Study of Caffeine as an Anticorrosion for API 5LX52 Steel in Geothermal Environment Simulation

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Abstract— **The research objective was to study the thermodynamics and kinetics of caffeine as anticorrosion in geothermal environment simulations. The weight loss method following the ASTM G31, and the Electrochemical Impedance Spectroscopy (EIS) method following the ASTM G59-91. The data obtained from this study are the value of polarization resistance (R_p), solution-electrode interface (C_{dl}), the electrolyte resistance (R_s), corrosion current density (i_{cor}), corrosion rate (*CR*), and inhibition efficiency. The results obtained are caffeine has a higher inhibition efficiency at lower temperatures. The caffeine inhibitor efficiency of 90% was achieved at a caffeine concentration of 20 ppm in a 3.5% of NaCl + 500 ppm of H_2S solution at a temperature of 70°C, pH 4, and stirring speed of 250 rpm. The ΔG_{ads}, ΔS^o, and Q_{ads} prices for caffeine are negative, while the E_a and ΔH^o prices for caffeine are positive. This shows that the adsorption strength of the caffeine molecule with iron (Fe) is good in the test environment. The nitrogen (N) atom in caffeine is considered to be alkaline as in ammonia (NH_3) which can accept a proton to give NH_4^+. The minimum Cdl value that occurs at a caffeine concentration of 20 ppm, indicating a double layer at the steel interface with the solution, is considered an electric capacitor. This happens because there are four N atoms in the caffeine molecule. This research is useful for manufacturing green inhibitors in hydrogen sulfide environments such as geothermal environments.**

Keywords— **Thermodynamic; kinetics; caffeine; corrosion inhibitor; mild steel; geothermal.**

I. INTRODUCTION

In Indonesia, geothermal energy is considered an alternative to replacing energy sources because it is consistent in availability and reliability, so there is much attention. In the geothermal industry, the problem of corrosion in the pipeline is always very important because the internal parts of the pipeline often suffer damage [1]–[3]. The type of API5LX52 steel is one of the pipes used for geothermal flow pipelines [4], [5]. Damage due to corrosion often occurs in the internal geothermal flow pipeline because the pipeline transports geothermal fluid from the wellhead to the processing facility [6]-[11]. Geothermal fluids contain high concentrations of corrosive agents passed in the gas stream, such as carbon dioxide, hydrogen sulfide, chloride, and salt compounds that cause corrosion in steel pipes, mainly due to pitting corrosion [2]. The availability of H_2S in the solution causes a decrease in the pH value due to the decomposition of H^+ and HS^- ions related to an expansion in the steel corrosion rate [2]. Several factors can influence the growth in the corrosion rate of steel that has been studied previously, such as the influence of pH, temperature, and concentration of dissolved H_2S [12]–[17], so it needs to be investigated how to minimize or decrease the corrosion rate of the steel.

Corrosion inhibitors as anticorrosion are used to minimize corrosion in the geothermal industry [18]. To achieve optimal inhibition, inhibitors must be added above a certain minimum concentration. Many corrosion inhibitor studies have been reported, such as the use of inorganic and organic compound inhibitors [19], [20]. The negative effects of most inorganic and organic inhibitors on the environment have limited their use in inhibiting metal corrosion [21], [22]. Currently, corrosion researchers are exploring corrosion inhibitors that are safe for the environment. Some examples of the use of organic inhibitors in dissolved H_2S environments, such as benzotriazole [13], *ctylpalmamide*, *octylsteramide*, *octylcaprylamide*, *Octylbenzamide* [23], and caffeine [24]–[26]. This organic inhibitor is a type of film-forming inhibitor that can be used in the oil and gas field to make molecular layers on the face of steel and aliphatic tails as the second film in hydrocarbons preventing water from sticking to the steel

surface, which can cause corrosion [27]. However, this article will report the performance of caffeine as a green inhibitor against API 5LX52 steel corrosion inhibition, and the performance of the inhibitor was reviewed in terms of thermodynamics, kinetics, and adsorption.

