Effects of H_2SO_4 and HCL Concentration on the Corrosion Resistance of Protected Low Carbon Steel

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Astract

Investigations were carried out to study the corrosion behavior of unprotected and protected low carbon steel using carburizing and hard chrome plating in different concentrations of H_2SO_4 and HCL solutions. Weight loss method was used for estimation the corrosion rate in the current study.

The results show that protected low carbon steels samples by hard chrome plating had better corrosion resistant (less corrosion rate) than unprotected and carburized low carbon steel samples. Also, the corrosion rate increases with increasing acid concentration from (1 to 5)M. for both types of acid used. The corrosion rate of low carbon steel in acid environments indicate that the hydrochloric acid solution was more corrosive media than that of sulphuric acid solution under the same conditions.

Keywords:Corrosion rate; Acid environments;Low Carbon Steel; weight loss method.

تأثير تركيز حامض الكبريتيك وحامض الهيدروكلوريك على مقاومة التآكل للصلب منخفض الكاربون المحمي

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الخلاصة

تم في هذا البحث دراسة سلوك تآكل الصلب منخفض الكاربون غير المحمي من التآكل والمحمي من التآكل باستخدام الكربنة والطلاء بالكروم في تراكيز مختلفة لمحلول حامض الكبريتيك ومحلول حامض الهيدروكلوريك. طريقة فقدان الوزن استخدمت لتقدير معدل التآكل في هذه الدراسة .

من النتائج التي تم الحصول عليها ، تبين ان نماذج الصلب منخفض الكاربون المحمي من التآكل بطلاء الكروم أعطت أفضل مقاومة للتآكل(اقل معدل تآكل) من نماذج الصلب غير المحمي ونماذج الصلب المحمي بالكربنة. كما ان معدل التآكل يزداد مع زيادة نسبة تركيز الحامض من (1 الى 5) مولالي لنوعي المحاليل الحامضية المستخدمة . وان نتائج معدل التآكل للصلب منخفض الكاربون في الأوساط الحامضية تبين بان محلول حامض الهيدروكلوريك كان وسطاً تآكلياً أكثر تأثيرا من محلول حامض الكبريتيك تحت نفس ظروف الاختبار.

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Introduction:

Corrosion is both costly and dangerous. Billions of dollars are spent annually for the replacement of corroded structures, machinery, and components. Premature failure of bridges or structures due to corrosion can also result in human injury, loss of life, and collateral damage. Taking all these factors into account, it becomes obvious why those persons involved with the design and/or maintenance of structures and equipments should have a basic understanding of the steel corrosion process [1]. Steel is one of the major construction materials, which is extensively used in chemical and allied industries for the handling of acid, alkali and salt solutions. Acid solutions are extensively used in industry, the most important applications are acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. The commonly used acids are hydrochloric acid, sulphuric acid, nitric acid, etc [1][2]. Hydrochloric and sulphuric acids are the most difficult of the common acids to handle from the standpoints of corrosion and materials constructions. Extreme care is required in the selection of materials to handle the acid by itself, even in relatively dilute concentrations or in process solutions containing appreciable amount of hydrochloric acid. These acids are very corrosive to most of the common metals and alloys. [3][4]. In carburizing, low-carbon steel acquires a high-carbon surface layer by heating in contact with carbonaceous materials. On quenching after carburizing, the high-carbon skin hardens, whereas the low-carbon core remains comparatively soft. The result is a highly wear-resistant exterior over a very tough interior. This material is particularly suitable for gears, cam-shafts, etc. [5]. Hard chrome plating is an electrolytic method of depositing chrome for engineering applications, from a chromic acid solution. Deposits can be applied from (0.25 – 1000) microns thickness for a wide range of applications. The thinner deposits being used to substantially increase the life of components in wear applications or corrosive environments, and the thicker deposits being used for salvage and repair of worn, damaged or mis-machined components. Hard Chrome has an extremely high resistance to atmospheric oxidation, and a good resistance to most oxidising and reducing agents, hence it is extensively used in the food and chemical industries [6].

