

## Study and optimize the corrosion inhibitor of sodium sulphate in water media at different conditions

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### Abstract

The objective of this research was to study and optimize the conditions of using sodium sulphate as a corrosion inhibitor in water media through estimating the corrosion rate with and without the inhibitor in re-circulated water pilot plant. In this work, three variable studies were the temperatures between 40 to 60 °C, inhibitor concentrations between 10 to 90 mg/l, and pH between 6.5 to 7.5. A mathematical model expressing the effects of variables on the corrosion was obtained by using SPSS program. The accuracy of mathematical model was very high and reached 97% comparing with the experimental results. The optimization by Lagrangian-multipliers was used to get the best condition to produce minimum corrosion for the specimens. The efficiency of inhibition of the inhibitor was 86%.

**Key words:** corrosion, sodium sulphate, inhibitor, corrosion efficiency, Lagrangian.

### Introduction

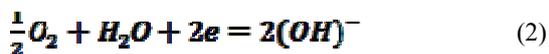
(Taha *et al.*, 2006). cited that the corrosion is an electrochemical process in which a metal in its element form returns to its native; it consists of an anodic reaction, a cathodic reaction, and transfer of electrons. There are many factors effecting on the rate of corrosion, these factors relating with the metal and the.

(Choi Dong-Jin, 2002 and DeWaard *et al.*, 2005). showed that the factors relating to the metal or alloy include position in the emf series, structure, contact with dissimilar metals and the presence of internal stresses originated from fabrication procedures. On the other hand, factors relating to the environment include; humidity, impurities in the atmospheric, rate of supply and distribution of oxygen, rate of flow of liquid and the presence of external stresses

The mechanism of corrosion can be expressed by the following reactions; at the anodic area anodic reaction occurs and produced ion.



On the other hand, a cathodic reaction takes place consuming electrons released in the anodic reaction.



(Smith and Kenneth, 1975 and Awadh and Turgoose, 2002) showed that both reactions must take place or occur simultaneously and at the same time on the metal surface. The solution on the cathodic area shows an increase in PH. The hydroxyl ions and ferrous ions diffuse away and where they meet ferrous hydroxide will be precipitated by adding equations (1) and (2) gives equation (3).



The ferrous hydroxide is oxidized further to a partially hydrated ferric oxide (which is the familiar of brown rust).



There are many factors effecting on the corrosion like environmental temperature, PH,

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dissolved salts , and types of inhibitor used for reducing the corrosion rate .

(Martinez, 2003 and John, 1984). suggested that like most chemical reaction, the corrosion of iron and steel in aqueous solution change with change the temperature.

Previous studies reported that the effect of temperature on the corrosion of metal and alloys which were exposed to portable waters increasing with increasing temperature.

(Edwards *et al.*, 1994; Rippon, 2001 and DeWaard *et al.*, 1991). studied the influence of PH on the rate of corrosion of metal is not constant in recirculation system, In acid solution, iron dissolves freely with evolution of hydrogen. Within the PH range between 4 and 9 the rate of corrosion is slightly changed. Out the pH range between 4 and 9, the rate of change decrease with increase PH below this range while the rate of change increase with increase PH.

(Obot and Obe-Egbedi, 2008 and DeWaard, 1991). defined the inhibitor as chemical substance when it added in small concentration to an environment decreases or prevents the reaction of the metal with the environment. Corrosion inhibitor are added to many system including; cooling systems ,refinery unit , pipelines, and steam generator.

(John *et al.*, 1984). Inhibitors fall into several classes as (passivators, vapor phase, cathodic , anodic, naturalizing, organic and inorganic inhibitors). Inorganic chemicals are certainly useful for controlling corrosion.

(Refaey *et al.*, 2006 and Landold, 2007). The corrosion testing methods classified as; corrosion test method with full scale plant equipment exposed to the corroding medium, corrosion test method with pilot –scale equipment ,laboratory test on sample exposed to actual plant liquid or simulated environment, electrical–resistance method, and linear polarization-resistance.