Literature studies of caffeine as a corrosion inhibitor have been reported previously. Caffeine has a chemical structure and formula as in Fig. 1. Caffeine consists of one unsaturated Nitrogen (N) atom and two oxygen (O) atoms which are not covered by alkyl groups and cause rings to tend to be negatively charged. Carbon due to interactions between electron-π and free electron pairs of nitrogen (N) and oxygen (O) at the triazole ring of caffeine with d iron (Fe) orbitals forming a protective film on the surface of carbon steel needs to be investigated more continued. Caffeine has been previously reported as anticorrosion inhibited for metal materials in various environments. Used caffeine as an inhibitor for metals and alloy corrosion in several solutions [24]–[26], [28]. Caffeine was used as an inhibitor for zinc (Zn) corrosion in ethanol [29]. Trindade and Goncalves [30] use caffeine as an inhibitor of corrosion for mild steel in ethanol. The research results show that the efficiency of caffeine inhibition for low carbon steel in the ethanol environment reaches 81.9% for caffeine concentrations of 20 mM, and 48.8% for 5 mM caffeine [31]. In the presence of a caffeine inhibitor, the steel does not corrode. This is due to the interaction between the caffeine molecules and the steel surface, forming a protective layer. Solehudin et al. [12] reported that 0.01 mmol/L of caffeine achieves 90% inhibition efficiency of mild steel corrosion in a chloride environment containing dissolved H_2S. Beda et al. [31] investigated the aluminum alloy's corrosion inhibition in 1.0 M HCl solution. The results showed that the efficiency of the inhibitor increased with increasing caffeine concentration but decreased with increasing temperature [21]. Recently, Xuan et al. reported caffeine as anticorrosion inhibited for corrosion of mild steel in seawater conditions. The results show that the corrosion rate of mild steel decreases with the addition of caffeine in the test environment [24].
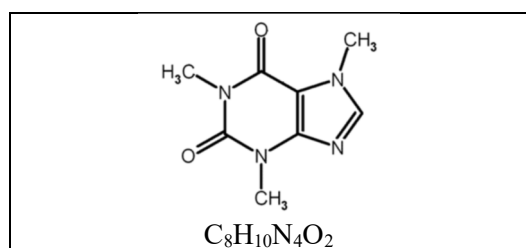

$C_8H_{10}N_4O_2$

Fig. 1 The molecular structure and chemical formula of caffeine

All previous researchers have not presented studies on the thermodynamics, kinetics, and performance of caffeine adsorption as a corrosion inhibitor in an artificial geothermal environment, where H_2S gas is dissolved in sodium chloride solution [32]-[38]. Knowledge about thermodynamic parameters related to inhibitors is very important, especially the mechanism of adsorption processes that inhibit the corrosion rate. Adsorption and thermodynamic behavior of organic inhibitors, mainly plant extracts in low carbon steel in a sour environment, have been widely reported [18], [19], [39]–[41]. The activation energy (*Ea*) and Gibbs free energy

($\Delta G°$) obtained from the analysis results are parameters to determine the mechanism of adsorption and its spontaneity, which is supported by kinetic data of the reaction.

All researchers reported the results of electrochemical linear polarization showing that the extract from natural sources functions as a varied type of inhibitor. Adsorption of *Bridelia ferruginea* Extract to the surface of low carbon steel follows the Langmuir adsorption isotherm model [42], as well as the other research by Abeng et al. [43] on the adsorption of methanolic extracts of Erigeron fluribus onto the mild steel. Meanwhile, recently, Olatunde Alaba Akinbulumo et al. The results showed that the adsorption of Euphorbia heterophylla L. on low carbon steel in 1.5 M of HCl media was compatible with physical adsorption according to the Flory-Huggins isotherm model. This extract is more effective in inhibiting the corrosion of low carbon steel in acidic media at temperatures below 343 K [44].

Conceptually, the research was conducted to measure caffeine's performance as a corrosion inhibitor in an artificial geothermal environment. The variables measured were thermodynamic parameters of caffeine during the experiment. The results will contribute to developing green inhibitor methods in the industry. Green inhibitors are needed because they are environmentally friendly and have been used as a substitute for toxic synthetic chemical inhibitors. In this case, a green inhibitor is the extraction of organic compounds obtained from leaves that contain lots of phenolic compounds or in the form of caffeine compounds. So that the use of green inhibitors as an alternative method of corrosion protection is expected to be used to help inhibit the corrosion rate of carbon steel as a pipeline or flowline material with sweet corrosion, such as in a geothermal environment.

This research aimed to study the behavior of caffeine as an anticorrosion agent in an environment containing hydrogen sulfide. Thermodynamic and kinetic studies of caffeine were also studied. We use the method of mass loss and electrochemical impedance. The thermodynamic parameters such as free energy values, enthalpy, entropy, and activation energy are calculated. The value of the inhibition efficiency was obtained from the two methods.