Khadom Anees A.[4] studied the effect of temperature and acid concentration on the corrosion of low carbon steel in hydraulic acid media by using a nonlinear regression method. He observed that the corrosion rate increased with the increase of the temperature and hydraulic acid concentration.

Owate Osarolube, E. [7] studied the corrosion behavior of mild and high carbon steels in various acidic media, and found that the rate of metal dissolution increased with the increase of concentration of the corrosion media and exposure time. Also, the corrosion rates of high carbon steel in all the acidic media were higher than that of mild steel because of carbon contents.

Oluwole [8] studied the corrosion resistance of medium carbon steel (un-plated) , nickel- plated medium carbon steel , and 18/8 stainless steel samples in cassava fluid environment for thirty days by Wight loss method. The result showed little corrosion attack (corrosion rate) on the nickel-plated steel and very high corrosion attack on the un-plated steel .

The aim of the present work is to study the effect of H_2SO_4 & HCL solutions as a corrosive media with different concentrations on the corrosion rate of low carbon steel for the three cases; un-protected, carburized, and hard chrome plated samples.

Experimental Work

1. Materials:

The materials used are low carbon steel. The chemical analysis was carried out using (X-Ray method type X-MET-3000TX and ARC-MET-8000 method) in AL-Basrah electrical station/Iraq, and compared with the composition of the DIN standard.

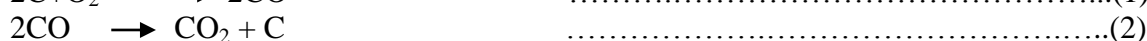Table -1- The chemical analysis of the used steel CK15

Element	AL-Basrah electrical station/Iraq	(DIN) standard.
C%	0.14	≤ 0.2
Si%	0.4	≤ 0.55
Mn%	0.38	≤ 1.5
P%	0.029	0.03
S%	0.03	0.05
Cr%	-	-
Mo%	-	-
Ni%	-	-
Cu%	-	-
V%	-	-
Fe%	Pure	Pure

2. Samples Preparation:

The samples were cut out in dimension of $(6\times1\times1)$ cm according to ASTM designation (G1-90) [4], critical preparations were used also by both chemical and mechanical means. The first portion of the preparation process which was used involves an abrasive surface treatment to remove any build up of material by used emery paper to remove the outer surface layer and roughen up the surface. The next portion involves more chemical means, this helps in dissolved contaminants that reach the surface externally from the environment such as oils, dust and grease that usually came from prior processing or handling. The final portion involves washed the samples with running tap water followed by distilled water, dried with clean tissue, immersed in acetone, and kept in desiccators over silica gel bed until used.

3. Carburizing Process:

Solid carburizing process was used in this work . Involve a solid carbon – rich medium packed around the samples into heat treatment mild steel box, so that, the space of approximately 50 mm exists between the components. The lids of the box closed tightly and luted with fireclay. The box heated in Electrical Muflle furnace / Model: RKB-101 to the carburizing temperature (915) ^{o}C and maintained in this temperature for up to five hours according to the depth of case required. Carburizing process depends upon the presence of the gas carbon monoxide (CO) to carry carbon to the surface of the work pieces,

$$2C+O_2 \longrightarrow 2CO \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$
$$2CO \longrightarrow CO_2 + C \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

4. Heat Treatments After Carburizing:

After the component has been carburized, heat treatment will be necessary both to strengthen and toughen the core and to harden the surface[8]. The heat treatment was carried out in a muffle furnace, Hardening carburized low carbon steel samples at 200 ^{0}C /for one hour, after water quenching was used in furnace to 840 ^{0}C /for 30 second.

5. **Hard Chrome Plating Process:**

        The plating process used involves bonding chrome onto a surface through electrolytic means. The part is placed in a bath of a solution called an electrolyte at $(50\text{-}60)^o$C which is primarily 300 g/L chromic acid along with other additive like 3g/L sulfate (SO_4) which acts as catalysts and can affect coating post-plate. The plated low carbon steel sample is connected to the negative terminal of a power source (battery or rectifier) and acts as a cathode. An anode is attached to the positive side and is placed in the tank, the anode is lead based. As a current is run through the circuit, cations from the plating solution become positively charged and travel to the negatively charged cathode and bond. It provides electrons to reduce the positively charged ions to metallic form.

