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The Effect of Adding Carboxymethyl Cellulose and Zinc Sulfate on the Corrosion Characteristics of the Drilling Fluid

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Abstract

Drilling solutions can be considered as an intricate mixture comprising of number of chemical additives which aid specific needs such as controlling the rheological properties and reducing corrosion. Inhibitors are substances that are added in small concentrations to corrosive environment to decrease the corrosion. Their applications can be found in drilling equipments. The effect of adding Zinc Sulphate and Carboxymethyl Cellulose to study their influence on the corrosion of carbon steel in Bentonite mud has been evaluated using Weight Loss Technique. This study focuses on determining rheological properties and corrosion characteristics. Results show CMC and $ZnSO_4$ work as inhibitors when added to the Bentonite with inhibition efficiency was approximately equal to 50%.

Keywords: *Bentonite Mud, Corrosion, Carboxymetyl Cellulose, Carbon Steel, Zinc Sulfate.*

1. Introduction

The term corrosion is linked to the degradation of a metal owing to its reaction with surrounding aggressive environment. Metal dilapidation is implied by declining of physical properties of the metal. This process either involves losing weight, cracking or stress corrosion. The corrosion process costs billions of dollars to the manufacturing every year, however some can be avoidable. The corrosion of oil and gas drilling tools is a common phenomenon where drilling fluid is widely applied and may cause severe deterioration to these tools. In addition, the presence of dissolved gasses (such as O_2, H_2S and Cl_2) in drilling fluids may worsen the problem and damagingly affect the trustworthiness of drilling equipment. Other parameters including: the flow rate, acidity, temperature and mud composition may give to drilling equipment corrosion [1,2].

Usually, conventional protection practices (such as coating, deactivating environment, using inhibitors, and mud de-aeration techniques) have been generally applied for the deterrence of corrosion. However, the protection process is also possible expanded by adjusting the properties of the mud to decrease corrosion rates. Thus, it averts the metal deterioration by forming a protective layer on the surface of the metal as a passivation. Corrosion inhibitors such as organic compounds that containing atoms like oxygen, nitrogen, phosphorus, have been used to control the metals from corrosion for a long time [3-10].

Carboxymethyl Cellulose (CMC) is one of the most important additives to drilling mud. It is considered as a water soluble polymer with many practical advantages. CMC solution has good properties of thickening, adhering, emulsifying, and stabilizing membrane forming, moisture-holding, shape-holding, and dispersing. In addition, this important additive has been used as corrosion inhibitor for medium steel in various destructive environments [11-13]. Moreover, the application of many other polymers in corrosion controlling of metals and alloys in various aqueous environment have also been investigated by various researchers [14-17].

Furthermore, it has also been shown that $ZnSO_4$ as a soluble material may inhibit the corrosion of steel in salted solution fluid flow environment. $ZnSO_4$ had relatively low efficiency in stagnant conditions but its influence improved significantly under hydrodynamic conditions. It is mainly attributed to an increase in Zn^{2+} ions mass transport towards electrode surface. This leads to the formation of more protective films and therefore, enhances the protection against corrosion [18-23]. Finally it is worth mentioning that literature revealed that effective used concentration of $ZnSO_4$ should be between 0.1 to 0.5 lb/bbl[20].

The objective of this work can be put as following:

(i) examining the effects of some of the common additives added to the drilling mud on its rheological properties. This is important to select the right concentrations for the next study.

(ii) investigating the corrosion characterization of CMC and $ZnSO_4$ and its contribution towards weight loss of carbon steel coupons in a static condition.

(iii) comparing finding to other studies.

The choice of this research is limited to water based muds and only at room temperature.

2. Material and Methods

Four different types of mud were made: the base *Bentonite mud*, *Bentonite+CMC* mud, *Bentonite+*$ZnSO_4$ mud and *Bentonite+CMC+*$ZnSO_4$ mud. The base mud sample was prepared using commercial Iraqi bentonite supplied by the South Oil company, containing only water and bentonite clay. The first set of experiment was done to measure and record the Rheological properties using different concentrations of bentonite (mass fraction between 0-10%). Then the concentration of bentonite was fixed at an optimum of 20 g with 300 ml of water to attain a bentonite weight fraction of 6 % and a bentonite-to-water ratio of 8%. The bentonite-to-water ratio was maintained constant for all subsequent mud samples used in this work. Other mud samples with CMC and $ZnSO_4$ additives were arranged and their Rheological properties were also determined and their effects on carbon steel corrosion were monitored. All measurements were carried out at room temperature of 290K (see figure 1 & 2).

