

A Thermodynamic Investigation on Corrosion of Cu-bearing Steel in Aqueous Solutions

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Abstract

This paper investigated the corrosion behavior of Cu-bearing steel using thermodynamic methods and presented the results in the graphical information widely known as “Calculated Potential-pH Diagram”. The chemical and electrochemical reactions which potentially occur during the corrosion process of Cu-containing steel and significant thermodynamic data such as standard Gibbs free energy of ions or compounds were first evaluated. Nernst’s equation and Van’t Hoff’s equation were then employed to establish two sets of thermodynamically important equations. Later, these equations were used to construct a potential-pH diagram, which can be used as a guideline to investigate the corrosion behavior of Cu-bearing steel. It is found from the obtained diagram that CuFeO_2 can be formed on the steel substrate for almost pH value. Fe_3O_4 appears from the middle to high pH value. The region in which CuFeO_2 and Fe_3O_4 overlap is found, indicating that two compounds potentially coexist in the rust layers covering on the steel substrate. The presence of copper ions in the rust can decrease the rust conductivity and retard oxygen ingress. Thus, this rust can would enhance the corrosion resistance of Cu-containing steel in a slightly acidic to a high alkaline environment.

Keywords: Anti-corrosion assessment; Thermodynamic; Steel

1. Introduction

Steels are generally utilized in numerous applications in different industries due to their low cost and attractive mechanical properties. Nevertheless, a major obstacle to the use of steel is the environmentally degraded mechanisms known as corrosion. Corrosion of steel is the detrimental attack caused by the reaction between steels and their surrounding environments, leading to the deficiency in load carrying capacity of the steel structure and subsequently endangering human life and the environment. Thus, the improvement of the anti-corrosion performance of steel is obviously required. Basically, the anti-corrosion performance of steels can be obtained by

adding alloying elements, such as copper (Cu), nickel (Ni) and chromium (Cr). Among many, Cu is an effective element which can help improve the corrosion resistance of steels. T. Misawa et al [1] used X-ray diffraction (XRD) to study the corrosion of steel with the Cu addition and found that rust of steels containing Cu was fine and compact, resulting in the increased anti-corrosion performance of steels. L. Hao et al [2] utilized XRD, Electrochemical Impedance Spectroscopy (EIS), and rust morphology analysis to examine the steel containing Cu. Their results pointed out that the corrosion resistance of this steel was significantly improved with the Cu addition. Ch. Thee [3] used the corrosion monitoring technique to study Cu-bearing steel and found that the rust containing Cu can retard the oxygen transport to the surface of the steel. Obviously, there have been many works revealing the effect of Cu on the corrosion resistance of steel. However, less work related to the thermodynamic study was conducted. Generally, corrosion of steel involves the transformation of iron to ore states, the formation of rust and compounds, and the flow of electrons [4]. Evidently, all of them are related to chemical and electrochemical reactions. Thus, to gain a better understanding of the corrosion behavior of Cu-bearing steel, chemical and electrochemical thermodynamic of corrosion reactions should be taken into consideration.

In recent years, the thermodynamic analytical approach purposed by Marcel Pourbaix has been developed [5-6]. The method can indicate the specific ranges of potential and pH in which metals are subjected to corrosion and other ranges where metals can be protected against corrosion [7]. This method has been proven to be useful and accepted for over 70 types of metals [8]. Thus, applying this approach to investigate the corrosion behavior of Cu-bearing steel is of great interest and the obtained would be useful to fill some research gaps. In this work, the thermodynamic consideration of possible electrochemical and chemical reactions was performed using Nernst's equation and the calculated free energy change and the results were presented in the graphical information. Besides, the analysis based on the graphical information was given and discussed.

2. Investigation approach

The investigation approach used in this research was composed of the chemical and electrochemical thermodynamic considerations as follows:

2.1 Electrochemical thermodynamic consideration

The corrosion process of steel is always related to the electrochemical reaction dealing with the transport of electrons. Equation 1 shows the general equation of the electrochemical reactions considered in this work [9].