6.   **Corrosion Rate Measurements**:

        The metal samples were completely immersed in glasses vessel containing 100 mL solution of HCl and H_2SO_4 in different concentrations; 1, 3, and 5M. They were exposed for 2 hours period at room temperature, then the metal samples were cleaned, washed with running tap water followed by distill water, dried, then immersed in acetone, and dried again. The weight loss method was used to calculate the corrosion rate (C.R.) by the following relationship and according to ASTM designation(G31-72) [4] [9] [10][11].

$$\textbf{C.R.(mdd)} = \textbf{(2.4} \times \textbf{10}^6 \textbf{ W)} / \textbf{(A} \times \textbf{T)}$$ ………………….…………………….(3)

Where W, A and T are weight loss (g), area of the specimen (cm^2) and exposure time (hr.) respectively. The mdd is milligrams per square decimeter per day.

Results and Discussion

        The corrosion rate of unprotected low carbon steel samples and protected low carbon steel samples by carburizing and hard chrome plating with using HCL and H_2SO_4 solutions as a corrosive media with different concentrations(1,3 and 5 M.) for 2 hr. duration time are investigated , and summarized separately:

1. Corrosion behavior of unprotected and protected low carbon steel samples:

        Figure (1) and Fig.(2) show that protected low carbon steel samples by hard chrome plating are more resistant to corrosion (less corrosion rate) than unprotected and carburized low carbon steel samples
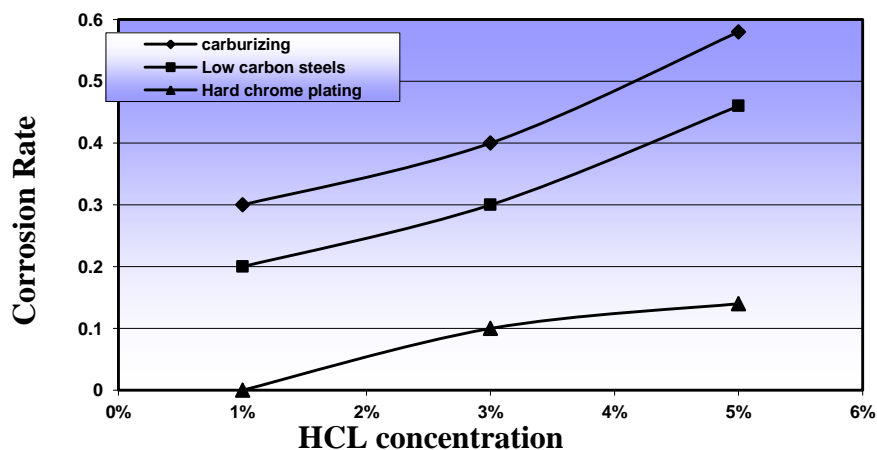

Fig.(1) : Corrosion behavior of unprotected and protected low carbon steel samples on HCL
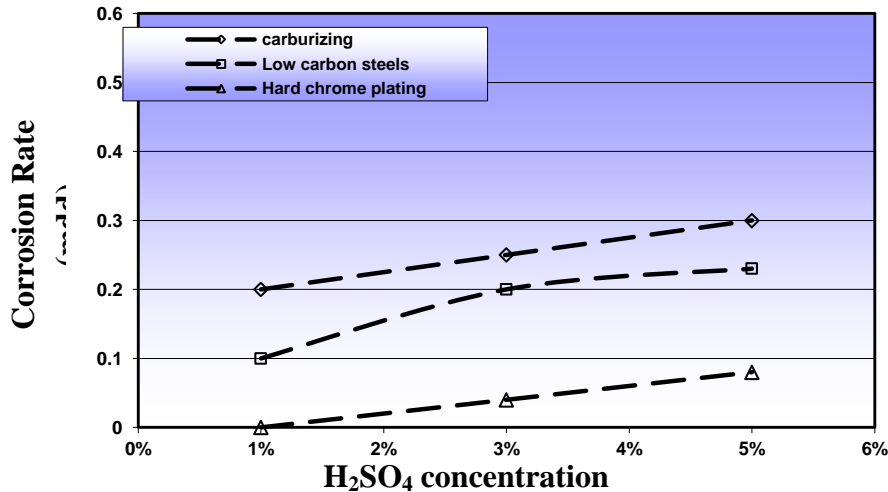
**Fig.(2): Corrosion behavior of unprotected and protected
low carbon steel samples on H₂SO₄**