The test specimens used for this work were medium carbon steel coupons obtained from the local market. The coupons were of uniform dimension (25 mm diameter and 3 mm thickness with surface area of 1217 mm^2 and volume of 1472 mm^3). We have made sure that all the surface area was immersed in the mud sample during the experiments. The chemical composition of the chemicals used as supplied by the manufacturer. The initial weights of the coupons were taken to the nearest 0.0001 g on a digital electronic weighing balance (KERN ABS, German made), then immersed in 15% HCl to remove any rust products, degreased and dried in acetone and finally rinsed with de-ionized water before total immersion in the different storage containers containing the mud samples. The procedure of using 15 % HCl had only been done at the first stage of preparing the testing coupons, well ahead only acetone and water were enough to remove any rust formed from the uniform corrosion as will be seen later. Corrosion rates of the coupons were monitored by weight loss technique. The weight loss of each of the coupons was determined at intervals between 24 hours to 400 hours. After that, the coupon was taken from each container and washed with acetone and de-ionized water. They were then dried and weighted to get the new mass. The weight loss within the immersion period was determined as the difference between the initial weight prior to immersion and final weight after immersion, and the corresponding corrosion rate calculated using appropriate equation. The coupons were visually examined progressively with the aim of identifying the nature of the oxide scales clinging to the surfaces of the specimens and the type of corrosion occurring.

Diagnostic tests were carried out in the laboratories of the department of Petroleum Technology/University of Technology using the standard drilling labs equipments such as mud balance (OFITE), the rotational viscometer (OFITE Model 900), Hamilton Beach Mixer, pH-meter and Ultrasonic Bath. The value of pH was measured at the beginning of each run and was found to be fixed at approximately 8. This procedure was done for all experimental samples to reduce its effect on the corrosion during our work. Figure 1 shows some of the equipment and materials that were used in this work.

Both XRD-6100/7000 X-ray Diffractometer and XRF-1800 Sequential X-ray Fluorescence Spectrometer (Geological Survey/Central Laboratory Department) were used to analyze the bentonite clay and the medium Carbon steel, as shown in tables 1 & 2. It has been revealed that the main constituent of this commercial bentonite is montmorillonite and Quartiz. Medium carbon steel typically has a carbon of 0.38% and a manganese content of 0.4%. This product is stronger than low carbon steel, and it is more difficult to form, weld and cut. Medium carbon steels are quite often hardened and tempered using heat treatment.

Table 1,
Composition of the Iraqi bentonite clay used in this study.

Const.	SiO_2	Al_2O_3	CaO	Na_2O	MgO	K_2O
Weight	64.97	12.59	1.03	2.75	2.49	1.12

Table 2,
Composition of Carbon steel coupons used in this study.

Const.	C	Si	Mn	P	S	Fe	
Weight	0.38	0.14	0.4	0.03	0.02	98.98	0.01

The carbon steel investigated in this work was found to undergo uniform corrosion in all the experiments. Thus the corrosion rates were calculated using the following standard expression [24]:

$$CR\ (mpy) = \frac{W(g)\ 3.45 \times 10^7}{\rho(g/cm^3)\ A(cm^2)\ \ t(hrs)}$$

Where:

CR is the corrosion rate (mile per year),
W is the weight loss (g),
A is the coupon area (cm^2),
ρ is the coupon metal density (g/cm^3),
t is the contact time in the corrosive environment (h),
and 3.45×10^7 is a conversion factor.

