted to the protected metal, which becomes the cathode. The cathode is protected from corroding, i.e., oxidizing, because reduction rather than oxidation takes place on its surface [12, 13]. For example when magnesium and iron are put together (in contact) in the presence of oxygen and water, the magnesium will lose electrons and go into solution as magnesium cations. Electron released from the magnesium atoms flow by metallic conduction to the iron where, on the surface, dissolved oxygen is reduced, by gaining the electrons released by the zinc, to hydroxide anions. When the magnesium not present, the same reduction of oxygen to hydroxide would occur on the iron surface, however in that case the electrons for reduction would be furnished by the iron thus oxidizing the iron. Therefore, the magnesium, when present, is "sacrificed" by being oxidized instead of the iron. The iron is "safe" until all of the magnesium has corroded. As magnesium is more costly than iron, this method of protecting iron, or steel, would not be cost effective were it not for secondary chemical reactions that form coatings on the iron surface thus shutting

down the electrochemical reaction to a trickle and thus greatly prolonging the life of the magnesium anode [14, 15, 16]

Magnesium has an equilibrium potential of (-2.61V) Vs SEC and there for theoretically can provide a very large driving voltage. Practical measurement indicates reactively more noble corrosion potential probably due to the electrochemical inefficiency of the metal as a sacrificial anode.

The theoretical current capacity for magnesium anode is approximately (2200 Ah /kg) .The galvanic series shows that magnesium heads the list as the most anodic metal and it is widely separate from iron. Magnesium coupled to iron provides sufficient galvanic potential to provide positive protection [17, 18].

A prospective sacrificial anode must possess large number of electrons per unit mass and should deliver these electric charges efficiency .This electrical output of anode is given by current capacity which is determined by electrochemical equivalent which is depend on the atomic weigh and valance [19].

2. Experimental work
2.1 materials

The steel pipe used in this work was carbon steel analyzed by Geology Scan Company (composition of wt% C:0.025;Mn:0.26;Si:0.015;S:0.012;Cr:0.03 8;and Fe to 100) with (2.5cm)OD and (8cm) in length. For all experiments, the carbon steel samples were polished with 220,500,800 mesh grinding, cleaned with distilled water. Carbon steel sheets with double side's surface area of (2) cm^2 were used for weight loss measurement (coupon).The sacrificial anode in this work was magnesium electrode (63 cm^2 surface area).The corrosion medium was 3.5% NaCl solution (sodium chloride with 99.99 in purity).

2.2 procedures

The specimens were weighed using electronic balance and then immersed in

the solution for (72) hr. The specimens were raised from the solution and washed after that brushed with tap water (using smooth brush) in order to remove the entire corrosion product from the metal surface .The specimens were washed again with tap water followed by distilled water and dried with clean tissue paper and kept in a desiccators for 1 hr before being weighed again.

The electrical circuit was connected as shown in Figure (2) to measure the open circuit potential. The electrochemical measurement were performed which current and voltage were measured with digital multimeters (type E7000). The electrode potentials are presented with reference to saturated calomel electrode (SCE). The current values reported in are expressed per unit area, i.e., current density. The cathode (pipe) and the (anode magnesium) immersed in the electrolyte

In order to obtain the effect of mixing speed on protection current density the above procedure was repeated with various mixing speed (zero to 2220) rpm. The electrolyte was stirred by using a glass rod in order to obtain a homogenous solution, then using the heater controller in the bath to set the solution at the required temperature to achieve thermal equilibrium before starting the experimental run. The cathodic current density was recorded with each rotation speed for (25°C) then the same procedure repeated for (35, 45, 55, and 65)$^{\circ}$C.

3. Results and discussion

The corrosion behavior of carbon steel in sodium chloride (NaCl) solution was studied using the weight loss technique the results show that the corrosion behavior of carbon steel is significantly different under the different liquid media solutions, such as its salt concentration, corrosion rates (*mpy*) mils penetration per year was calculated by using the following expression

$$ mpy \quad = \quad \frac{\Delta w}{t} \cdot \frac{K}{r A} ....(\ 1\ ) $$

The schematic effect of NaCl concentration on corrosion rate of carbon steel in (25°C) temperature solution is shown in Figure (3), the corrosion rate first increases when salt concentration increase, then decrease, the falling below that for distilled water when saturation is reached (3.5 %NaCl) Uhlig showed the effect of NaCl concentration on corrosion of iron in air-saturated water at room temperature. He showed that corrosion first increases up to concentration of 3.5%, above this concentration, the corrosion begins to decrease. The increase in corrosion rate is due to increase of the conductivity, while the decrease is due to the decrease of oxygen solubility with increasing NaCl concentration [2].