Chromium, regardless of form or condition, has a natural ability to prevent corrosion. This is due to how it attracts oxygen and forms a protective oxide layer on its external boundary. The oxygen layer formed is Cr_2O_3. This process of passivation allows the chromium - oxygen layer to form on the outside of the chromium coating and prevents any other harmful agents, such as acids or more oxygen, from attacking the chromium metal or any underlying metal [9].

Also, the carbon rich surface layer in carburizing low carbon steel samples are higher than hard chrome plating and unprotected low carbon steel samples causes' high rate of corrosion, because of the corrosion rate increases with the increase of the carbon contents[11][12].

2. Effect of acid type (H₂SO₄ & HCL solutions) on the corrosion rate of samples:

Figures (3,4, and 5) show that the hydrochloric acid as a corrosive media is more effective solutions on the samples than sulphuric acid. This is an indication to the effect of chloride ions on the samples comparable with the sulphate ions($SO4^{-2}$). The chloride ions had more aggressive effect and responsible for pitting on the surface of metal than sulphate ion [13] .
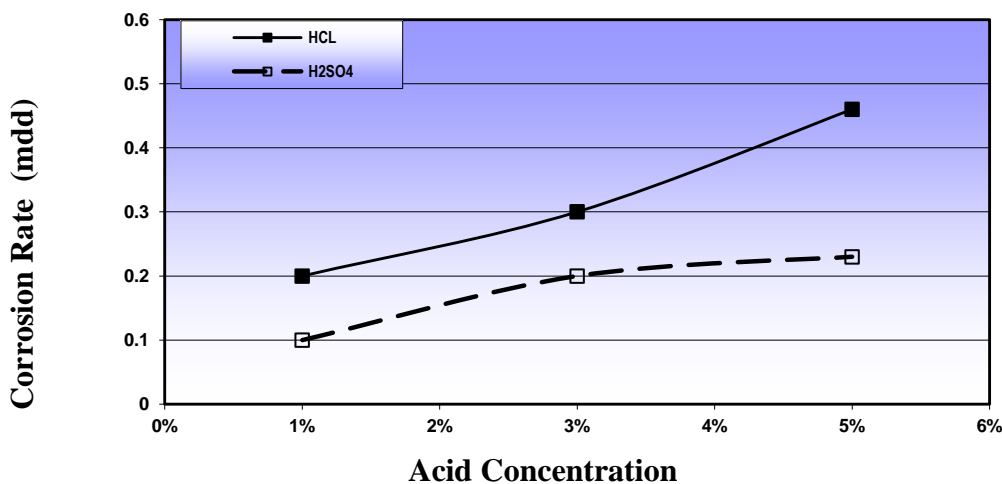

