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Review of the Usefulness of Inhibitors for Reducing the Corrosion of Iron in H_2S Environments

Hansang Kim† **and Eunsub Yoon**

Nuclear Engineering & Technology Institute, Korea Hydro & Nuclear Power Co.,
25-1 Jang-dong, Yuseong-gu, Daejeon 305-343, R. of Korea

The influence of H_2S on the corrosion of iron and the corrosion prevention mechanism of an inhibitor was investigated with a differential capacitance measurement and a weight loss measurement method. The results show that H_2S accelerates both the anodic iron dissolution and the cathodic hydrogen evolution in most cases. However, H_2S acts as an inhibitor of the corrosion of iron under certain special conditions. An EIS method is proposed to explain the ability of inhibitors.

Keywords *: hydrogen sulfide, inhibitor, capacitance measurement, impedance measurement*

1. Introduction

Hydrogen sulfide (H_2S) acts as an accelerator of anodic dissolution and cathodic hydrogen evolution in iron corrosion but, in some environments, can prevent iron corrosion by forming an iron sulfide (FeS) film on the iron surface. If a corrosion inhibitor is added to media to prevent corrosion, it reacts with iron to form a protective film composed of different FeS crystals, such as pyrite, troilite, pyrrhotite, and mackinawite, whose properties depend on the sulphuration temperature, the pH of the solution, the H_2S concentration, and the immersion time.[1),2)]

Many inhibitors can prevent metals from deteriorating under H_2S corrosion environments. In this work, two traditional methods such as differential capacitance measurements and weight loss measurements are investigated to evaluate the performance of inhibitors in iron corrosion under a H_2S environment. Moreover, a new evaluation method is proposed to verify the effectiveness of inhibitors.

2. Background

2.1 Functions of inhibitors

Corrosion inhibitors are added to media to prevent structures or equipment from corroding in corrosive environments. Most inhibitors are organic compounds that work in the following three ways:[3)]

- Cathodic inhibitors impede the cathodic half cell reactions of the corrosion,
  e.g., $2H^+ + 2e^- \rightarrow H_2$.
- Anodic inhibitors limit the anodic half cell reactions of the corrosion,
  e.g., $Fe \rightarrow Fe^{2+} + 2e^-$.
- Adsorption inhibitors form a physical barrier on the metal surface and prevent corrosion.

When a corrosion inhibitor is added to a system, the inhibitor molecule adheres to the metal-solution interface, thereby causing a change in the potential difference between the metal-solution interface. The metal-solution interface is characterized by an electrical double layer. The inhibitor may become effective as a result of changes in the properties of the electric double layer, particularly by the following means:[4)]

- reducing metal reactivity
- participating in a partial electrode reaction
- forming a physical barrier.

Filming corrosion inhibitors are complex mixtures of organic and inorganic molecules designed to adhere to metal surfaces to protect them from an environmental attack. Table 1 shows corrosion inhibition data of iron coupons of several inhibitors under a H_2S environment.

2.2 Influencing factors on the inhibition effects

2.2.1 Temperature

Gomes[5)] performed a study on the crystal size of pyrite as a function of temperature. The data in Fig. 1(a) clearly shows that the crystallite size increases when the sulphuration temperature increases.