Based on the literature review above, there are still limited studies on thermodynamic parameters, kinetics, and adsorption characteristics, especially for caffeine as an anticorrosion agent in API5LX52 steel in a sodium chloride medium containing dissolved hydrogen sulfide. The novelty of this research is the evaluation of the thermodynamic, kinetic, and adsorption parameters of the caffeine inhibition mechanism in the test medium. Then, the activation energy, enthalpy change, entropy change, and free energy change are determined. The inhibitor efficiency of caffeine for API5LX52 steel in a hydrogen sulfide-containing environment was calculated.

II. Materials and Methods

This research stage begins with the preparation of materials and tools. Furthermore, experiments were carried out for corrosion inhibition using caffeine at various temperatures, with H_2S concentration, pH, and stirring speed under constant conditions, which were carried out using Electrochemical Impedance Spectroscopy (EIS) and weight loss methods. Qualitative data support is carried out through surface

analysis with SEM, EDS, and XRD. After obtaining the corrosion rate of steel with an inhibitor, the thermodynamic parameters and the efficiency of the inhibition were calculated. Furthermore, the discussion is carried out by comparing the corrosion rate with the addition of an inhibitor and the corrosion rate without an inhibitor.

A. Materials and Standard

API5LX52 steel was used as the specimen. API 5L X52 steel is a type of carbon-manganese (C-Mn) steel with a very low content of carbon (0.2%), sulfur (1.6%), silicon (0.3), and other elements. Corrosion and inhibition tests used the weight loss method (ASTM: G31) and the electrochemical method (ASTM: G59-91). The stages of experiments consisted of making specimens, specimen surface treatment, corrosion testing, inhibition tests, and analysis of test results. Surface examination with X-ray diffraction (XRD), Energy Dispersive Spectroscopy (EDS), and Scanning Electron Microscopy SEM were also carried out. Detailed explanations in the analysis of XRD and SEM are well-documented elsewhere [47], [48]

B. Experiment with Weight Loss Method

The specimens were cut with dimensions of 20 x 10 x 4 mm. Then, the test object's surface is rubbed with a polishing machine using sandpaper with grit 120, 300, 600, and 1000 gradually. The specimens were cleaned with distilled water, rinsed with acetone, dried, and stored in a desiccator for 24 hours. The corrosion and inhibition tests used an autoclave filled with sodium chloride solution containing dissolved hydrogen sulfide with and without caffeine inhibitor. The weight loss was obtained from the difference in weight before and after immersion during the corrosion and inhibition tests. The experiment was carried out with a series of geothermal environment simulation tools, as shown in Fig. 2.
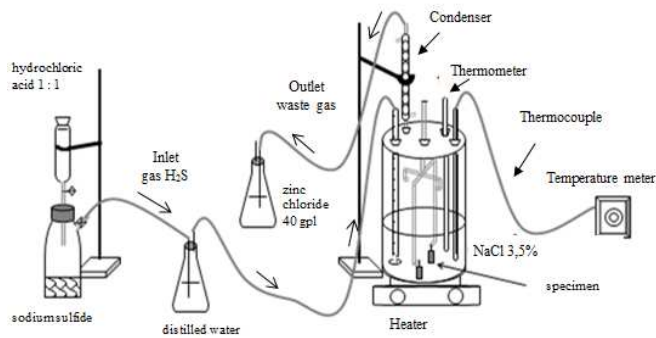

Fig. 2 Schematic of a series of corrosion experiments for simulating the geothermal environment

C. Experiment with the Electrochemical Method

The electrochemical method used is impedance Spectroscopy (EIS). The specimens were cut with dimensions of 1.2 x 1.0 x 4 mm. The specimens are connected with copper wires using solder. Then, the specimen was fixed with epoxy resin to form a circle with a diameter of 40 mm. The surface of the specimen is rubbed with a polishing machine using sandpaper with grits of 120, 300, 600, and 1000 in stages. The specimens were cleaned with distilled water, rinsed with acetone, dried, and stored in a desiccator for 24 hours. Experiments were carried out with a potentiated to obtain electrochemical parameter values. The Ag/AgCl electrode is used as the reference electrode.