**Fig.(3) : Effect of H₂SO₄ & HCL solutions on the corrosion rate
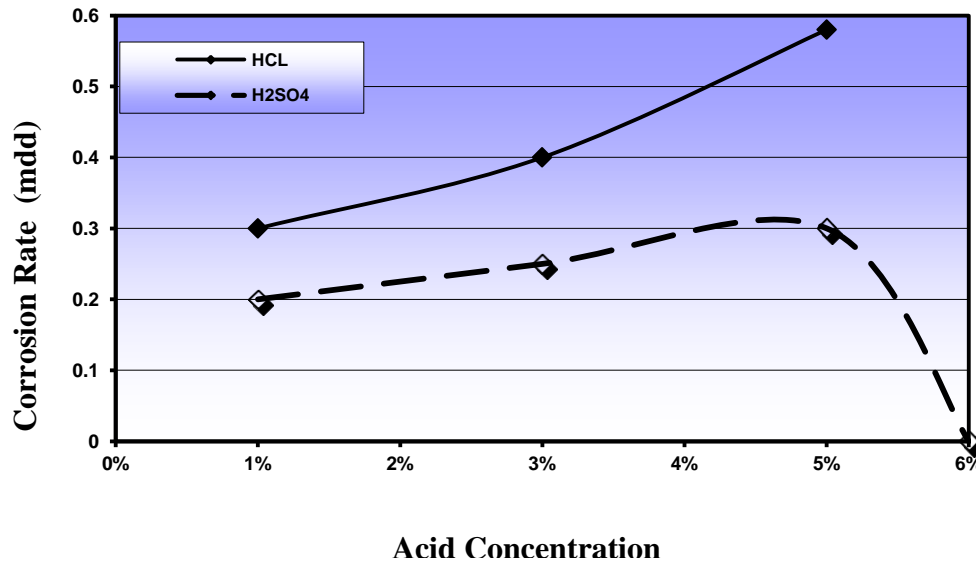of low carbon steel samples in different concentrations**

Acid Concentration

Fig.(4): : Effect of H$_2$SO$_4$ & HCL solutions on the corrosion rate of carburizing samples in different concentrations

3. Effect of acid concentrations on the corrosion rate of samples:

As the concentrations of a corrosive acid media (HCL and H$_2$SO$_4$ solutions) are increased, the corrosion rates are likewise increased, as show in Fig.(1) to Fig.(5). This is primarily due to the fact that the amounts of hydrogen ions, which are the active species, are increased; as acid concentration is increased [13]. The corrosion of metals in natural and acidic solution is cathodically controlled by the hydrogen evolution reaction. Corrosion rate data as a function of acid concentration can be used to show the rate dependence of acid concentration [4].

Figure (5), shows minimum corrosion rate at 1% of acid concentration for hard chrome plating sample, because of less effect of active species (hydrogen ions) at 1% of acid used (H$_2$SO$_4$ & HCL solutions) and ,on the other hand, the chromium - oxygen layer in hard chrome plating surface has natural ability to prevent corrosion and prevents any other harmful agents at these concentration
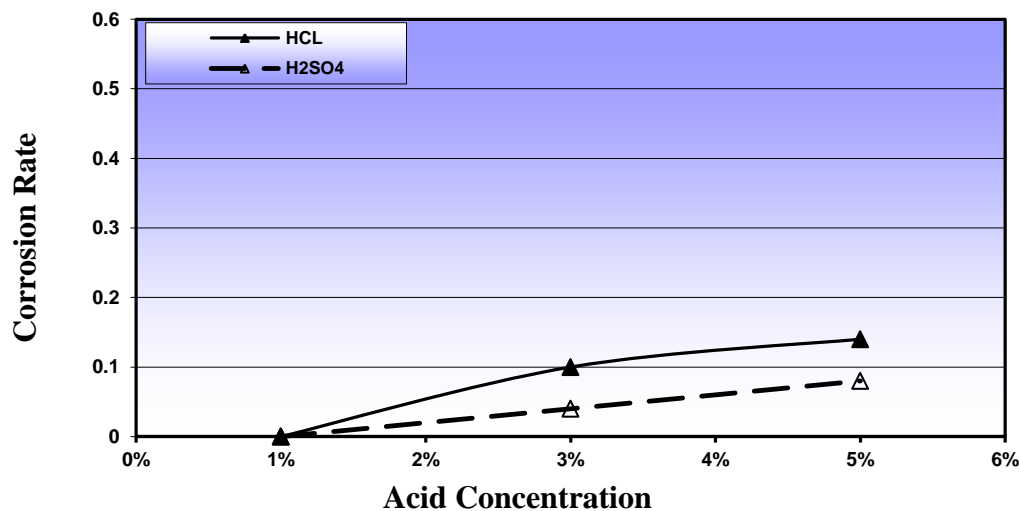
Fig.(5) : Effect of H$_2$SO$_4$ & HCL solutions on the corrosion rate of hard chrome plating samples in different concentrations