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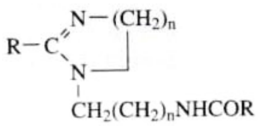
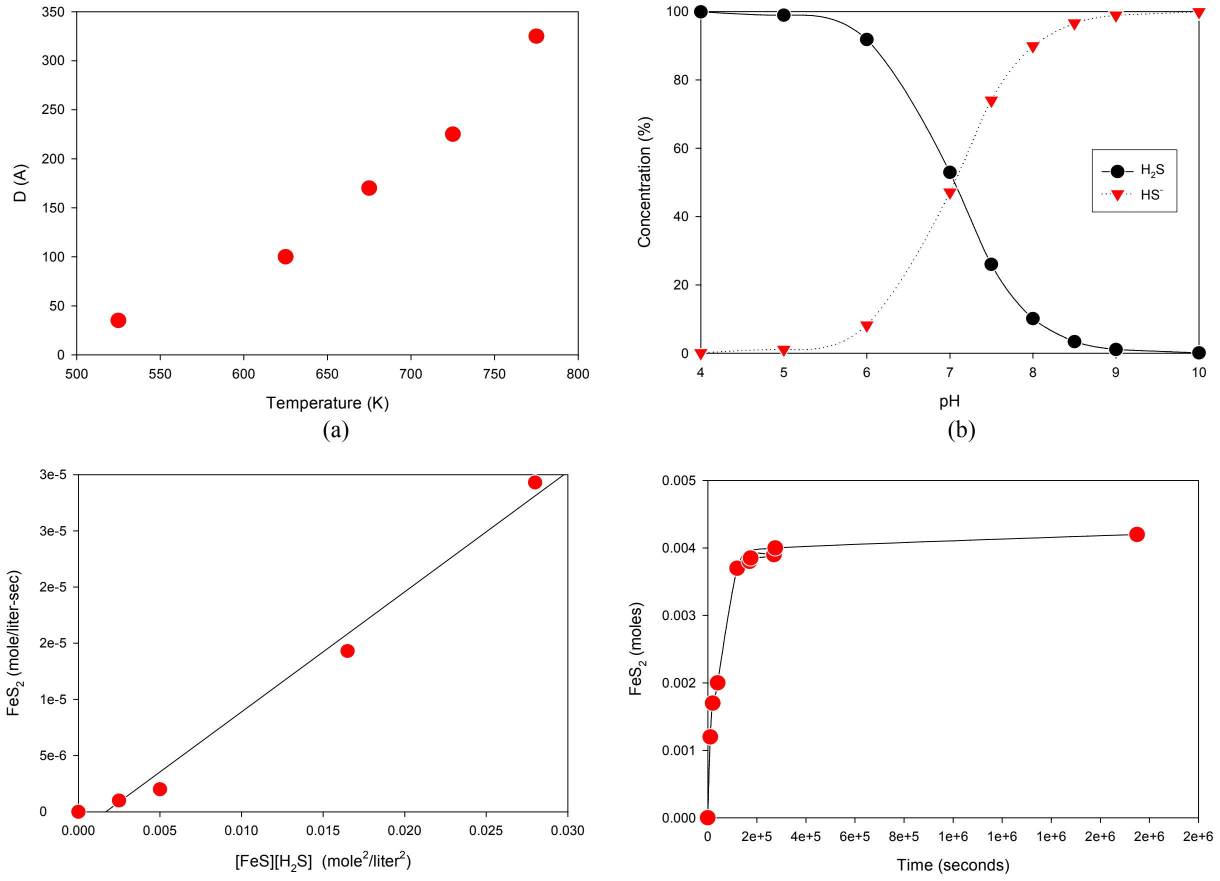
† Corresponding author: hanskim@khnp.co.kr

Table 1. Corrosion inhibition data for hydrogen sulfide environment[4]

Material	Medium	Inhibitor	Effect
Iron sheet	3% NaCl, 50% gasoline saturated with H_2S and CO_2 at 80 ℃	250 ppm of  (n=1 or 2; R=$C_{7\text{-}25}$ alkyl or akenyl) mixed with sulfur	75% Inhibition
	CO_2, H_2S water-oil emulsions (3% NaCl)	250 ppm of 1 aminoethyl - 2 isoctyl - 2 imidazoline reacted with 5% sulfur at 150 ℃ for 2 h.	70% Inhibition
	50:50 emulsion of mineral spirits (3% NaCl) + CO_2 + H_2S	250 ppm of 1 - 2 oleamidoethyl - 2 imidazoline with 10% sulfur	83% Inhibition
	50:50 emulsion of mineral spirits (3% NaCl) + CO_2 + H_2S	250 ppm of 1 - 2 oleamidoethyl - 2 imidazoline	77% Inhibition



(a)

(b)

(c)

(d)

Fig. 1. (a) Pyrite crystal size vs. sulphuration temperature; (b) percentage of H_2S species vs. pH; (c) rate of pyrite formation vs. FeS and H_2S concentrations; and (d) the amount of pyrite produced vs. time