**Experimental Part**

**Experimental Arrangement and procedure**

The inhibition efficiency of reducing corrosion rate of the specimens was studied by using weight loss method utilizing the pilot plant cooling tower system. The corrosion rate was calculated with and without inhibitor for

comparing the changes in results. The corrosion rate was calculated at different temperatures, inhibitor concentration, and PH.

| Temp.<br>(°C) | Sodium Sulphate<br>Na <sub>2</sub> SO <sub>4</sub> |                    |                    |                    |                    |
|---------------|--|--------------------|--------------------|--------------------|--------------------|
|               | PH=7.5   |                    | PH=7               |                    | PH=6.5             |
|               | Inhibitor concentration(mg/l)                      |                    |                    |                    |                    |
|               | 10   | 30                 | 50                 | 70                 | 90                 |
| 40            | Test <sub>1</sub>                                  | Test <sub>2</sub>  | Test <sub>3</sub>  | Test <sub>4</sub>  | Test <sub>5</sub>  |
| 45            | Test <sub>6</sub>                                  | Test <sub>7</sub>  | Test <sub>8</sub>  | Test <sub>9</sub>  | Test <sub>10</sub> |
| 50            | Test <sub>11</sub>                                 | Test <sub>12</sub> | Test <sub>13</sub> | Test <sub>14</sub> | Test <sub>15</sub> |
| 55            | Test <sub>16</sub>                                 | Test <sub>17</sub> | Test <sub>18</sub> | Test <sub>19</sub> | Test <sub>20</sub> |
| 60            | Test <sub>21</sub>                                 | Test <sub>22</sub> | Test <sub>23</sub> | Test <sub>24</sub> | Test <sub>25</sub> |

**Table (1):** The experimental design of this research this experimental repeated for each PH (6.5,7,and 7.5).

**Composition of specimen’s metal**

The steel was used as specimen for testing corrosion on it, which had the following compositions shown in table (2);

|          |                 |
|----------|-----------------|
| Carbon   | C <0.006%       |
| Silicon  | Si 0.366%       |
| Nickel   | Ni 11.15%       |
| Copper   | Cu 0.342%       |
| Chromium | Cr 17.18%       |
| Fe       | Remaining wt. % |

**Table (2):**Composition of the steel (specimens)

The specimens used had the following dimensions 103 mm long, 13 mm width, with a hole of a 7 mm diameter with its center about 8 mm from one end of the specimens. The specimens were degreased with an benzene and acetone; then annealed in a vacuum furnace at 600 Co for 1 hour .The furnace was switched off and allowed to be cooled to room temperature. The procedure was done for removing mechanical stresses. Finally, the specimens were stored in desiccators, which contain silica gel.

The specimens were abraded with emery paper: 200, 320, 400, and 600, under running top water, then immersed with a piece of cotton, dried by a tissue paper.

**Composition of the test water**

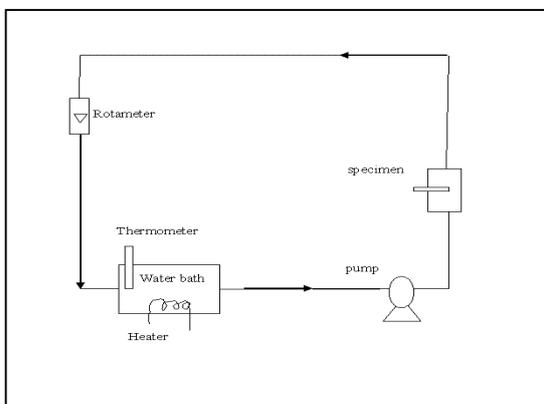
Table (3) shows the composition of the test water. The composition of water done in the laboratory of AL-Mustansiriya University College of Engineering Environmental Eng. Dept.

| Specification         | Sodium | Chloride | Sulfate | Total hardness | Total dissolved salt |
|-----------------------|--------|----------|---------|----------------|----------------------|
| Water analysis (mg/l) | 36     | 0.8      | 201     | 120            | 1530                 |