Where a and b refer to the number of moles of reactant R and H₂O

c and d refer to the number of moles of product P and H⁺

n refers to the number of electrons transferred in this equation

Then Nernst's equation at 25 °C and 1 atm can be used as given in Equation 2.

$$E = E^0 + \left(\frac{0.059}{n}\right) \log \left(\frac{a_P^c a_{H^+}^d}{a_R^a a_{H_2O}^b}\right) \quad (2)$$

Where

E and E⁰ refer to the electrode potential and standard electrode potential (Volt)

a_i is the activity of the ith species, which can be described as follows [6]:

- For solid, a = 1
- For liquid H₂O, a = 1
- For other liquid and ions, a = concentration

and

$$pH = -\log a_{H^+} \quad (3)$$

$$E^0 = \frac{\Delta G^0}{nF} \quad (4)$$

Where

ΔG⁰ is standard free energy change

F is Faraday's constant (23,060 Cal Volt⁻¹)

Then, the equation for electrochemical reactions used in this investigation can be obtained.

$$E = \frac{\Delta G^0}{nF} + \left(\frac{0.059}{n}\right) \log \left(\frac{a_P^c}{a_R^a}\right) + \frac{[-0.059d]}{n} pH \quad (5)$$

2.2 Chemical consideration

The general equation of chemical reactions involved in the corrosion of steel can also be referred to Equation 1. To consider the change of standard free energy (ΔG⁰) at 25 °C in equation 1, Van't Hoff equation was employed as displayed in Equation 6. The equilibrium constant (K) for reactions which involve dissolved species or solid species is also given in Equation 7.

$$\Delta G^0 = -RT \ln K = -2.303 \times 1.987 \times 298 \log K \quad (6)$$

$$K = \left(\frac{a_P^c a_{H^+}^d}{a_R^a a_{H_2O}^b} \right) \quad (7)$$

2.3 Thermodynamics information of species related to corrosion of Cu-bearing steel

To use the thermodynamic approach to investigate the corrosion behavior of Cu-bearing steel, standard Gibbs free energy of species related to the corrosion process of interest should be well prepared. For iron corroded in water at 25 °C, its corrosion process is mainly related to the reaction of iron and H₂O, resulting in the formation of important dissolved ions, such as Fe²⁺, Fe³⁺, and HFeO₂⁻ [10]. The solid species, i.e. Fe₃O₄ and Fe₂O₃ are also formed in the corrosion process of iron in water [11]. Thus, obtaining standard Gibbs free energy values of formed species is vital for the corrosion behavior of iron in water at 25 °C and they are concluded in Table 1. For the corrosion of Fe containing Cu, the corrosion reaction causes the formation of Fe²⁺, Cu²⁺ and CuFeO₂. The reaction of CuFeO₂ with H₂O can form FeOOH and CuO₂²⁻ [12]. Table 2 provides standard Gibbs free energies of species related to the corrosion of steel containing Cu in water at 25 °C.

Table 1 The standard Gibbs free energy of species formed in Fe-H₂O system at 25 °C [13-14]

	Formula	ΔG° (Cal/mole)
Solvent	H ⁺	0
	H ₂	0
	H ₂ O	-56,474
	O ₂	0
Solid	Fe	0
	Fe ₃ O ₄	-241,774
	Fe ₂ O ₃	-176,425
Dissolved species	Fe ²⁺	-18,786
	Fe ³⁺	-2,530
	HFeO ₂ ⁻	-90,282

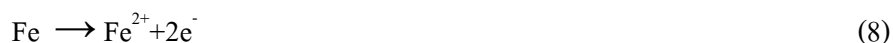
Table 2 The standard Gibbs free energy of species formed in Fe-Cu-H₂O system at 25 °C [13-14]

	Formula	ΔG° (Cal/mole)
Solvent	H ⁺	0
	H ₂ O	-56,474
Solid	Cu	0
	Fe ₃ O ₄	-241,774
	CuFeO ₂	-127,512
	CuO	-30,880
	FeOOH	-115,548
Dissolved species	Fe ²⁺	-18,786
	Cu ²⁺	-15,593
	CuO ₂ ²⁻	-43,714

3. Results

3.1 Thermodynamic consideration of Fe-H₂O at 25 °C

As Fe is subjected to corrosion in water, reactions listed below may occur [5-6, 15].