2.2.2 pH

In the metal-H_2S solution system, H_2S can be present in the forms of H_2S, HS^-, and S^{2-}. The percentage of the two main species is shown as a function of pH in Fig. 1(b).[5] At a pH of 4, H_2S presents almost entirely in the molecular form; in contrast, at a pH value higher than 6, HS^- ions appear and increase as the solution becomes strongly alkaline, leaving only small amounts of H_2S. The work of Hughes et al.[6)] shows that the surface scale in the metal-solution interface does not form at the lowest pH value in the system but builds up rapidly at a pH of 4.5 before reaching a maximum at a pH of 5.0.

2.2.3 H_2S concentration

The H_2S concentration has great influence on the protective ability of sulfide film.[7)] From the work of Rickard,[8)] the hypothesis that the H_2S concentration is proportional to the production rate of pyrite is easily confirmed. The result in Fig. 1(c) demonstrates that there is good linearity between the H_2S concentration and the formation rate of FeS film.

2.2.4 Immersion time

Rickard[8)] measured the pyrite weight as a function of time. We can see the pyrite weight produced is asymptotic to 4 *m*mol of pyrite in Fig. 1(d). The pyrite forming reaction is $FeS + H_2S = FeS_2 + H_2$. These species form more protective films on the iron surface as time goes on.

3. Theory

3.1 Dissolution mechanism

The dissolution mechanisms in the environment of a H_2S solution involve the surface complex $Fe(H\text{-}S\text{-}H)_{ads}$. This compound plays a very important role in preventing the metal surface from corroding in the presence of H_2S and organic inhibitors. Elboujdaini et al.[2)] suggested the following mechanisms:

$$Fe + HS^- \rightarrow Fe(HS^-)_{ads} \tag{1}$$

$$Fe(HS^-)_{ads} + H_3O^+ \rightarrow Fe(H-S-H)_{ads} + H_2O \tag{2}$$

$$Fe(H-S-H)_{ads} + e^- \rightarrow Fe(HS^-)_{ads} + H_{ads} \tag{3}$$

Cheng et al.[9)] also suggested the following mechanism of iron dissolution in the presence of H_2S:

$$Fe + H_2S + H_2O \leftrightarrow \left(FeSH^-\right)_{ads} + H_3O^+ \tag{4}$$

$$\left(FeSH^-\right)_{ads} \leftrightarrow \left(FeSH\right)_{ads} + e^- \tag{5}$$

$$\left(FeSH\right)_{ads} \rightarrow FeSH^+ + e^- \tag{6}$$

$$FeSH^+ + H_3O^+ \leftrightarrow Fe^{2+} + H_2S + H_2O \tag{7}$$

In this mechanism, H_2S adheres to the surface of iron where it forms a monolayer of H_2S molecules. As a result of the interaction between $Fe(HS^-)$ and inhibitor cations (I^+), a stable surface compound of Fe(H-S-I) appears on the surface of the metal.

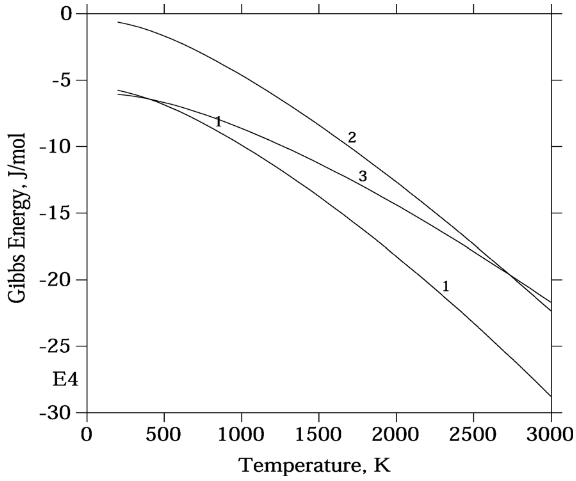


Fig. 2. Gibbs energies of pyrrhotite(1), troilite(2), and pyrite(3) as a function of temperature (calculated by THERMO-CALC^{TM})

3.2 FeS film formation

According to Shoesmith et al.,[10)] the species $FeSH^+$ at an electrode surface may be incorporated directly into a growing layer of mackinawite as follows:

$$FeSH^+ \rightarrow FeS_{1-x} + xSH^- + (1-x)H^+ \tag{8}$$

If the reaction leads to local supersaturation at the electrode surface, then the nucleation and growth of one or more of the iron sulfides, such as mackinawite, pyrrhotite, and troilite, occurs. The troilite transfers into pyrrhotite or pyrite according to the temperature to minimize Gibbs energy in Fig. 2.