Since oxygen depolarization controls the rate throughout the sodium chloride concentration range, it is of some interest to understand why the rate first increases, reaching a maximum at about 3.5%NaCl (seawater concentration) [3, 13], and then decreases. Oxygen solubility in water decreases continuously with sodium chloride concentration, explaining the falling off of corrosion rate at a higher sodium chloride concentration. The initial rise appears to be related to change in the protective nature of the diffusion barrier rust film that forms on the corroding carbon steel .Solubility of oxygen in water decreases rapidly with increasing salt concentration that the decreased solubility of oxygen with increasing salt concentration is the reason for the reduced rate of corrosion[4-6] .

Figure (4) shows effect of immersion time of open circuit potential of carbon steel pipe immersed in 3.5 %(NaCl) .It can be seen that the potential decrease with time until the study state potential is

1644

Eng. &Tech. Journal. Vol. 27, No. 8, 2009

**Theoretical Aspects of some
Mechanical Properties of Composites**

reach at (-625mV) Vs SCE which represent the corrosion potential .This evidence that the sample is which in corrosion zone under these conditions.

As shown in Figure (5) magnesium anode coupled to carbon steel provides sufficient galvanic potential to provide positive protection, the protection potential that supply by magnesium anode is equal to (-950mV), that is referred to as sacrificial system, since the magnesium sacrifice itself to protect the structure (carbon steel pipe) from corrosion, therefore the pipe does not corrode at this condition [7].

The change from static condition to mixing effect shows sharp rise in cathodic protection current density for first condition of temperature equal to ($25^{o}C$) as shown in Figure (6).This can be attributed to the increase of oxygen flux arriving to the metal surface and the decrease in all resistance that hinder the transfer of oxygen, when the mixing speed increase the cathodic current density increase too and this due to dispersion of the accumulation of (OH^-) ions by stirring action. These ions were generated at cathodic side as:

$$O2 + 2H_2O \rightarrow 4OH^- \quad \dots (2)$$

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \quad \dots (3)$$
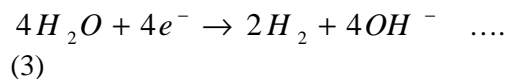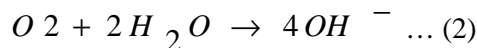
At cathodic region and as shown in equation(1and 2) the generation of (OH^-) ions tends to increase the pH of solution, as a result of cathodic alkalinity increasing at this region adequate protection will occur.

Oxygen evolution occurs at anodic region as shown:

$$2H_2O \rightarrow O + 4H^+ + 4e^- \quad \dots (4)$$
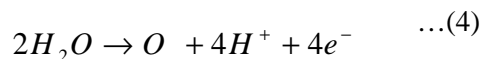
The mixing process leads to removes the corrosion products from the surface of the metal that causing clean surface to appear to the medium (NaCl solution) and hence

increase the corrosion rate of magnesium (sacrificial anode) that's mean more electrons to be formed in the electrical circuit (increasing the current density) as long as the current (free electrons) is arriving at the cathode (steel) faster than oxygen is arriving, no corrosion occurs [8]

The mixing process of the salt solution leads to increase the movement of positive ions which are generated near the surface of magnesium anode towards the electrolyte, this heavy movement will be accelerated of the electrons flow rate and the circuit was closed, so the current will be increasing through the circuit.

The results show clearly that the cathodic current density increase with bulk temperature increase; this can be attributed to the increase of oxygen supplying to the surface and decrease all the resistance that hinder the transfer of oxygen especially at the boundary layer, and the increasing of temperature leads to increase of the electrical conductivity of (NaCl solution) as we know there is a linear relation ship between temperature and conductivity of salt solution, resistivity of solution decrease with increasing of temperature and this leads to allow more current to flow from the sacrificial anode (Magnesium) (that corrodes more rapidly)towards the carbon steel through the electrolyte .This electrical current which magnesium discharges is controlled by (ohm's law)that is: $I=E/R$ …………..(5) [9,10,12]

That the current resistance includes both the water path and the metal path, including any cable in the circuit, for most applications the metal resistance is so small compared to the water resistance that it can be ignored [13]

Figure (7) shows the influence of temperature on solution conductivity .It can be seen clearly that the conductivity increase with an increases the solution temperature [15, 21].

With an increasing in solution temperature the rate of chemical reaction

and solubility of some corrosion products increase, decreasing of gases solubility in the solution, therefore increasing the electrical conductivity of the electrolyte, that mean increasing in the current flow through the circuit.

Figure (8) shows the relation between the mixing speed and protection current density with different solution temperature .It can be seen that the protection current density increasing with increasing of mixing speed .With increaseing solution temperature from (25 to 65)^o C the protection current density increases as shown in Figure; for zero r.p.m (static conditions) the cathodic protection current density increase about (3 μ A/cm^2) per ^{o}C but with mixing speed increase 10 μA/cm^2 per ^{o}C was found. These results mean that the effect of mixing speed is better than the effect of temperature on the cathodic protection current density.