III. Results and Discussion

Carbon steel specimens API 5LX65 have been immersed in 3.5% NaCl + 500 ppm of H_2S solution for 3 hours with various caffeine concentrations from 0 to 2000 ppm at pH 4, temperature 70°C, and stirring speed 250 rpm. The results show a semicircular spectrum of the Nyquist curve for an increase in caffeine concentration from 0 to 2000 ppm. However, upon further caffeine additions of up to 2000 ppm, the semicircular spectrum of the Nyquist curve shrank back. The widening of the semicircular spectrum indicates an increase in polarization resistance (R_p), which means a reduction in the current density of corrosion. An increase in the height of the imaginary impedance peak indicates a decrease in the capacitance value of the solution-electrode interface (C_{dl}). With the addition of 10 to 2000 ppm of caffeine concentrations into the solution, there is an inductive loop. This shows that caffeine organic molecules' adsorption is the beginning of forming a protective film [45].

Table 1 shows that the addition of caffeine to 20 ppm has increased the value of polarization resistance (R_p), decreased the capacitance value of the solution-electrode interface (C_{dl}), and decreased the corrosion current density (i_{cor}). However, adding more caffeine, from 200 to 2000 ppm, caused a decrease in Rp again, an increase in Cdl, and an increase in the corrosion current density (i_{cor}). This is due to the formation of oxides on the steel surface with the addition of large concentrations of caffeine. This shows that the electrolyte resistance value (R_s) is almost unchanged with changes in caffeine concentration. Thus, it is concluded that caffeine does not play a role in the conductivity of the solution.

The addition of caffeine, as much as 20 ppm does not form FeO (OH, Cl), and the maximum polarization resistance value lies at 20 ppm of caffeine. As a result, the corrosion current density (i_{cor}) and the lowest corrosion rate were found in solutions containing 20 ppm of caffeine. Whereas in solutions containing 200, 1000, and 2000 ppm of caffeine, the corrosion current density (i_{cor}) and the corrosion rate of carbon steel specimens tended to increase but were still below the current density of corrosion and the corrosion rate in solutions without the addition of caffeine.

A decrease in the value of C_{dl} at a caffeine concentration of 0 to 20 ppm, indicates caffeine adsorption on the steel surface. Meanwhile, at a caffeine concentration of 200 to 2000 ppm, the C_{dl} price increases, indicating desorption occurs on the steel surface. The minimum C_{dl} value that occurs at a caffeine concentration of 20 ppm, indicates that there is a double layer on the steel interface with a solution that is considered an electric capacitor [46].

Because the caffeine variation interval is too far from 20 ppm to 200 ppm, the effect of caffeine concentration at that interval cannot be seen. However, the results of experiments with the weight loss method can provide data support. The experiment's results with the weight loss method stated that adding caffeine concentration in solution ranging from 10 to 80 ppm could reduce the corrosion rate of steel in 3.5% sodium chloride solution with 500 ppm of H_2S during 24 hours of immersion at pH 4. The caffeine concentration of 160 to 320 ppm resulted in an increased corrosion rate of steel, but

it was still below the corrosion rate of carbon steel in the test solution that was not added with caffeine. The results of this experiment were supported by Trindade and Goncalves [30], who examined the corrosion of carbon steel in 99% ethanol + 1% water with the addition of caffeine at room temperature (25°C) at pH 4.5, which the corrosion rate of steel decreased with increasing caffeine content in ethanol from 0, 20, 40, 60 ppm [30]. Other researchers also support this result [24]–[36]. The temperature effect on the corrosion rate of API 5LX65 steel in NaCl 3.5% + 500 ppm of H₂S + 20 ppm of caffeine at pH 4 and stirring speed of 250 rpm was also studied using the EIS method. In Table 2, it appears that the values of Rs and Rp decrease with increasing temperature. The decrease in the value of electrolyte resistance (Rs) is caused by an increase in temperature, which can increase the conductivity of the solution

TABLE I

ELECTROCHEMICAL PARAMETERS OF EIS MEASUREMENT RESULTS ON API 5LX65 STEEL IMMERSED IN 3.5% OF NACL + 500 PPM OF H2S SOLUTION FOR 3 HOURS WITH VARIATIONS IN CONCENTRATION OF CAFFEINE AT PH 4, TEMPERATURE 70OC AND STIRRING SPEED OF 250 RPM