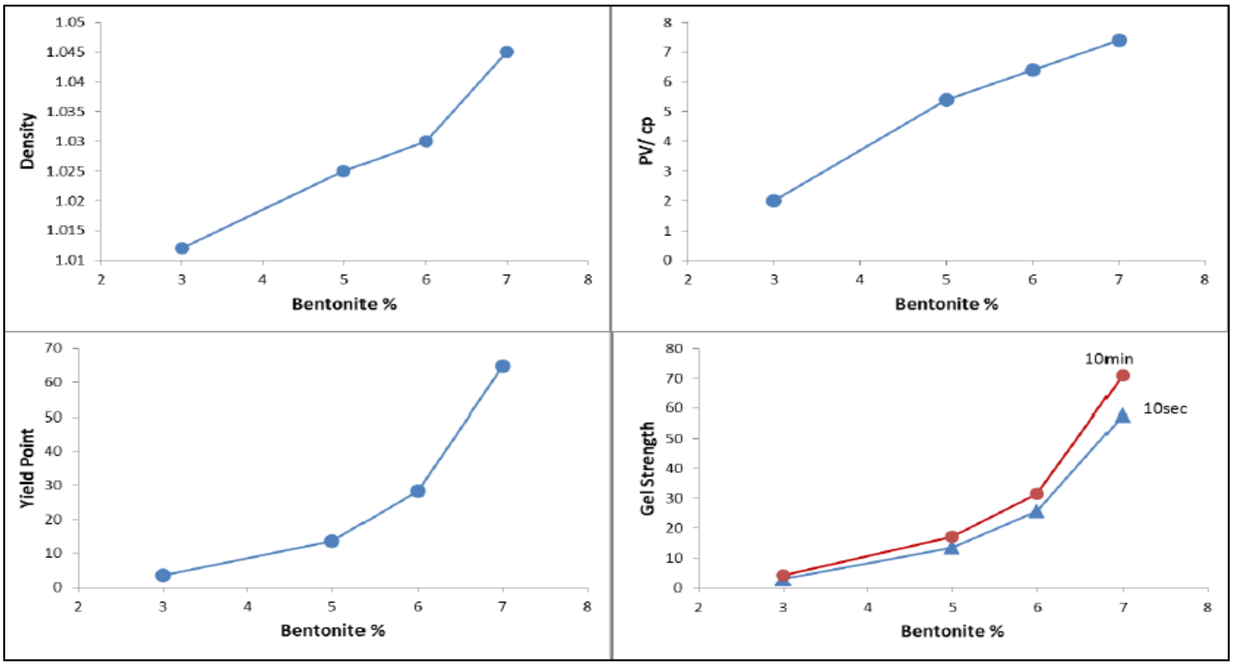

Fig. 1. Rheological properties of bentonite base mud.