Figure (9) reveals approximately to linear relation between the potential supply by magnesium anode and different temperature of the solution from (25-65) ^{o}C shifts the potential to more negative value .Temperature rise increases the rate of almost all-chemical reactions .For most metals (magnesium anode) a rapid rise of corrosion rate with increasing temperature was observed. Generally an increase in temperature of corroding environments increases the rate of chemical reaction , decreases the solubility of gases in solution This is due to the increasing of the rate of reaction on magnesium surface which also increasing the decay of magnesium metal [17-22].

4. **Conclusion**

Carbon steel pipe immersed in 3.5 %sodium chloride solution at (25° C), it will be under the risk of corrosion. It can be prevent corrosion of carbon steel in 3.5% Nacl solution by sacrificial anode cathodic protection system, connected it with a sacrificial anode such as (magnesium).Cathodic protection current density increases with increasing the

solution temperature. A large increase happened to protection current density with the increase in mixing speed. The effect of mixing action on cathodic protection current density is more sensible than the effect of temperature solution .An increasing in temperature shifts the potential supplies by the magnesium anode to more negative values indicating a decreased the resistance of the solution.

References
[1] Mars G. Fontana "Corrosion engineering", 3rd edition McGraw-HILL, (1986).
[2]H.H. Uhlig .and R. Winston "Corrosion and corrosion control" John Wiley and sons', (1985).
[3] J. Liu, Y. Lin, X. Yong, and X. Li " Study of Cavitation Corrosion Behaviors and Mechanism of Carbon Steel in Neutral Sodium Chloride Aqueous Solution, Corrosion—Vol. 61, No. 11,(2007)1061-1068
[4] J.C. Scully, "The fundamentals of corrosion" 3rd edition, Pergamon, NY (1990).
[5] Deny A. Jones, "Principles and Prevention of Corrosion", 2nd edition, Prentic hall Ltd., 1996.
[6] Stansbury, E.E. and Buchanan, R.A., "Fundamentals of Electrochemical Corrosion", ASM International, (2000).
[7] Gretz, W.Z.and Bayer, G., "Cathodic Protection", Matoco Associates Inc, (2004).
[8] R. T. Kenneth and J. Canber "corrosion for scince and engineer" Longman ,1996.
[9] David Talbot, James Talbot "Corrosion Science and technology "CRC Press, (1998).
[10] S.S. Abd El- Rahim, S.A.M.Refay, F.Taha, M.B.Saleh, R.A.Ahmed, J.Appl.Electrochem. 31(2001) 429
[11] V. Ashworth "Corrosion industrial problems treatment, and control techniques"Pergmon Press, 1984.
[12] Deny A. Jones, "Principles and Prevention of Corrosion", 2nd edition, Prentic hall Ltd., 1996.

Eng. &Tech. Journal. Vol. 27, No. 8, 2009

Theoretical Aspects of some
Mechanical Properties of Composites

[13] Abdul Salam Hamdy, M.A. Shoeib1, A.G. Sa`eh2 and Y. Barakat" The Electrochemical Behavior of Mild Steel in Sulfide Polluted NaCl at Different Velocities" Int. J. Electrochem. Sci., 3 (2008) 1142 - 1148

[14] Alan A. Lou and bob R. Powell "tensile and compressive creep of Magnesium (PDF).Material and processes laboratory, G.M. R &Development Center, 2007

[15] William H.H. and Weichu, R., " Design of Cathodic Protection Systems for deep water Compliant Petroleum production rises", Final Report, (2005).

[16] H. T. Kiim ,C. H. Paik,B.W. Cho,K.S.Yun,Y.H.Kim,J.B.Ju,M.S.Kang and K.Y.Kim"Effect of dissolved oxygen and hydrogen ion on corrosion rate and passivation of carbon steel ,Journal of Ind.& Chemistry, Vol. 3,No.1,March 1997,51-55

[17] L.L. Shreir, R.A. Jarmon and G.T. Burstein "Corrosion metal/Environment and reaction" 3rd edition Plant Tree. (1998).

[18] Nestor Perez "Electrochemistry and corrosion science" K.A.P (2004).

[19] Peabody, A, W." control of pipe line corrosion, National Association of Corrosion Engineers, Houston TX. (1997).

[20] Nestor Perez "Electrochemistry and corrosion science" K.A.P (2004).

[21] L.L. Shreir, R.A. Jarmon and G.T. Burstein "Corrosion and corrosion control" 3rd edition PLANTA TREE. (1994).