Concentration of caffeine (ppm)	Rs (ohm)	R_p (ohm)	Cdl (Farad) x 10-6	icor (µA/cm2)	Corrosion rate (mm/y)
0	21,15	6,12	945,30	136,52	1,58
10	13,86	13,82	617,20	64,15	0,74
20	17,06	61,24	265,50	14,48	0,17
200	20,34	30,81	350,00	28,77	0,33
1000	14,99	15,26	562,60	58,10	0,67
2000	17,80	13,82	829,40	64,15	0,74

The increase in temperature causes a decrease in polarization resistance (Rp) which also means an increase in icor and subsequently increases the corrosion rate. The rise in the corrosion rate due to temperature increases can be explained by Arhenius' theory, which states that the chemical reaction rate constant depends exponentially on temperature, so chemical reactions (corrosion) are very sensitive to temperature. Carbon steel's polarization resistance value (Rp) at 30 and 50°C in the test solution was much greater than at 70°C. This is because at temperatures of 30 and 50°C no desorption may occur, while at temperatures of 70°C there is desorption on the metal surface. The Cdl value supports this phenomenon at 70°C higher than 30 and 50°C. As a result, the corrosion current density (i_cor) and the corrosion rate at temperatures of 30 and 50°C in the test solution were lower than those at 70°C. This suggests that caffeine protection against carbon steel in this environment is better when used at temperatures below 70°C.

TABLE II

ELECTROCHEMICAL PARAMETERS OF EIS MEASUREMENT RESULTS ON API 5LX65 STEEL IMMERSED IN 3.5% OF NACL + 500 PPM OF H2S + 20 PPM OF CAFFEINE FOR 3 HOURS AT PH 4, TEMPERATURE OF 30, 50, 70°C AND STIRRING SPEED 250 RPM

Tempe-rature (°C)	Rs (ohm)	Rp (ohm)	Cdl (Farad) x 10⁻⁶	icor (µA/cm²)	Corrosion rate (mm/y)
30	20,77	81,16	255.80	10,92	0,13
50	17,56	68,75	259,60	12,90	0,15
70	17,06	61,24	256,50	14,48	0,17

The influence of caffeine on the corrosion process of steel in the sodium chloride solution containing dissolved H₂S has

also been studied using the open-circuit potential (OCP) method. The results presented that the corrosion potential of carbon steel in a solution without the addition of caffeine was stable at -516 mV. While the addition of 10 ppm of caffeine, the corrosion potential is stable at -505; with the addition of 20 ppm of caffeine, the corrosion potential is stable at -501 mV; with the addition of 200 ppm of caffeine, the corrosion potential is stable at -520 mV; at the addition of 1000 ppm of caffeine, the corrosion potential is stable at -522 mV; and the addition of 2000 ppm of caffeine, the corrosion potential is stable at -500 mV.

Based on the potential change in the OCP curve, it can provide data about the adsorption rate between the caffeine compound and the steel surface after adding caffeine concentration. With the addition of 10 and 20 ppm of caffeine, the electrode potential changes in a more positive direction than the electrode potential without the addition of caffeine. Whereas at the addition of 200 and 1000 ppm of caffeine, it is seen that the electrode potential changes towards a more negative direction than the electrode potential without the addition of caffeine. This shows that the addition of 10 to 20 ppm of caffeine can increase the stability of the adsorption between caffeine and the surface.

The influence of temperature on the corrosion process of carbon steel in a chloride environment containing dissolved H₂S and caffeine has also been studied using the OCP method. The results presented that the corrosion potential of carbon steel at temperatures of between 30 and 50°C in the test solution was -519 mV vs Ag / AgCl more stable than the corrosion potential at 70°C (-522 mV vs Ag / AgCl). Thus, based on the potential change in the OCP curve, it can provide data about the adsorption rate between caffeine compounds and the steel surface at temperatures of 30 and 50 °C better than 70 °C. This shows that the effect of temperature is proven to be more dominant than the effect of adding a caffeine inhibitor.

Inhibitor performance parameters are expressed as (*IE%*). That calculated the inhibition efficiency of the corrosion test using the weight loss method following equation (1):

$$IE(\%) = \left(\frac{CR_o - CR_i}{CR_o}\right) x\ 100 \qquad (1)$$

where CR_i is the metal mass loss in the presence of an inhibitor, and CR_o is the metal loss without the inhibitor.