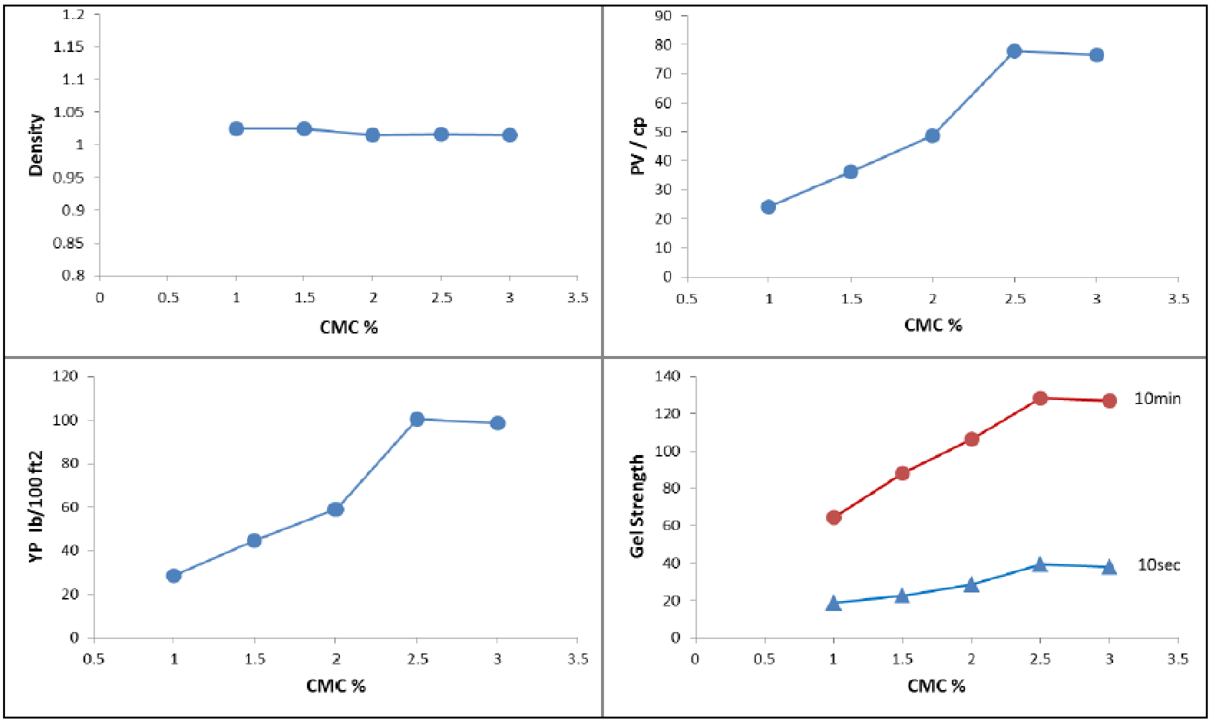

Fig. 2. Rheological properties of bentonite and CMC mud.

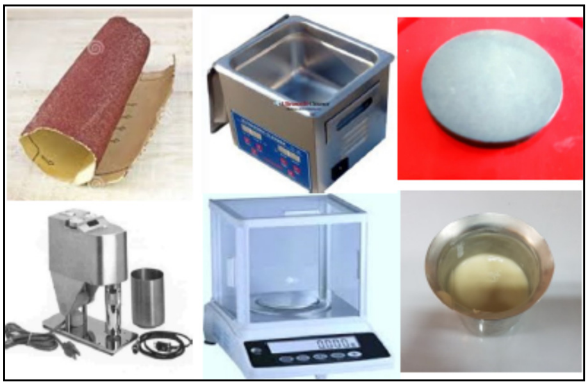

Fig. 3. Equipment and material used in the experiments.

3. Results

The corrosion rate results aid field engineers to predict the lifetime of metallic working components. Most drilling fluid preparations comprise of a base liquid and additives. These must be dissolved or mechanically distributed into the liquid to produce a homogenous fluid. The resulting mud may contain one or more of the following: water-dispersible (soluble) polymers or resins, clays or other insoluble but dispersible fine solids and soluble salts.

In this work the three parts of the drilling fluid have been chosen and studies. The base liquid has been selected as commercial Iraqi bentonite, the additives have been selected as CMC polymer and $ZnSO_4$ soluble salt.

Figure 1 shows the first set of preparation experiments which concentrated on choosing the best bentonite base liquid and the best additives concentrations. A number of Rheological properties were measured and compared. Obtained results were showing a Herschel-Bulkley model which is apparent for most of the prepared fluids. In addition, the concentration of the commercial bentonite was varied to study the Rheological properties of the drilling fluid. Figure 2 demonstrates that the density, plastic viscosity, yield point and gel strength are increased sharply with increasing the bentonite concentration. In order to study the effect of CMC on the rheological properties, CMC was added at different concentrations to the blank solution of 6 wt% (20 Bentonite and 300 fresh water). The results have shown that the density has not been changed within experimental error and its average value was about 1.01±0.02 gm/cm^3. In addition, the data show that there has been a sharp increase in the Plastic Viscosity (PV) and Yield Point (YP) with the CMC. As for the gel strength the effect was apparent and with a change in the trend of the curves. As far as the effect on viscosity is concerned, the increasing of CMC increases the viscometer dial reading at 600 r/min and plastic viscosity. This increase of viscosity in solution refers to adding polymer. Increasing of CMC concentration increases the

Yield Point (YP) and Gel Strength (GS) and at low value of CMC concentration, the bentonite reaches API specification of YP/PV ratio. Results show that the increase of CMC increases the shear stress. This increase of shear stress is attributed to the increase of drilling fluid viscosity.

After finding the optimum values for the drilling mud, it's time for the corrosion study. The experiments were carried out to find the effect of bentonite drilling mud (without any additives) on carbon steel corrosion. The second part of the study was done on the influence of adding $ZnSO_4$. The results of corrosion experiments of adding $ZnSO_4$ to the bentonite base liquid are shown in Figures (4 & 5).