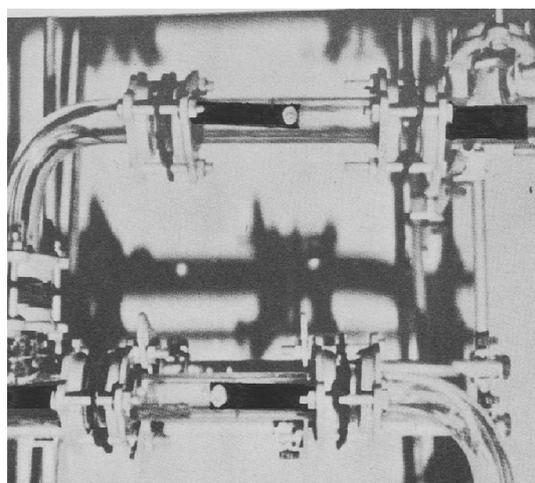
**Table (3):** Composition of water analysis

The used system was a open recirculation water flow, figure (1) showing the main components of this system. The main components were rotameter (used for measuring and controlling water flow rate), thermometers (a mercury in glass thermometers to get the temperature in the system), water bath (with heater) for controlling water temperature, pump, and specimens.

The positions of specimens in the system were shown in figure (1) and in figure (2). The testing zone consisted of three-tubes that were connecting with each other. The prepared and weight specimens attached to the holders (for added protection the specimens were attached to the holders using plastic nuts and bolts), the specimens assemblies were installed in the center of the pipe (figure, 2).



**Fig.(1):**Corrosion testing system



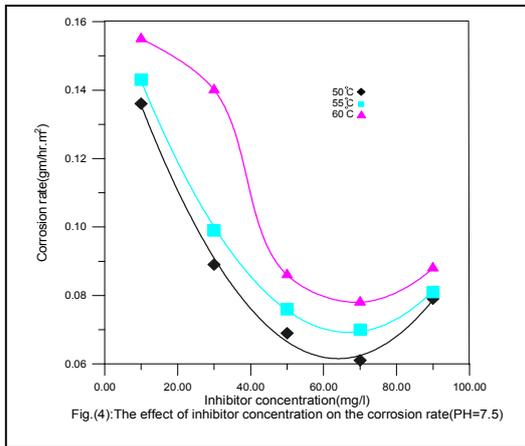
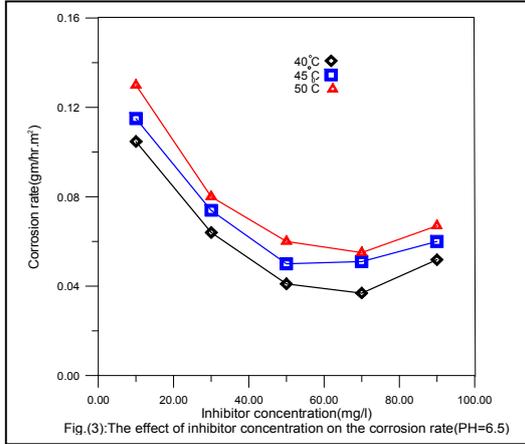
**Fig.(2):**Corrosion testing section(place of putting specimens in the system)

After each test, the specimens were washed with running tap water, drying with piece of cotton to remove corrosion products, washed with distilled water, dried by cotton again, rain with acetone, drying, and then weighed accurately to the forth decimal.

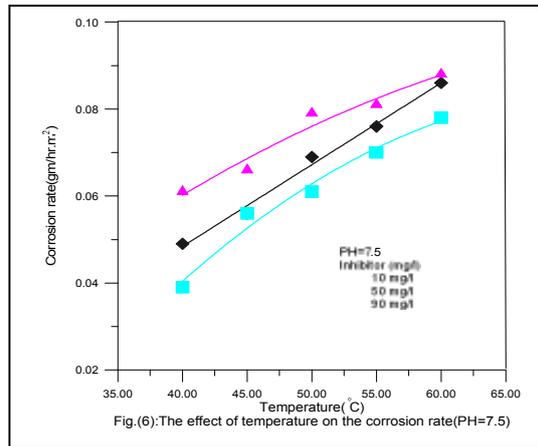
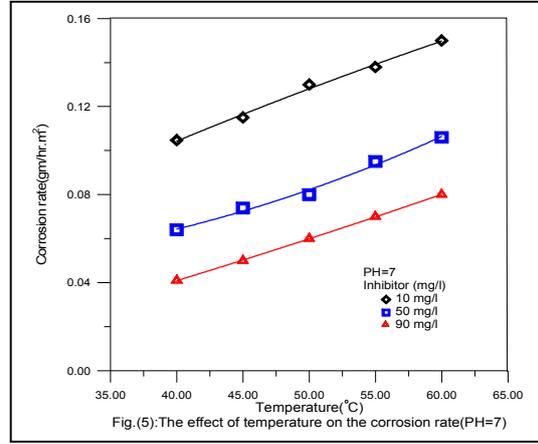
**Results and Discussion**