In addition, they calculated the inhibition efficiency of the corrosion test using the Electrochemical Impedance Spectroscopy (EIS) method following equation (2):

$$IE\ (\%) = \frac{R_p - R_p^o}{R_p} x\ 100 \qquad (2)$$

Analysis of several thermodynamic parameters such as adsorption free energy (ΔG_{ads}) inhibitor, adsorption heat (ΔQ_{ads}) inhibitor, activation energy (ΔE_a), enthalpy (ΔH^o), and entropy (ΔS^o) corrosion reaction and inhibition of carbon steel in NaCl (3.5%) + 500 ppm of H₂S at pH 4, temperature 80°C, stirring speed 50 rpm. The thermodynamic analysis is needed to study the inhibitor adsorption mechanism on the carbon steel surface under these conditions. The mechanism of corrosion inhibition can be explained by the theory of adsorption inhibitor behavior, based on equation (3):

$$\Delta G_{ads} = -RT \ln 55,5\ K \qquad (3)$$

where T is the absolute temperature (K), R is the gas constant (8.314 J/mol.K), and 55.5 is the concentration of water in solution (mol/L), assuming the addition of variations in the inhibitor concentration into the solution is neglected because the concentration is very low compared to water concentration. K is the equilibrium constant, which can be calculated using equation (4):

$$K = \frac{\theta}{C(1-\theta)} \qquad (4)$$

where θ is the surface coverage rate of carbon steel and C is the concentration of the inhibitor caffeine (mol/L). The substitution of equation (4) in equation (3) will give an equation (5):

$$\frac{\theta}{C(1-\theta)} = k\, C \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \qquad (5)$$

When equation (5) when logged is, then obtained:

$$\log\frac{\theta}{C(1-\theta)} = \log(kC) - \frac{\Delta G_{ads}}{2,303\,RT} \qquad (6)$$

The surface coverage rate (θ) for various concentrations of caffeine has been calculated from experimental data with the weight loss method. Furthermore, the adsorption heat (ΔQ_{ads}) for steel in the solution of 3.5% of NaCl + 500 ppm of H_2S, pH 4, and stirring speed of 50 rpm with the addition of caffeine can be determined based on equation (6) by making a curve as in Fig 3. Based on the $log\ (\theta/((1-\theta)))$ relationship to $1/T$, the value (ΔQ_{ads}) can be obtained as the slope of the curve multiplied by 2.303 R. The adsorption heat price (ΔQ_{ads}) obtained for caffeine is -41.2 kJ/mol, as shown in Table 3.

TABLE III
THERMODYNAMIC PARAMETERS FOR STEEL IN SOLUTION OF 3.5% OF NACL + 500 PPM OF H2S AT PH 4 WITH AND WITHOUT INHIBITORS

Condition	Thermodynamic parameters (kJ/mol)				
	ΔE_a	ΔH^o	ΔS^o	ΔG_{ads}	Q_{ads}
Without caffeine	21,27	18,59	-0,16	-	-
With caffeine	33,56	30,88	-3,86	-29,86	-41,2

Since the ΔQ_{ads} value for caffeine is -40 kJ/mol caffeine may be chemically adsorbed. If it looks at the molecular structure of caffeine as shown in Fig. 1, it appears that there is a place most likely to act as a proton acceptor in the caffeine molecule. The nitrogen (N) atom in caffeine is considered to be alkaline as in ammonia (NH_3) which can accept a proton to give NH_4^+. With this in mind, the caffeine molecule has four N atoms. Three N atoms are considered tertiary amines because each is bonded to three carbon (C) atoms. The fourth nitrogen atom has one double bond attached to one carbon atom (C) and one single bond with another C atom. This position is most likely to accept a proton so that it can bind to the iron (Fe) atom on the surface of the steel. The bond between caffeine molecules and steel (Fe atom) can be proven from the results of EDS analysis, where there is a Nitrogen (N) content on the surface of steel which is added with 20 ppm of caffeine of 8.15 - 10.62%. This is confirmed by the results of the EIS analysis, where the presence of an inductive loop indicates the Nyquist curve. The corrosion activation energy of carbon steel in the test solution is based on the following Arrhenius equation approach:

$$CR = k \exp\left(-\frac{E_a}{RT}\right) \qquad (7)$$

where CR as corrosion rate (mm/y), k is the factor constant for Arrhenius pre-exponential, E_a is the activation energy of the corrosion process, where R is the gas constant (8.314 J/mol.K), T is the absolute temperature (K).