The concept of electrochemical thermodynamic and chemical consideration should be applied to gain the insight in the corrosion behavior of iron in the water. Some examples of calculation to gain the significant equations can be considered as follows:

Computation of Equation 8

As iron is dissolved, oxidation can occur, as shown in equation 8. This reaction is related to the transfer of electrons and electrochemically proceeds without H^+ as a reactant. Thus, equation 4 can be applied. Because a_{Fe} is equal to 1, no H^+ involves in the reaction, and E^0 is known as -0.44 Volts [8]; equation 4 can be modified as given in Equation 17. After computing, we obtain Equation 18.

$$E = -0.44 + \left(\frac{0.059}{2}\right) \log\left(\frac{a_{Fe^{2+}}}{1}\right) + \frac{[-0.059 \times 0]}{2} pH \quad (17)$$

$$E = -0.44 + 0.0295 \log(a_{Fe^{2+}}) \quad (18)$$

Computation of Equation 9

The reaction of iron and water can from Fe_3O_4 [15] as shown in Equation 9. Evidently, this reaction also involves the release of H^+ and e^- as products of the reaction. Using Equation 4, we obtain Equations 19 and 20.

$$E = \frac{-15,878}{8 \times 23,060} + \left(\frac{0.059}{8}\right) \log\left(\frac{a_P^c}{a_R^a}\right) + \frac{[-0.059 \times 8]}{8} pH \quad (19)$$

$$E = -0.085 - 0.059 pH \quad (20)$$

Computation of Equation 16

The reaction of Fe^{3+} with H_2O causes the formation of Fe_2O_3 and the release of H^+ [15]. Obviously, there are no electrons transferred in this reaction. Thus, the equilibrium constant (K) listed in Equation 7 can be applied as rewritten in Equation 21.

$$K = \left(\frac{a_{H^+}^6}{a_{Fe^{3+}}^2}\right) \quad (21)$$

$$\log K = -6 \log(pH) - 2 \log(a_{Fe^{3+}}) \quad (22)$$

Modifying Equation 6, we obtain Equation 23.

$$\log K = \left(\frac{-\Delta G^0}{2.303 \times 1.987 \times 298}\right) = \left(\frac{1,943}{1,363.67}\right) = 1.425 \quad (23)$$

Substituting in Equation 22, we gained Equation 24.

$$\log(a_{Fe^{3+}}) = -0.72 - 3pH \quad (24)$$

Table 3 Reactions, equations and line number used in the thermodynamic consideration of Fe-H₂O at 25 °C

Reactions	Equation	Line number
$Fe \rightarrow Fe^{2+} + 2e^-$	$E = -0.44 - 0.0295 \log(a_{Fe^{2+}})$	1
$Fe^{2+} \rightarrow Fe^{3+} + e^-$	$E = 0.77 + 0.059 \log(a_{Fe^{3+}} / a_{Fe^{2+}})$	2
$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+$	$\log(a_{Fe^{3+}}) = -0.72 - 3pH$	3
$2Fe^{2+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 2e^-$	$E = 0.73 - 0.18pH - 0.059 \log(a_{Fe^{2+}})$	4
$3Fe^{2+} + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 6e^-$	$E = 0.98 - 0.24pH - 0.089 \log(a_{Fe^{2+}})$	5
$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e^-$	$E = -0.085 - 0.059 \log(a_{Fe^{2+}})$	6
$2Fe_3O_4 + 2H_2O \rightarrow 2Fe_2O_3 + 2H^+ + 2e^-$	$E = 0.22 - 0.059pH$	7
$3HFeO_2^- + H^+ \rightarrow Fe_3O_4 + 2H_2O + 2e^-$	$E = -1.8 + 0.03pH - 0.09 \log(a_{HFeO_2^-})$	8
$Fe + 2H_2O \rightarrow HFeO_2^- + 3H^+ + 2e^-$	$E = 0.49 - 0.089pH + 0.03 \log(a_{HFeO_2^-})$	9

Table 3 shows a list of equations, which can be used to plot the potential-pH diagram for Fe corroding in water at 25 °C. The concentration of related species was assumed to be 10⁻⁴ mol/L.