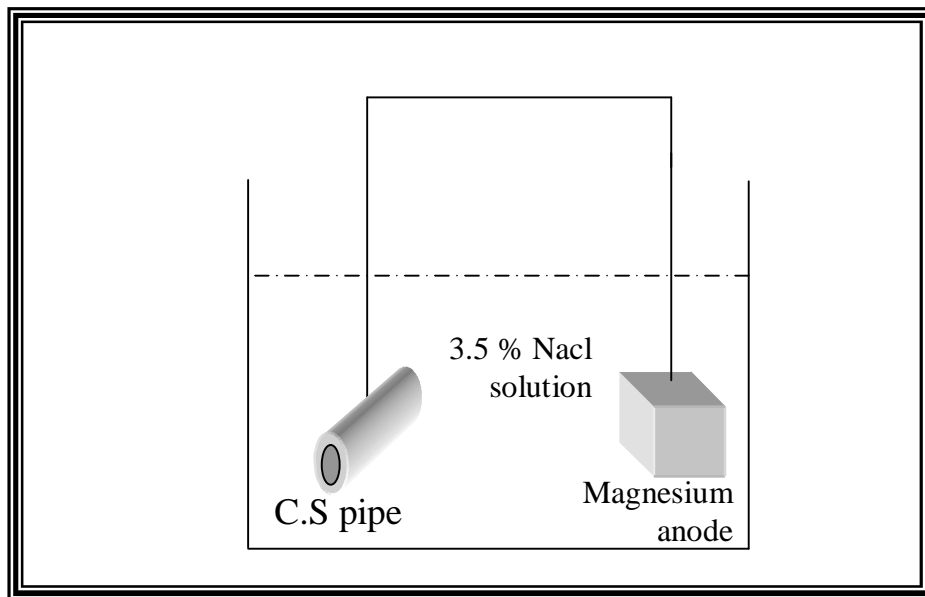[22] Stansbury, E.E. and Buchanan, R.A., "Fundamentals of Electrochemical Corrosion", ASM International, (2000).

Eng. &Tech. Journal. Vol. 27, No. 8, 2009

Theoretical Aspects of some
Mechanical Properties of Composites

Figure (1) Protection of immersed carbon steel pipe with a magnesium anode in 3.5%NaCl solution at temperature (25°C)
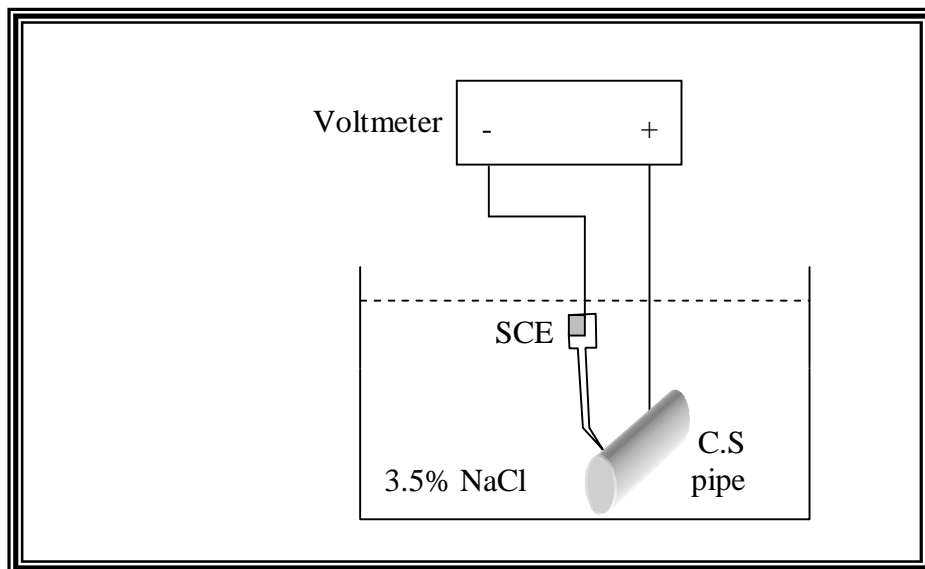