4. Traditional evaluation methods of the usefulness of inhibitors

4.1 Differential capacitance measurements

Podobaev and Shalygin[11)] used differential capacitance

Table 2. Sequence of adding the inhibitors and H_2S

Test 1	Test 2	Test 3
- Immerse a coupon in 200 ppm PKU-6 inhibitor - No H_2S	- Immerse a coupon in 200 ppm PKU-5 inhibitor - Hold 60 minutes - Add $5x10^{-3}$ *M* NaS	- Immerse a coupon in $5x10^{-3}$ *M* Na_2S solution - Hold 60 minutes - Add PKU-6 inhibitor

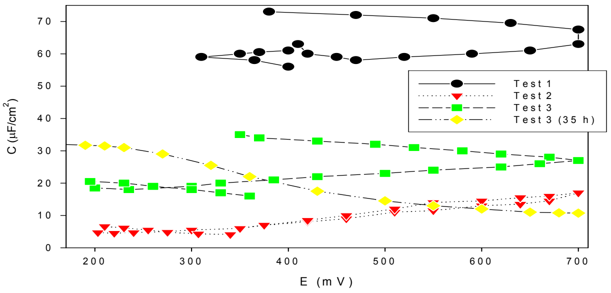


Fig. 3. Film capacitances of an iron surface as a function of potential

measurements to measure the adsorption of an inhibitor by Armco iron from sulfate solutions. Table 2 shows the experimental sequence for measuring the effect of the FeS film.

Test 1 shows the cathodic polarization curve in the absence of H_2S. Holding the potential at 700 mV for 10 minutes reduced the capacitance. This outcome may be caused by the formation of a secondary film as a result of alkalization of the metal layer. The low capacitance values mean that a compact chemisorbed film is formed on the electrode surface. In test 3, FeS on the metal surface also increases the capacitance in the presence of an inhibitor. A protective film is gradually formed and, after 35 hours, the capacitance of the electrode is reduced to the values found in test 2. When an inhibitor is added to the sulfide layer, the corrosion products are gradually replaced by a film of the inhibitor. The degree of surface coverage of the iron by the inhibitor is calculated by means of the following expression,

$$\theta = \frac{C_0 - C}{C_0 - C_1} \tag{9}$$

where C_0, C, and C_1 are the capacitances without an inhibitor, with an inhibitor, and at $\Theta = 1$, respectively. The results of which are plotted below.

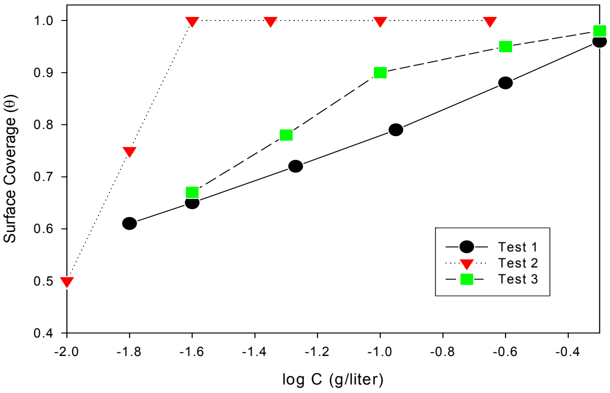


Fig. 4. Isotherms of the adsorption of the PKU-6 inhibitor on an iron surface at the corrosion potential (E_{corr})

When the inhibitor is added in tests 2 and 3, the curves display a break at $\Theta \rightarrow 1$. The slopes of the first linear sections are higher than the slopes of curve 1, showing that the protective actions of the inhibitor and H_2S are synergistic. The results suggest that H_2S increases the capacitance of FeS. In the absence of FeS, the inhibitor has less influence on the capacitance of the iron-solution interface; however, in the presence of FeS, the inhibitor increases the capacitance by up to 20 $\mu F/cm^2$ to 30 $\mu F/cm^2$.