The activation energy (E_a) is obtained as the slope of the $log\ (CR)$ curve concerning $1/T$ as in Fig. 3. Fig. 4 shows that when adding caffeine to the test solution, there is a reduction in the corrosion rate ($\Delta log(CR)$) at low temperatures greater than at high temperatures. Determination of the enthalpy (ΔH^o) and entropy (ΔS^o) of the corrosion reaction and inhibition of steel in a solution of 3.5% of NaCl plus 500 ppm transition as below:

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S^o}{R}\right) \exp\left(-\frac{\Delta H^o}{RT}\right) \qquad (8)$$

With CR, the rate of corrosion (mm / yr), h is the constant of Plank's, where R is the gas constant and N is Avogadro's number. The enthalpy value (ΔH^o) is obtained as the slope of the $log\ (CR/T)$ curve concerning $1/T$, while the entropy (ΔS^o) is calculated from the intersection of the curve on the log axis (CR/T) which is equal to the $log\ (R/Nh) + (\Delta S^o/2.303R)$, as shown in Table 3.
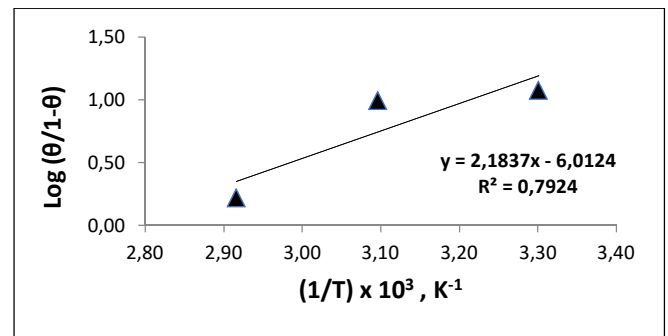

Fig. 3 Isotherm adsorption curve to determine the adsorption heat (ΔQ_{ads}) of the inhibitor on the surface of temperature 80°C, stirring speed 50 rpm

The enthalpy value (ΔH^o) is positive, indicating that the corrosion reaction or dissolving process is endothermic, meaning that it requires high temperatures (see Fig. 4).
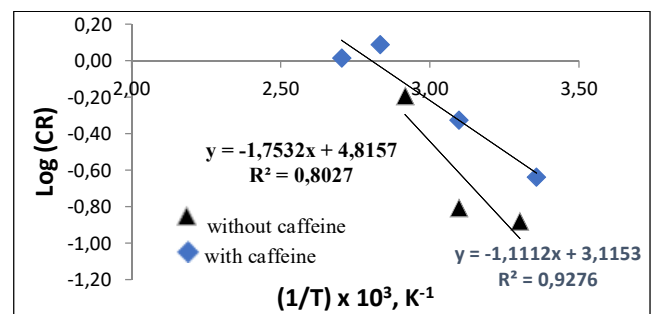

Fig. 4 Adsorption isotherm curves to determine the activation energy (ΔE_a) of corrosion and inhibition of steel in the solution of 3.5% of NaCl + 500 ppm of H_2S at pH 4, temperature 30, 50, and 70°C, stirring speed 50 rpm

Meanwhile, the negative entropy (ΔS^o) value for caffeine indicates that the rate-determining stage is a kind of association process. This incorporation process can be interpreted as the adsorption of caffeine inhibitors whose

irregularity decreases in the growth stage of the reaction from the reactants to the active complex layer.

The adsorption free energy (ΔG_{ads}) was determined using equation (6), which is shown in Table 3. Free energy adsorption (ΔG_{ads}) for caffeine is -29.86 kJ/mol. The ΔG_{ads} value for caffeine is negative, representing the spontaneous adsorption of caffeine on the steel surface [29]. This indicates that the caffeine molecule interacts with the steel in a semi-physisorption manner [11]. The value of free energy shows the strength of adsorption of the caffeine molecule and the Fe atoms from the surface of the carbon steel.

Phase analysis based on the XRD diffractogram indicated that the addition of 2000 mg/L of caffeine to the NaCl solution had formed FeO(OH, Cl) on the surface of the specimen (Fig. 5). As for the addition of 20 mg/L of caffeine, it was not formed. So it can be concluded that the increase in the corrosion rate with the increase in caffeine concentration is caused by leakage of the protective layer due to the dissolution of FeO(OH, Cl).
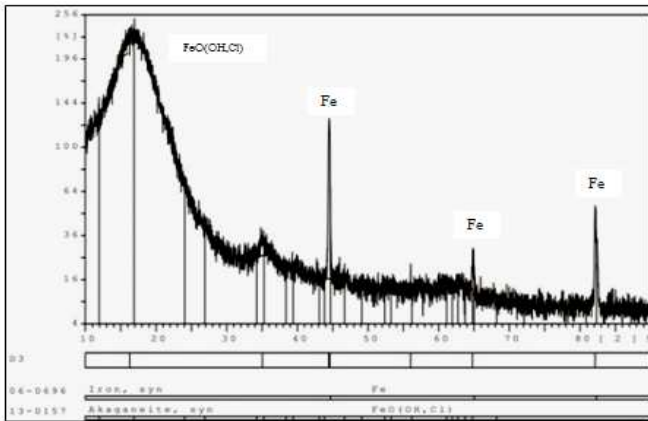