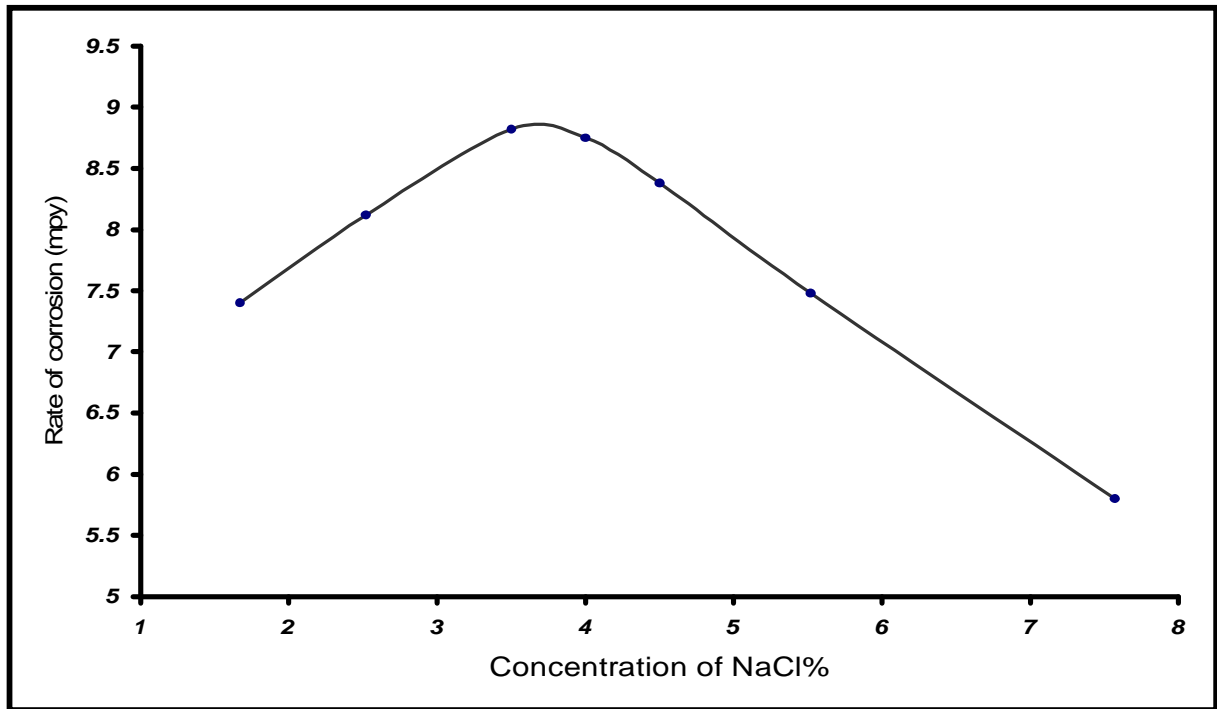**Figure (2) Measuring the open circuit potential for carbon steel pipe in 3.5% NaCl solution**

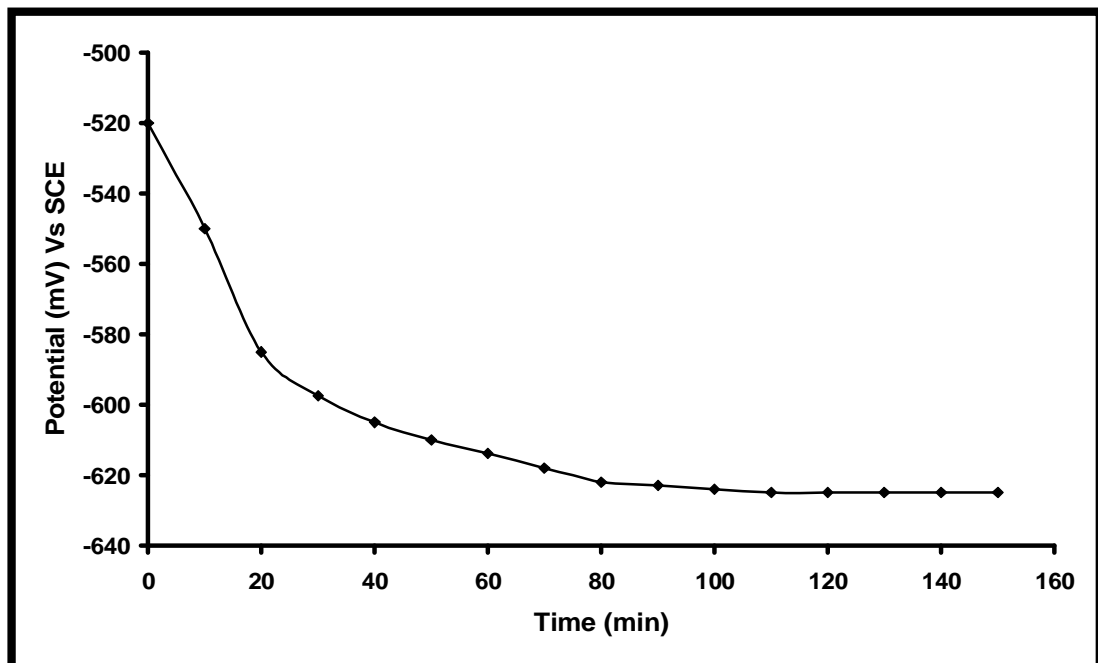**Figure (3) Effect of concentration of sodium chloride solution on corrosion rate of (CS) in 25° C**

Figure (4) Effect of time on open circuit potential for carbon steel in 3.5% NaCl solution