4.2 Weight loss measurements

Gardner[12)] measured the corrosion of iron in the aqueous solutions of H_2S in the absence and presence of inhibitors by using the weight loss measurement method during the formation of solid FeS. First, the experiments were performed to study the reaction between Fe and H_2S in the absence of inhibitors. The corrosion inhibitors were then added to the solutions. The experiments were performed for three different concentrations of the inhibitors, namely 20 ppm, 30 ppm, and 50 ppm, and the temperature was fixed at 80 ºC to maintain the same experimental conditions. The inhibitors used in the second experiment were an oil-soluble inhibitor (test 1) and an oil field sour well inhibitor (test 2).

Fig. 5 shows the difference in the corrosion rates for the absence and presence of inhibitors. The solution of the test 1 contained 4% of NaCl brine and 2000 ppm of H_2S. Without inhibitors, H_2S stimulates the corrosion rate of iron; however, with inhibitors, the corrosion is suppressed by the inhibitor effects.

Hughes investigated the corrosion inhibition effect of the sulfide film. This study used a 10 percent solution of sodium chloride; the solution had a pH of 6.5 and was saturated with H_2S. The investigation comprised four tests that were performed separately:

- Test 1 - coupons were placed in the solution without inhibitors

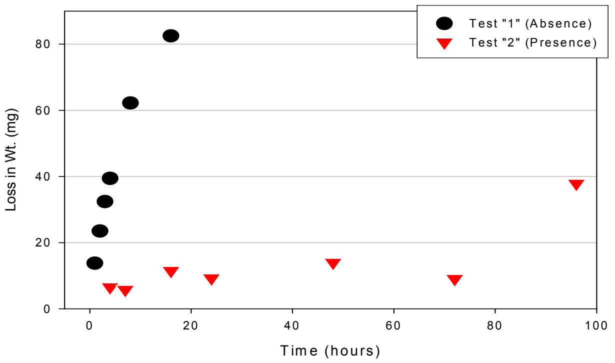


Fig. 5. Comparison of the loss of weight in the absence and presence (30ppm of oil field sour well inhibitor) of inhibitors

Table 3. Results of the weight loss experiments

Test	Total loss of wt.	Loss to solution	Distributed to Scale
Test 1	511 mg	447 mg	64 mg
Test 2	241 mg	48 mg	193 mg
Test 3	473 mg	123 mg	350 mg
Test 4	121 mg	18 mg	103 mg

- Test 2 - coupons were placed in the solution with 1% of inhibitor A
- Test 3 - coupons were placed in the solution with 50 ppm of inhibitor B
- Test 4 - the solution contains 1% of inhibitor A and 50 ppm of inhibitor B

This investigation was performed for 19 days with a repetitive process of weighing and dipping. The experimental results are shown in Table 3. The inhibitors represent two different types, A being an aldehyde sulfoxylate and B an amine material of the imidazoline type.

The results suggest that inhibitor A is superior to inhibitor B in forming films that are more impermeable to metal and that a synergistic effect can be expected when both inhibitors are mixed in the solution. We can observe that the formation of the FeS scale as a corrosion protection film is deeply influenced by corrosion inhibitors.

5. Application of the EIS Method to evaluate the weight loss

The adsorbed inhibitors react with the base metal to form an FeS layer and they also form a layer in the interface between the metal and the solution. These layers increase the capacitance in the interface in addition to the original electrical double layer, which is the layer that always occurs at the interface when an electrode is immersed in an electrolyte solution.[13)]

The equivalent circuit of the iron corrosion under an inhibitive environment without an FeS layer can be drawn the same as Randle's model in Fig. 6. For the mathematical derivations, the anodic and cathodic reactions are both assumed to be a Tafelian electron transfer; hence, the charge transfer resistance is identical to the polarization resistance.