Fig. 5 The diffractogram of XRD on the addition of 2000 mg/L of caffeine

The results of the EDS spectrum showed that on the surface of the specimens with the addition of 2000 mg/L of caffeine, oxides were formed, but a little nitrogen bond was formed with the addition of 20 mg/L of caffeine (Fig. 6). This indicates that caffeine is more effective as a corrosion inhibitor at a concentration of 20 mg/L.
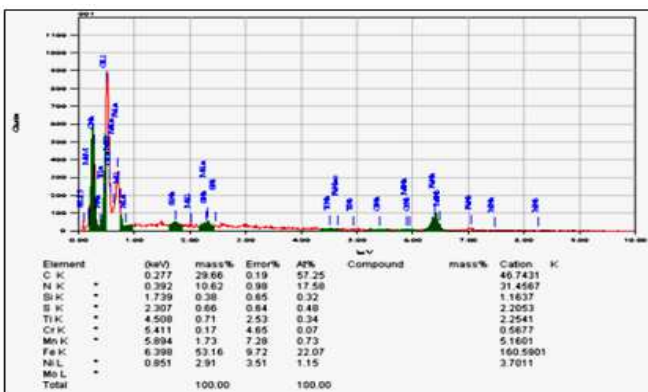

Fig. 6 The spectrum of EDS on the addition of 20 mg/l caffeine

The SEM image results show that a layer of iron sulfide (FeS) corrosion is formed on the surface of the carbon steel specimen. Meanwhile, with the addition of 20 mg/L of caffeine, there appears to be a cobweb structure on the surface of the carbon steel (Fig. 7). This indicates a bond between caffeine and the steel surface.
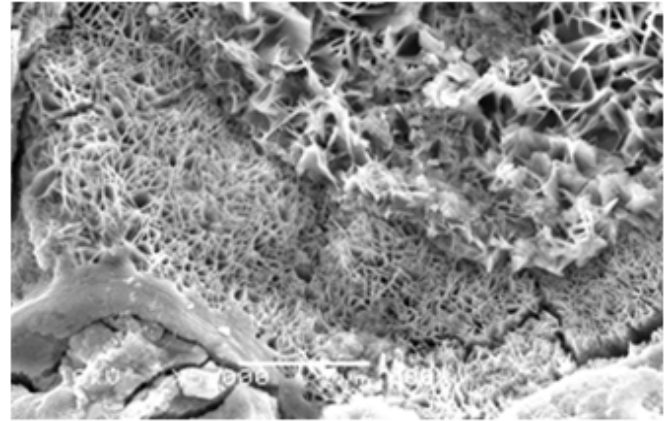

Fig. 7 The SEM image with the addition of 20 mg/L of caffeine, there is a cobweb structure on the corrosion product (5000x magnification)

IV. CONCLUSION

The addition of caffeine up to 20 ppm has increased the polarization resistance value (R_p), decreased the capacitance value of the solution-electrode interface (C_{dl}), and decreased the corrosion current density (i_{cor}). Caffeine has a higher inhibition efficiency at lower temperatures. The caffeine inhibitor efficiency of 90% is achieved at a caffeine concentration of 20 ppm in a 3.5% of NaCl + 500 ppm of H_2S solution at a temperature of 70°C, pH 4, and stirring speed of 250 rpm. The values of ΔG_{ads}, $\Delta S°$, and Q_{ads} for caffeine are negative, while the values of E_a and $\Delta H°$ for caffeine are positive. This shows that the adsorption strength of caffeine with iron (Fe) molecules is good in the environment with these conditions. This study's results contribute to the development of green inhibitors. This is because green inhibitors are expected to help inhibit the corrosion rate of carbon steel as a pipeline or flowline material with sweet corrosion, such as in geothermal environments.

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