

Review on theoretical calculation of the magnetite solubility

Myong-Jin Kim*, Hong Pyo Kim

Nuclear Materials Research Division, Korea Atomic Energy Research Institute, 1045 Daedeokdaero, Yuseong,
Daejeon, Republic of Korea

*Corresponding author: mjkim@kaeri.re.kr

1. Introduction

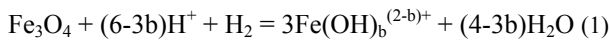
Flow accelerated corrosion (FAC) causes severe damage to secondary piping systems. An accident from FAC occurred at the Oyster Creek nuclear power plant (NPP) in 1978. Other NPPs like Surry 2 and Mihama 3 have also experienced an FAC that induced damage to the carbon steel piping [1]. FAC is influenced by many factors such as water chemistry (temperature, pH, dissolved oxygen (D.O.) in a solution, and etc.), chemical composition of carbon steel, and fluid dynamics [2]. Magnetite is formed at the inner surface of carbon steel, and protects the integrity of pipes from the damage. The magnetite has a stable state at each equilibrium condition, so that it can be dissolved into the fluid under conditions that satisfy the equilibrium state. The iron solubility can be calculated by considering the reaction equilibrium constants for prediction of a change in the magnetite layer.

In the present work, studies on the magnetite solubility were reviewed for the theoretical calculation of magnetite, and iron solubility data were compared to find the proper solubility values of each study.

2. Theoretical calculations and results

2.1 Theoretical calculations

P. R. Tremaine et al. [3] calculated the solubility of magnetite in H₂O and D₂O to 300°C from Gibbs free energy and entropy data for ferrous ions. The chemical reaction of the magnetite dissolution is expressed as follows.



The concentration of each ferrous species was calculated from the chemical reaction (2).

$$\log(m_b \gamma_b) = \frac{1}{3} \left[\frac{-\Delta G_R^\circ}{2.3025RT} - (6-3b)\text{pH}_T + \log\left(\frac{P_{\text{H}_2}}{0.10132}\right) \right] \quad (2)$$

where $0 \leq b \leq 4$ and γ_b is the activity coefficient.

The solubility calculation of magnetite was performed by K. Dinov et al. [4] on the thermodynamic data. The solubility of magnetite is given by the sum of all ferrous and ferric species as the following expression.

$$[\text{Fe}]_T = [\text{Fe}^{2+}] \left\{ 1 + \sum_{m'} \frac{K_{m'}}{[\text{H}^+]^{m'}} \right\} + [\text{Fe}^{3+}] \left\{ 1 + \sum_{n'} \frac{K_{3n'}}{[\text{H}^+]^{n'}} \right\} \quad (3)$$

where $m' = 1, 2, 3$, $n' = 1, 2$.

G. Rocchini [5] proposed the calculation equation of magnetite solubility using the equilibrium constants based on the work of Sweeton and Baes [6]. The concentration of iron and the equilibrium constants are expressed as follows.

$$Q = (K_0 x^2 + K_1 x + K_2 + K_3 x^{-1}) p^{1/3} \quad (4)$$

$$\ln K_b = -\frac{A_b}{RT} + \frac{B_b}{R} (\ln T - 1) + \frac{D_b}{R} \quad (5)$$

where K is the equilibrium constants, A, B, and D are constants, and R is a gas constant.

K. Fujiwara et al. proposed the FAC model in consideration of the diffusion of soluble iron and chromium species, dissolved hydrogen, and dissolved oxygen [2]. In this model, the solubility of iron was calculated using the equilibrium constants of Fe²⁺, Fe(OH)⁺, Fe(OH)₂, Fe(OH)₃⁻, Cr(OH)₄⁻, hydrogen ion concentration, and partial pressure of hydrogen. The derived equation of iron solubility, hydrogen ion concentration (pH effect), and P_{H₂} are expressed by Eqs. (6), (7), (8), respectively.

$$S_{\text{Fe}} = \frac{P_{\text{H}_2}^{1/3}}{K_{\text{Fe}_3\text{O}_4}^{1/3}} \left([\text{H}^+]^2 + K_{\text{Fe},1} [\text{H}^+] + K_{\text{Fe},2} + \frac{K_{\text{Fe},3}}{[\text{H}^+]} \right) \quad (6)$$

$$f(1) + f(2) - \frac{K_{\text{Cr},4}}{[\text{H}^+]} = 0 \quad (7)$$

$$P_{\text{H}_2} = \left\{ \frac{U K_{\text{Henry},\text{H}_2}}{C_{\text{H}_2\text{O}} K_{\text{Fe}_3\text{O}_4}^{1/3}} \frac{a_{\text{H}_2}}{a_{\text{Fe}}} f(3) \right\}^{2/3} \quad (8)$$

Where K_x is an equilibrium constant, and f(1), (2), and (3) are equations as a function of [H⁺].

The calculated magnetite solubility from above studies at pH_{298K} 7 is shown in Table 1. The variation is slightly

presented in the results of these studies because parameters such as equilibrium constants and thermodynamic data were used from different references.

Table I: The calculated magnetite solubility at $\text{pH}_{298\text{K}} 7$, log [Fe] mol/kg

T (K)	Tremaine	Fujiwara	Rocchini
373	-5.2 ~ -5.5	-6.0	-5.6
423	-5.2 ~ -5.7	-6.5	-6.1
473	-5.3 ~ -6.0	-7.0	-6.9

2.2 Magnetite solubility with Temperature

The equilibrium constant of iron is changed with an increase in temperature. F. H. Sweeton and C. F. Baes, Jr. performed a calculation of the solubility of magnetite at an elevated temperature [6]. The solubility of magnetite was at maximum at a neutral or base solution temperature of 363 K. K. Fujiwara et al. calculated the thermodynamic solubility of iron in a temperature range of 298 ~ 473 K [2]. In this calculation, the FAC rate by dissolving Fe_3O_4 had a maximum value at 413K. P. R. Tremaine and J. C. LeBlanc had reported the magnetite solubility decreased with an increase in a temperature range of 350 - 573 K at pH 9.3 [7].

2.3 pH effect

The iron solubility is influenced by the dissolved hydrogen concentration. F. Fujiwara et al. reported that the iron solubility decreased with an increase in pH at 298K [2]. Also, Bignold et al. [8], Heitman and Kastner [9] reached a similar result in that the FAC rate decreased at a $\text{pH}_{298\text{K}}$ higher than 9.2. caused by a reduction of the iron solubility.

3. Summary

The theoretical calculation studies of magnetite solubility were reviewed to predict the FAC rate. There are some variations in the calculated results caused using different sources of input parameters. The theoretical calculation will be compared with the experimental data at an elevated temperature in future work.

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