The effect of inhibitor concentration of sodium sulphate on the corrosion rate was shown in figures (3) and (4). Examination of these figures indicated that at a given temperatures, and PH, the corrosion rate decreased with the increase of the inhibitor concentration between 10 to 70 mg/l then it

started to increase slightly between 70 to 90 mg/l.

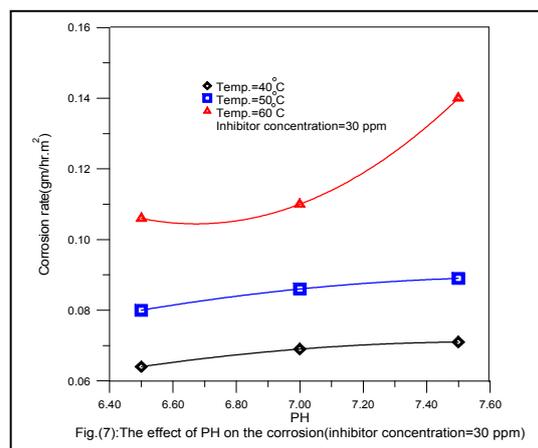


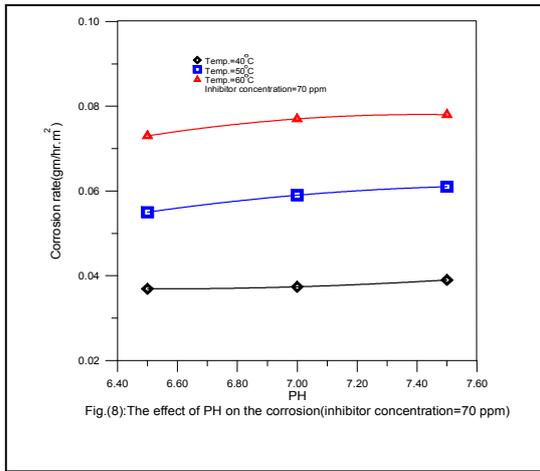
figures one can see that the decrease in corrosion rate was due to the influence of oxygen reduction at the cathode.



Examination of the figures (5) and (6) shows the variation of corrosion rate with the temperatures, it can be seen that the corrosion increases as the temperature increases, which is consistent with Arrhenius equation ( $corrosion\ rate = Ke^{\frac{-E}{RT}}$ ). Examining this figures one can see that the increase in corrosion rate was due to increase of diffusion rate of oxygen to the cathode sites on the metal surface. From the result, the results show that the maximum inhibition was at temperature 40 C<sup>0</sup> and PH=7.

The effect of PH on the corrosion rate was shown from figures (7) and (8). Examine these figures one can see that at a given temperature (45 ,and 50 C<sup>0</sup>),the corrosion rate decreased mildly with increase PH . Examining this

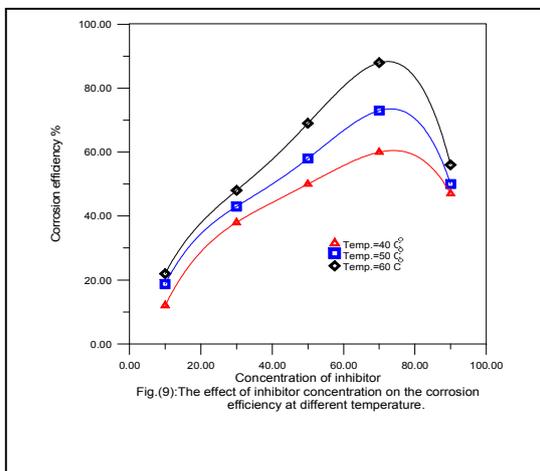




Corrosion inhibitor efficiency was calculated in terms of inhibited corrosion rate and uninhibited corrosion rate as shown in equation (5).

$$\text{Corrosion efficiency}\% = \frac{\text{corrosion rate}_{un} - \text{corrosion rate}_{in}}{\text{corrosion rate}_{un}} \quad (5)$$

Examination of figure (9) indicated that the inhibition efficiency increased with decrease temperature through all inhibitor efficiency and the maximum efficiency was at 86% at temperature 40 C°.