Conclusions

All the results can be concluded as follows:

1. Hard chrome plating samples are more resistant to corrosion (less corrosion rate) than unprotected and carburized low carbon steel samples.

2. The hydrochloric acid as a corrosive media is more effective solution on the carbon steel samples than the sulphuric acid.

3. The corrosion rate increases with increasing the concentration of a corrosive acid media (HCL and H_2SO_4 solutions).

References

[1] Schweitzer Philip A., "Fundamentals of Corrosion" , Taylor and Francis Group, LLC, United States of America, http://www.taylorandfrancis.com, (2010)

[2] Abdel Rehim Sayed S., Hazzazi Omar A. , and Amin Mohammed A. "The corrosion inhibition of low carbon steel in concentrated sulphuric acid solutions " , Corrosion Science Vol. 50 , pp (2258–2271), (2008)

[3] Nataraja S. E. , Venkatesha T. V. and Praveen B. M. "Corrosion inhibition of steel in acid media by S-Benzylthiuronium chloride" , Der Pharma Chemica , Vol. 3 , No. (1), USA, Pp (388-398), (2011)

[4] khadom Anees A. , Yaro Aprae S., "The effect of temperature and acid concentration on corrosion of low carbon steel in hydrochloric acid media", American journal for applied sciences ,Vol. 6, No.7,pp.(1403-1409),(2009).

[5] Myer Kutz , "Mechanical Engineers' Handbook," 2nd ed., John Wiley & Sons, Inc.,ISBN 0-471-13007-9 , (1998).

[6] Hard chrome Engineering, Pty Ltd ABN 97 005 291 083, ISO 9001 Lic. 2102Standards Australia, Victoria, Australia, www.hardchrome.com.au. (2007)

[7] Owate Osarolube, E., and Oforka, I. O." Corrosion behavior of mild and high carbon steels in various acidic media ",Scientific Research and Essay Vol.3 (6), pp. 224-228, June 2008

[8] Oluwole O.O., Atanda P.O. , and Odegbaju E., "Corrosion Behavior of 18/8 Stainless Steel and Nickel-Plated Low Carbon Steel in Cassava Fluid" , Journal of Minerals & Materials Characterization & Engineering, Vol. 8, No.10, pp.(803-811), 2009

[9] Leahey Matthew H."Replacement of hard chrome electroplating by tungsten carbide based high velocity oxygen fueled thermal spray" ,Msc. Dissertation. College of Engineering. Department of Mechanical Engineering , Rensselaer Polytechnic Institute Hartford CT December, pp(10-50), (2009)

[10] Malik, A.U., Mobin M., and Andijani, I. N.,"The effect of heavy metals ions on the localized Corrosion behavior of Steels ",saline water desalination research institute TR.3804/APP96010 , riyadh, Saudi Arabia march (2005).

[11] Winston R. , Uhlig's Corrosion Handbook, John Wiley & Sons, Inc., Canada, pp(100-125), (2000)

[12] ابراهيم. صبحي اسماعيل و عبدالله . ياسر عبدالوهاب "تأثير نسبة الكاربون على مقاومة التآكل للصلب الكاربوني في الاوساط المائية" ، مجلة هندسة الرافدين ،جامعة الموصل ،، المجلد 18 ، العدد 3، العراق ، ص،(25-37)،(2010).

[13] Singh V.B. and Ray Monali , "Effect of H_2SO_4 addition on the corrosion behaviour of AISI 304 austenitic stainless steel in methanol-HCl solution", Int. J. Electrochem. Sci.,Vol. 2 ,pp (329 – 340),(2007).