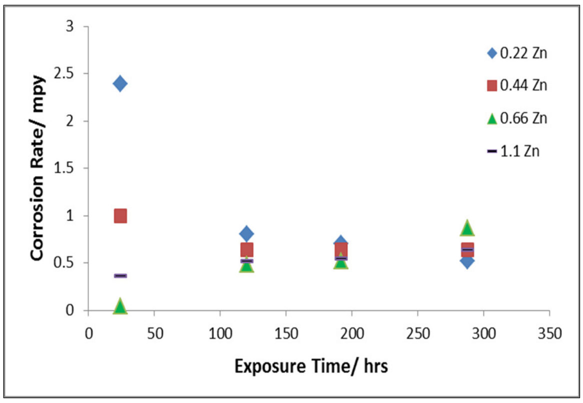

Fig. 4. The variation of $ZnSO_4$ (shown in the figure as Zn) on the corrosion Rate.

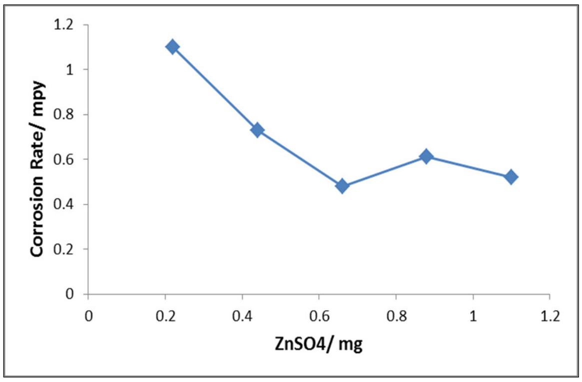

Fig. 5. Average Corrosion Rate with Variation of $ZnSO_4$ added to Bentonite.

Another set of experiments were carried out to study the outcome of adding CMC on the corrosion of carbon steel. This study included varying the concentration of CMC between 0.5% and 3% to examine the corrosion rate with exposure time. The results are summarized in Figures (6 & 7).

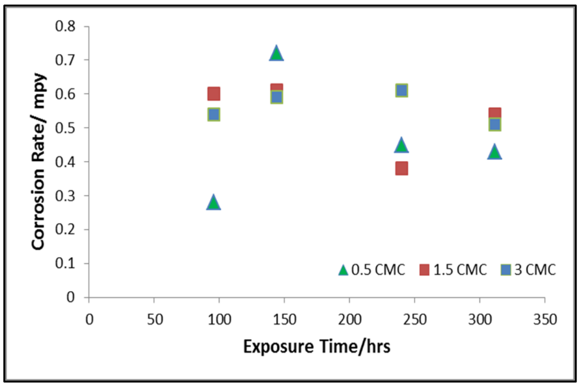

Fig. 6. The variation of CMC concentration on the corrosion Rate.

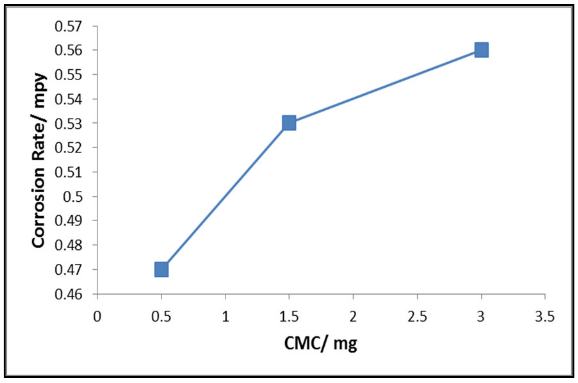

Fig. 7. Average Corrosion Rate with Variation of CMC added to Bentonite.

Finally, the last set of experiments has been tried, this time by mixing both CMC and $ZnSO_4$ with bentonite to check the values of corrosion rate. This has been done by choosing a fixed value of 20 gm for Bentonite and 1.6 gm for CMC and changing the values of $ZnSO_4$ between 0.05gm and 0.4gm. The results are illustrated in Figures (8 & 9).