1649

Eng. &Tech. Journal. Vol. 27, No. 8, 2009

**Theoretical Aspects of some
Mechanical Properties of Composites**
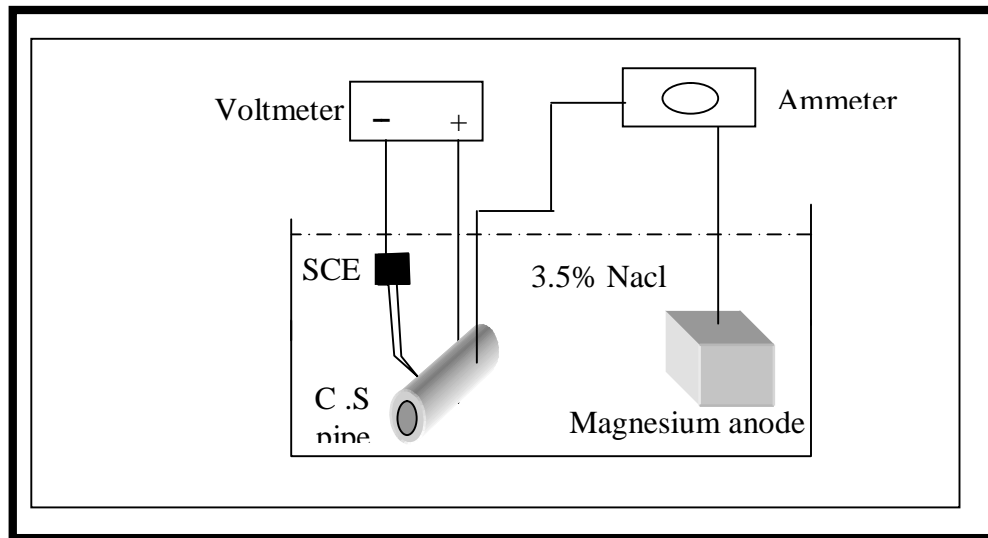
Figure (5) Protection of carbon steel pipe using magnesium anode
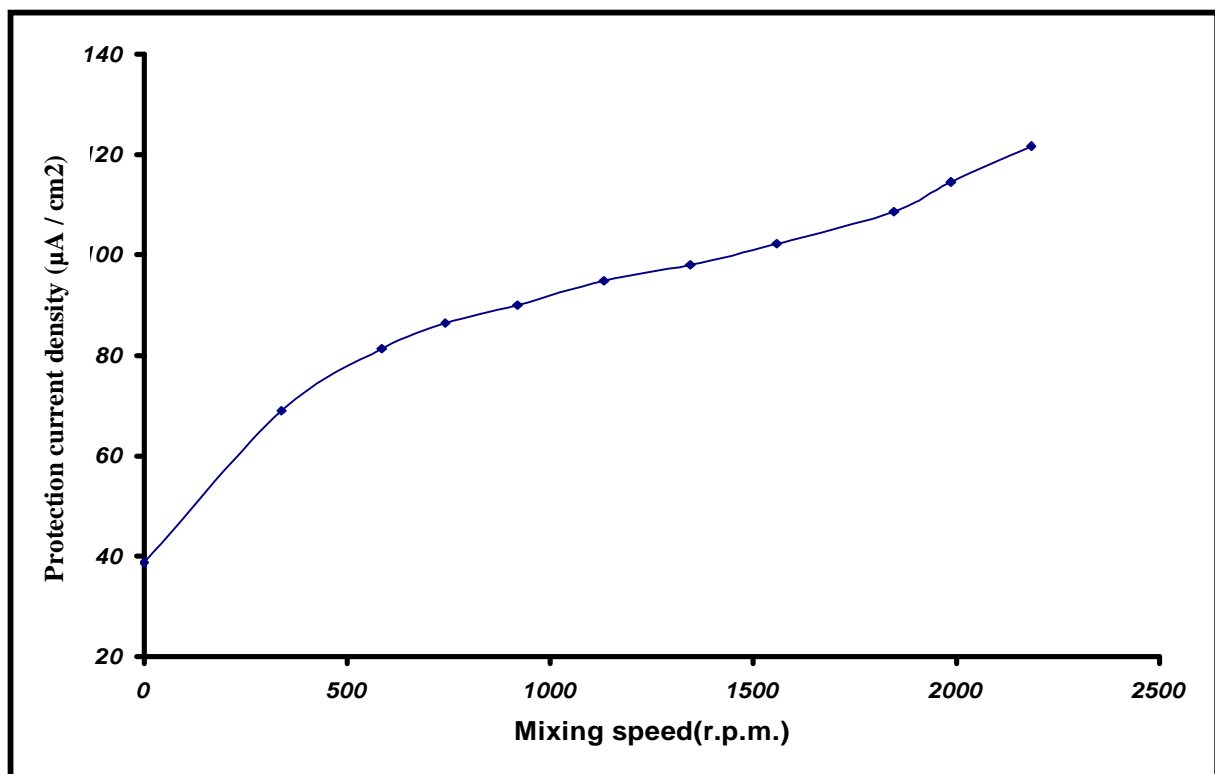
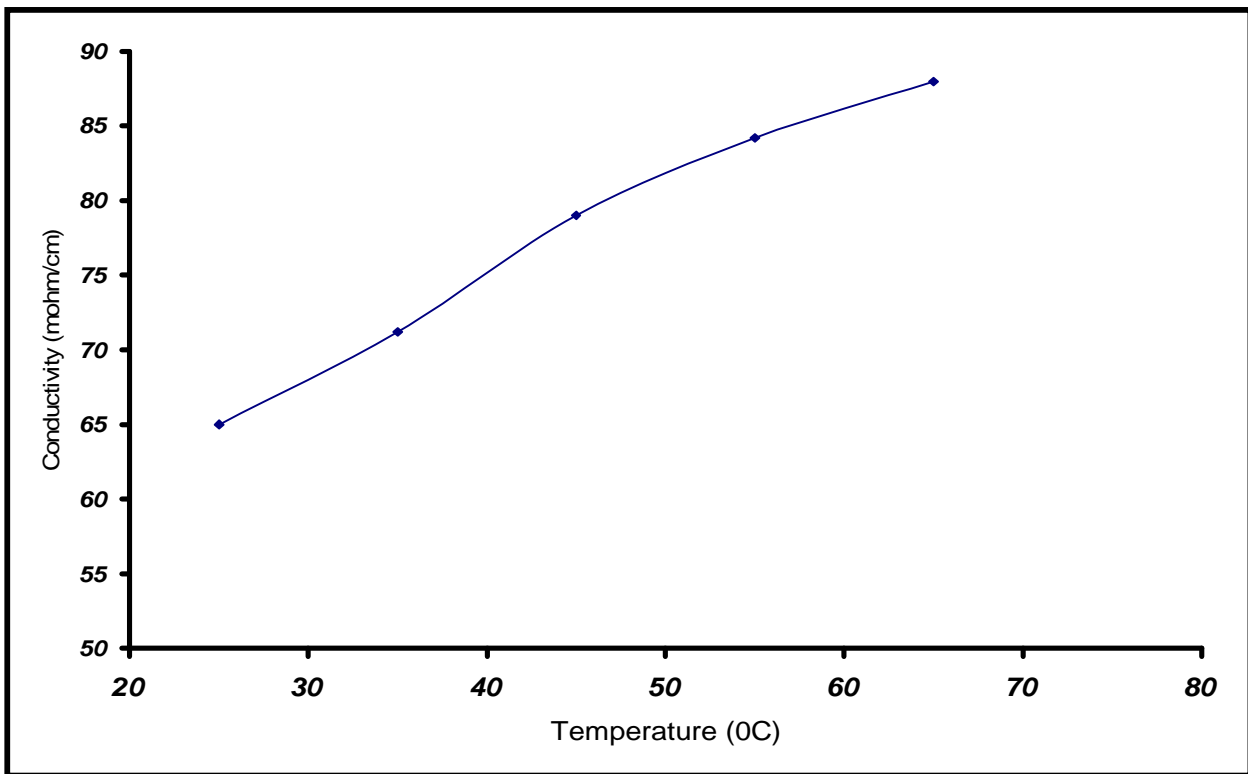**Figure (6) The relation between mixing speed and cathodic protection current density at (25^{0}C)**