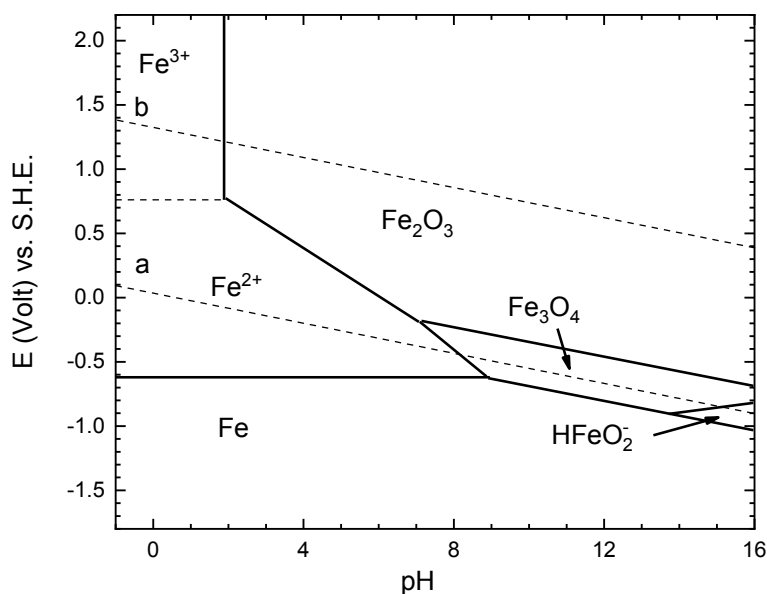


Figure 1 Potential-pH diagram of Fe corroding in water at 25 °C.

3.2 Thermodynamic consideration of Cu-bearing Steel in water at 25 °C

As steel alloyed with Cu is subjected to corrosion in water, Cu electrochemically reacts with Fe^{2+} -containing water and moist Fe_3O_4 to form CuFeO_2 [16]. Besides, the chemical reaction of Cu^{2+} and Fe^{2+} , including water, can provide the formation of CuFeO_2 [17]. Normally, CuFeO_2 is not stable and can further react with water and H^+ to form FeOOH [15]. All reactions can be considered in the same way as performed in Fe- H_2O system [18-22] and the reactions, the equations and line number are listed in Table 4.

Table 4 Reactions, equations and line number used in the thermodynamic consideration of CuFeO_2 at 25 °C

Reactions	Equation	Line number
$\text{Cu} + \text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{CuFeO}_2 + 4\text{H}^+ + 2\text{e}^-$	$E = 0.38 - 0.118\text{pH} - 0.0296\log(a_{\text{Fe}^{2+}})$	1
$3\text{Cu} + \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} \rightarrow 3\text{CuFeO}_2 + 4\text{H}^+ + 4\text{e}^-$	$E = 0.13 - 0.059\text{pH}$	2
$\text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{CuFeO}_2 + 4\text{H}^+$	$1.38243 = 4\text{pH} + \log[(a_{\text{Fe}^{2+}})(a_{\text{Cu}^{2+}})]$	3
$\text{CuFeO}_2 + \text{H}_2\text{O} \rightarrow \text{FeOOH} + \text{CuO} + \text{H}^+ + \text{e}^-$	$E = 1.06 - 0.059\text{pH}$	4
$\text{CuFeO}_2 + 2\text{H}_2\text{O} \rightarrow \text{FeOOH} + \text{CuO}_2^{2-} + 3\text{H}^+ + \text{e}^-$	$E = 2.96 - 0.18\text{pH} + 0.059\log(a_{\text{CuO}_2^{2-}})$	5
$\text{CuFeO}_2 + \text{H}^+ \rightarrow \text{Cu}^{2+} + \text{FeOOH} + \text{e}^-$	$E = 0.62 + 0.0592\text{pH} + 0.059\log(a_{\text{Cu}^{2+}})$	6