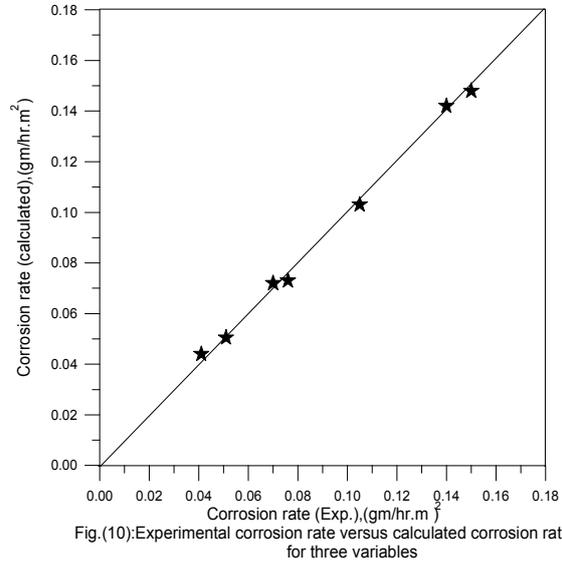
### Optimization and conclusions

The corrosion in this study was a function of three factors included in equation (6) where it described the behavior of the behavior process, which had been studied.

$$Y = 4.523 - 3.2297X_1^{0.034} - 1.761X_2^{0.034} + 0.508X_3^{0.711} \quad (6)$$

The error between the theoretical corrosion rate (calculated from equation (6)

and the experimental corrosion rate was 3%, and this could be seen in figure (10).



The results obtained by equation (6) gave error of 3% , it was due to many factors such as the presence of corrosion products in corrosive solution, dissolved solids which might cause erosion of the metal specimens, and the non uniformity of the metal shape.

To find the best conditions (temperature, inhibitor concentration, and PH) giving the minimum corrosion rate for the specimen, a method for optimization called Lagrangian-Multipliers was used for equation (6). The obtained conditions that resulted in minimum corrosion rate were as follows the temperature equal to 40 °C, the inhibitor concentration 67 mg/l, and the PH equal to 6.5. This results obtained from the process of optimization can be seen and notice in figures (3), (4), (5), and (6).

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#### Nomenclature

- $K$  Reaction rate constant
- E Activation energy (kcal/mol)
- R Gas constant (1.985 cal/mol.K)
- Y Corrosion rate (gm/hr.m<sup>2</sup>)
- X<sub>1</sub> Temperature (°C)
- X<sub>2</sub> Inhibitor concentration (mg/l)
- X<sub>3</sub> PH

الملخص العربي

### دراسة و احتساب الاختيار الأمثل كبريتات الصوديوم كمانع تاكل في الوسط المائي عند ظروف مختلفة

#### الخلاصة

يعنى البحث بدراسة كفاءة استعمال كبريتات الصوديوم كمانع تاكل بالوسط المائي من خلال حساب معدل التاكل بوجود و بدون وجود مانع تاكل ضمن منظومة ريادية يتم تدوير الماء و السيطرة فيها على درجات الحرارة و pH وتركيز مانع التاكل . تم احتساب معدل التاكل عند تراكيز مختلفة لمانع التاكل تراوحت بين ( 10 - 90 mg/l ) ودرجات حرارة تراوحت بين (40-60 °C) و pH تراوحت بين (5.6-5.7). تم إيجاد موديل رياضي باستخدام برنامج خاص (SPSS) لحساب معدل التاكل رياضيا" و تم مقارنة النتائج العملية مع النتائج النظرية حيث وجد تطابق بين النتائج يصل ال 97%. تم كذلك في هذا البحث دراسة الاختيار الأمثل (optimization) للعملية بطريقة Lagrangian-multipliers وتم من خلالها الحصول على أفضل الظروف التي تعطي أقل و أفضل معدل تاكل للعينة المعدنية قيد الدراسة. لقد وجد أن كفاءة منع التاكل لمادة مانع التاكل تصل الى 86%