Figure (7) Temperature effect on solution conductivity

Eng. &Tech. Journal. Vol. 27, No. 8, 2009

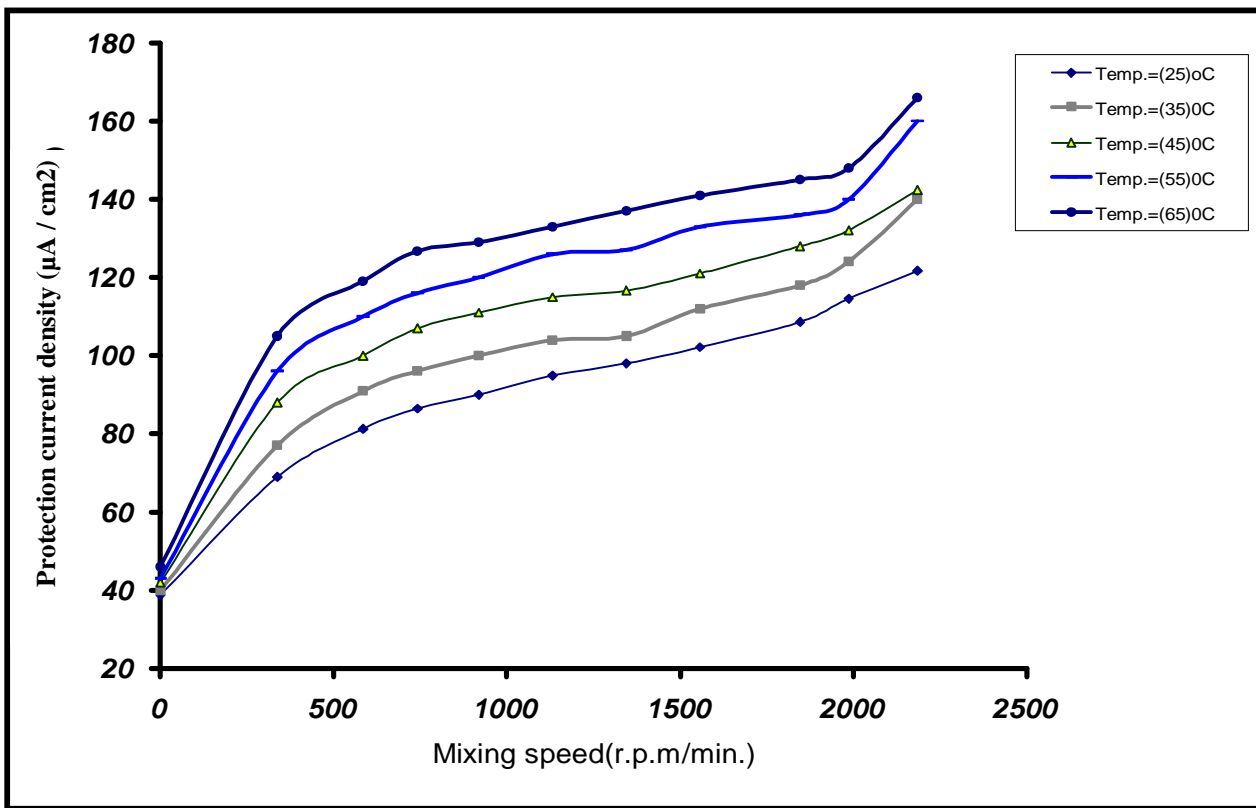**Theoretical Aspects of some
Mechanical Properties of Composites**