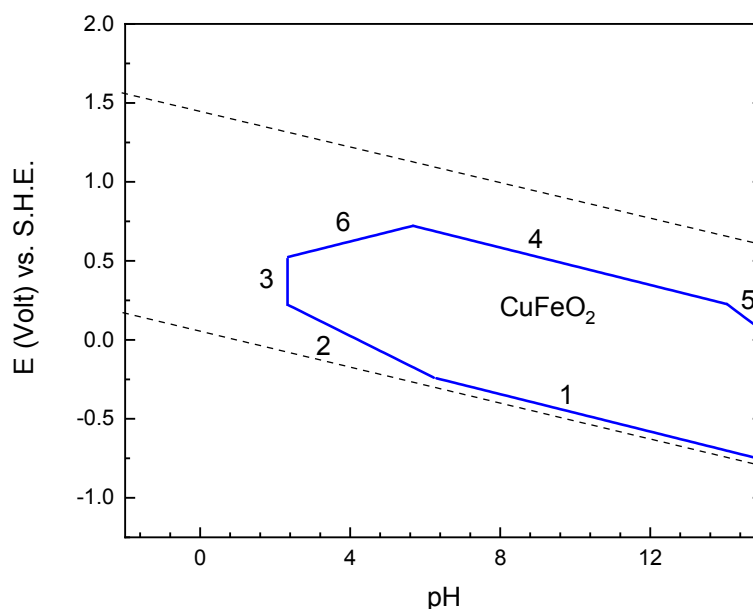


Figure 2 Potential-pH diagram of CuFeO_2 at 25 °C.

The potential-pH diagram of Cu-bearing steel in water at 25 °C can be obtained by placing Figure 2 over Figure 1, as displayed in Figure 3. The concentration of species related to the corrosion of Cu-bearing steel was supposed to be 10^{-4} mol/L.

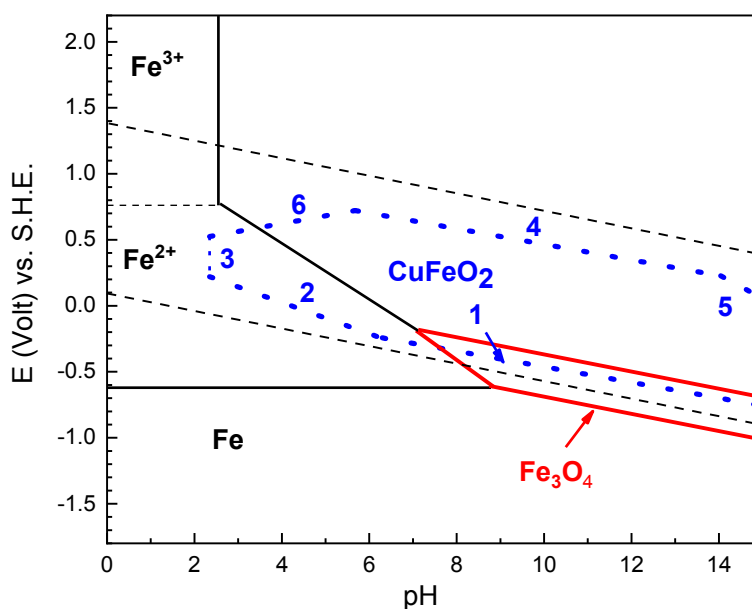


Figure 3 Potential-pH diagram of Cu-bearing Steel corroded in water at 25 °C.

It is obvious from Figure 3 that CuFeO_2 can be set up on the steel surface for almost pH value. At the same time, Fe_3O_4 can also be formed at the middle to high pH value. The overlap region of FeCuO_2 and Fe_3O_4 is clearly observed, meaning that both compounds would coexist in the precipitated rust covering the steel surface. Usually, the presence of Cu ions in the rust layers can lower the conductivity of the rust. In addition, Cu ions in the rust can retard the transport of oxygen. Therefore, this kind of rust would improve the anti-corrosion efficiency of Cu-containing steel in a slightly acidic to a high alkaline environment.

4. Conclusion

In this work, electrochemical and chemical thermodynamic considerations were conducted using Nernst's equation and Van't Hoff equation to set up two sets of thermodynamically significant equations. The obtained equations were then employed to construct potential-pH diagram, where the investigation of corrosion behavior of Cu-bearing steel can be performed. It is found from the obtained diagrams that CuFeO_2 can be formed on the steel substrate for almost pH value. Fe_3O_4 appears from the middle to high pH value. The region in which CuFeO_2

and Fe_3O_4 overlap is clearly found. The overlap region of both compounds indicates the enhanced anti-corrosion performance of Cu-containing steel used in the slightly acidic to high alkaline environment.

Acknowledgement

The authors would like to thank Professor Dawei Zhang, University of Science and Technology Beijing, for the useful discussion for establishing the equations.

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