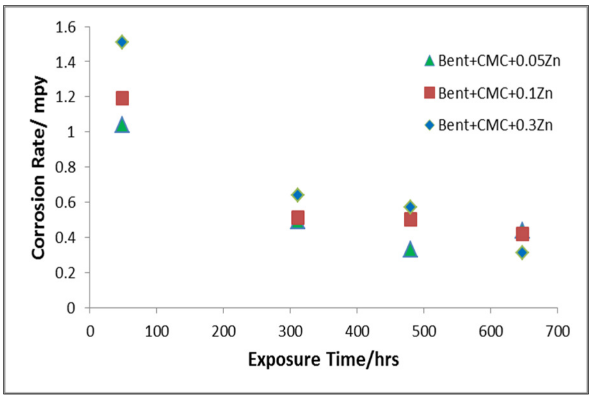

Fig. 8. The variation of $ZnSO_4$ (shown in the figure as Zn) on the corrosion Rate.

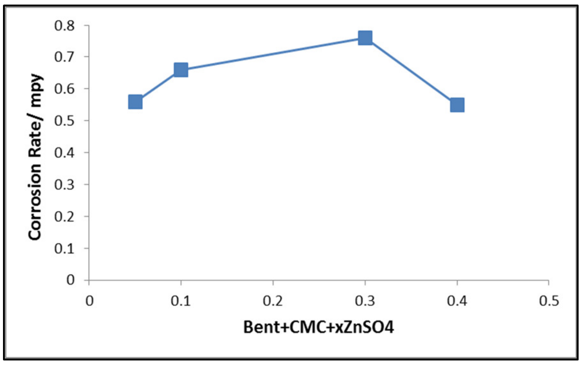

Fig. 9. Average Corrosion Rate with Variation of $ZnSO_4$ added to Bentonite.

4. Discussion

The corrosion of carbon steel which has been used to make most of the equipment in oil drill, oil refinery and vessels is affected by water, mud and reservoir constituents. In this study we focused on studying the corrosion rate of commercially available carbon steel in the water base mud (bentonite) and some common additives (CMC and $ZnSO_4$). The results show that the corrosion rate was decreased with adding $ZnSO_4$ and CMC especially at higher retention time. Visual inspection of the coupons showed that failure has not taken place and corrosion rust can easily be removed from the surface using water. The rust was more series only with bentonite base liquid experiments and need some treatment to be removed such as ultrasonic in acetone liquid. From this result, it seems that passive film was taken place in the case of *bentonite+ZnSO₄* and *bentonite+CMC*. CMC and $ZnSO_4$ work as corrosion inhibitors to reduce metal corrosion.

The aim of adding inhibitors in low concentrations to corrosive media is to delay the reaction between the metal and the corrosive species in the medium. Figure 10 shows the comparison result of using different concentrations of CMC and $ZnSO_4$ additives and their effect on corrosion rate. For the base mud, the corrosion rate started high then gradually fell to a constant value of 0.75 mpy. The same trend was found with *Bentonite+CMC+*$ZnSO_4$ where the corrosion rate was found to end at 0.35mpy. For $ZnSO_4$ the corrosion rate has started very slow at high concentration and later got steady with time. From figure 10, the average value of corrosion rate for *Bentonite+*$ZnSO_4$ is about 0.5mpy. As for the relationship between the weight loss and exposure time shown in figure 11, it seems that it is proportional.

The least corrosive mud was the mixture of *bentonite+CMC* then the mixture of *bentonite+CMC+*$ZnSO_4$ in comparison to the *bentonite base mud*. The work of CMC and $ZnSO_4$ as inhibitors can be explained as film forming corrosion inhibitors, known as barrier or interface inhibitors, which are more protective since these chemical substances do not need to interact with corrosive agents to be effective. Instead, these additives form a protective barrier on the metal surface through strong interactions such as electrostatic adsorption, chemisorption and π-orbital adsorption that significantly reduce penetration of corrosive substances [16]. Corrosion inhibition efficiency can be calculated based on mass of the metal surface lost due to corrosion. Corrosion inhibition efficiencies for both CMC and $ZnSO_4$ were found to be about 50% (calculated from 0.75-0.35/0.75).

A number of researchers studied the corrosion characteristics of CMC using medium carbon steel in various aqueous environments [11-13]. It has been reported that the use of corrosion inhibitors - chemicals added to the corrosive environment in small amount, in many cases, reduced the corrosion rate to approximately 5-10% of the corrosion rate with no inhibitors. However, research using CMC or $ZnSO_4$ as corrosion inhibitor in drilling mud environments has not been reported. Manimaran [13] used the inhibition efficiency of CMC in monitoring corrosion of carbon steel in ground water in the absence and presence of Zn^{2+}, it confirmed the formation of protective film on the metal surface.