Figure (8) The relation between mixing speed and protection current density at different temperatures
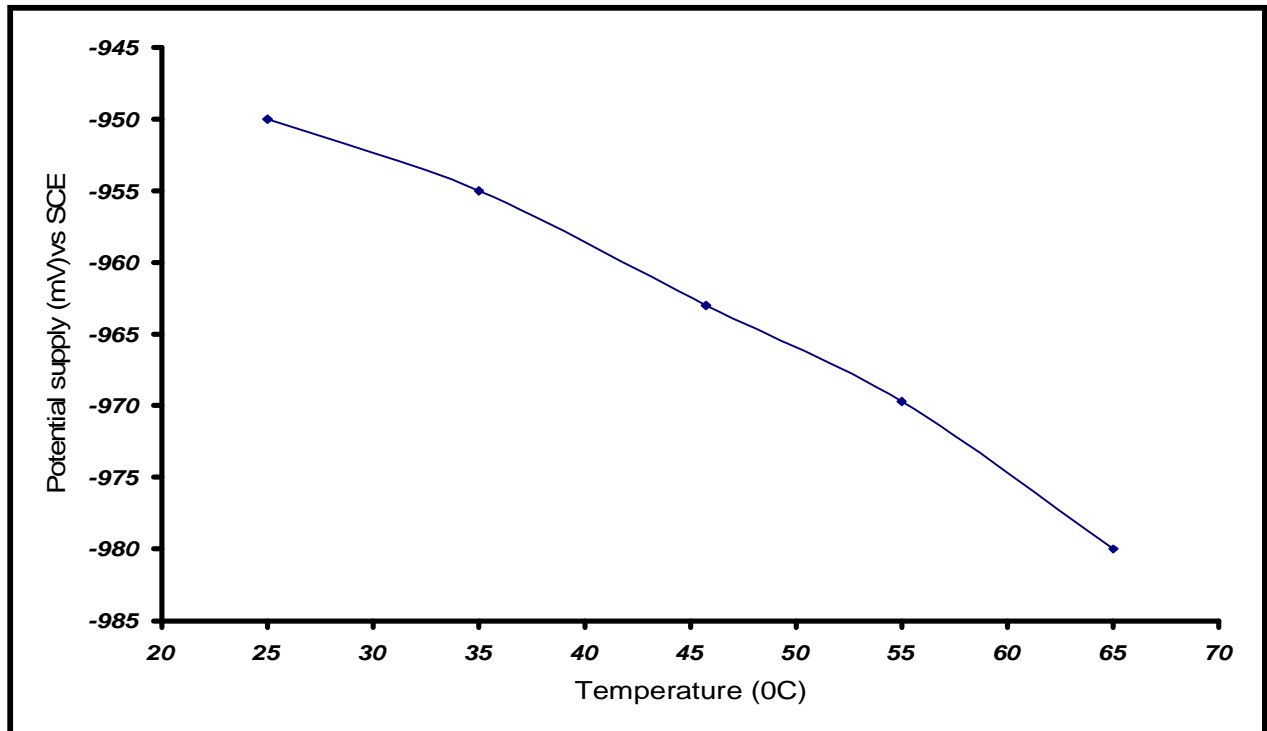
Figure (9) The relation between temperature and the potential supply by magnesium anode