For a true equilibrium potential, the impedance is expressed as follows:[13)]

$$\frac{1}{Z_F} = \frac{1}{R_p} = 2.303\left[\frac{I_a}{b_a} - \frac{I_c}{b_c}\right] \tag{10}$$

where Z_F is the frequency-dependent impedance, R_p is the polarization resistance, I_a and I_c are the anodic and cathodic currents, and b_a and b_c are the anodic and cathodic Tafel slopes. For an overall current of zero, where $I_a = -I_c = I_{corr}$, the relationship between impedance and the corrosion current (I_{corr}) is

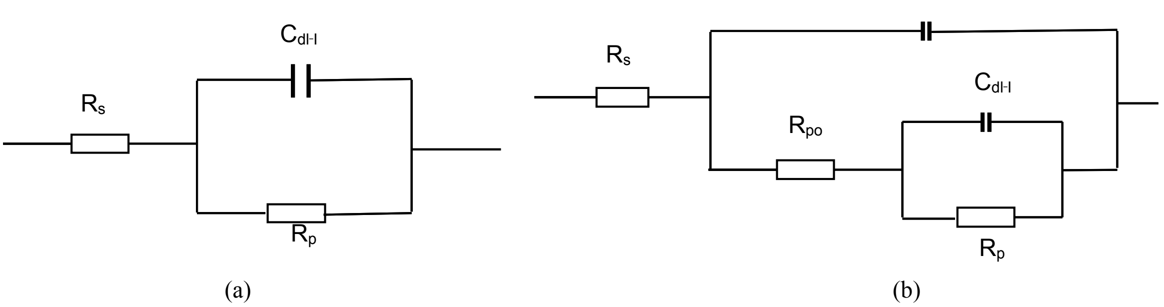
$$\frac{1}{R_p} = 2.303 I_{corr} \frac{(b_a + b_c)}{b_a b_c} \tag{11}$$

Therefore, the corrosion rate of the metal per unit area of the circuit of Fig. 6(a) is

$$\frac{dW}{dt} = \frac{MI_{corr}}{zF} = \frac{b_a b_c M}{2.303 zFR_p (b_a + b_c)} \tag{12}$$

where W is the weight loss of iron, M is the molecular weight, z is the number of electron balances, and F is the Faraday constant.

The effect of the FeS film is considered the same as the effect of failed paint coatings. Fig. 6(b) represents the simple equivalent circuit of a failed coating.[14)] In Fig. 6(b), C_{FeS} is the capacitance of a FeS film and R_{po} is the pore



(a) (b)

Fig. 6. Equivalent circuits to the iron corrosion under the H_2S and inhibitor environment (a) without a FeS layer and (b) with a FeS layer

resistance. The corrosion rate for this circuit is given as

$$\frac{dW}{dt}=\frac{MI_{corr}}{zF}=\frac{b_a b_c M}{2.303zFR_{ct}\left(b_a+b_c\right)} \tag{13}$$

6. Summary

Inhibitors are considered to act as a cation (I^+). As a result of the interaction between Fe(HS^-) and organic cations (I^+), the relatively stable surface compound Fe(H-S-I) appears on the surface of the metal. This compound is not able to supply protons for the cathodic process and impedes the anodic reaction of metal. Furthermore, the adsorbed cations of the inhibitor shift potential toward the positive, which also helps slow down the hydrogen-ion discharge.

A differential capacitance measurement technique was used to evaluate how PKU-5 and PKU-6 inhibitors inhibited the corrosion of iron under H_2S environments. This experiment shows that the inhibitors entirely suppress the effects of H_2S. In contrast, the FeS on the iron surface increases the capacitance in the presence of this inhibitor. In the absence of FeS, the inhibitors have less influence on the capacitance of the iron-solution interface; however, in the presence of FeS, they greatly increase the capacitance to around 20 µF/cm^2 to 30 µF/cm^2. The weight loss measurement technique is a very trustworthy method of measuring the corrosion rate in an aqueous solution. This experiment shows that H_2S stimulates the corrosion rate of iron without inhibitors; however, with inhibitors, the corrosion is suppressed by the inhibitor effects.

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