In general, most of the previous researches are in good agreement with this work concerning the used of CMC as a corrosion inhibitor for carbon steel in an aggressive environment.

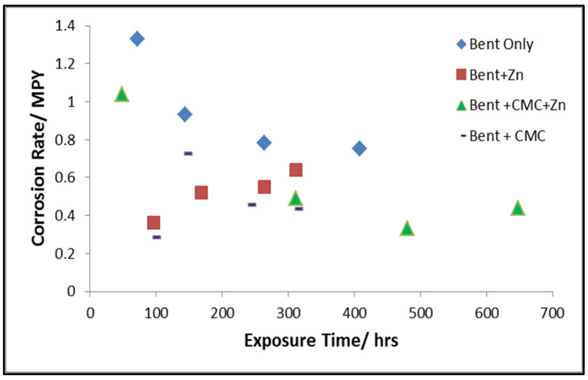

Fig. 10. Comparison Results of Corrosion Rate against Exposure Time

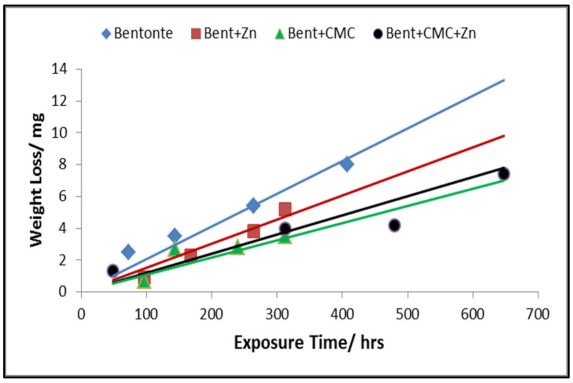

Fig. 11. Comparison Results of Weight Loss against Exposure Time.

5. Conclusions

The corrosion inhibition of medium carbon steel by CMC and $ZnSO_4$ in bentonite mud was studied by weight loss method.

The main conclusions of this study are summarized below:

1. In order to control the drilling mud rheological properties, determining the concentration of selected additives is vital. Changes in the concentration of the additives, added to the mud had significant outcome on mud density, plastic viscosity, yield point, and gel strength.
2. Carboxymethyl Cellulose was found to be a good inhibitor for medium carbon steel corrosion especially in low concentration of (0.5 mg) in water base bentonite mud.
3. ZnSO4 has small effect when used alone as corrosion inhibitor on medium carbon steel corrosion in water base bentonite mud.
4. The mixture of CMC/ZnSO4 shows considerable effect as corrosion inhibitor on medium carbon steel corrosion in water base bentonite mud.
5. The following average corrosion rates trend were estimated of medium carbon steel at room temperature:
   0.75 mpy> 0.55mpy > 0.47mpy>0.35 mpy for the following drilling mud:
   Bentonite only > Bentonite/ZnSO4 > Bentonite/CMC > Bentonite/CMC/ZnSO4.

6. Acknowledgement

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تأثير إضافة كربوكسيل ميثيل السيليلوز وكبريتات الخارصين على خصائص التآكل لسائل الحفر

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الخلاصة

سوائل الحفر هي سوائل معقدة تتكون من العديد من الإضافات التي تؤدي دورا محدداً مثل السيطرة على الخصائص الريولوجية والحد من التآكل .اما مثبطات التاكل فهي المواد التي تضاف في تراكيز صغيرة جدا لبيئة التآكل لتقليل عملية التآكل. وتعد معدات الحفر واحدة من تطبيقاتها. تم في هذا البحث تقويم تأثير إضافة كربوكسيل مثيل سيليلوز و كبريتات الخارصين لدراسة تأثيرها على تآكل الكربون الصلب في طين البنتونيت باستخدام تقنية فقدان الوزن. تركزت هذه الدراسة على تحديد الخصائص الريولوجية وخصائص التآكل .أظهرت النتائج ان اضافة مادة كبريتات الخارصين والكاربوكسيل المثيلي إلى البنتونيت بوصفها مثبط تاكل يعمل على تقليل التاكل الى نسبة مقدارها ٥٠٪ تقريبا.