Precipitation Kinetics of Ferrous Oxalate in Oxalic Acid Depending on Hydrogen Peroxide and Iron Catalyst for NPP Chemical Decontamination

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1. Introduction

Chemical decontamination is to remove the magnetite oxide film in PWR by dissolving it with a chemical reagent. The oxalic acid as a representative decontamination reagent, can dissolve magnetite oxide into aqueous ferrous oxalate, but the ferrous oxalate change slowly into ferrous oxalate hydrate which is subject to precipitation.

The previous studies so far have investigated the precipitation behavior of ferrous oxalate in the system containing chemical agents such as sulfuric and phosphoric acid which cause an increase in solubility of ferrous oxalate. In this study, the ferrous oxalate system consists of Fe^{2+}- oxalate - water by dissolving magnetite in oxalic acid. Therefore, the solubility of ferrous ions was limited by the concentration of oxalic acid which also influences its precipitation behavior.

2. Methods and Results

The precipitation behavior of aqueous ferrous oxalate in oxalic acid was studied changing the system concentration and temperature experimentally and also theoretically.

2.1 Chemical equilibrium and solubility characteristics of ferrous-oxalate system.

Ferrous oxalate system was prepared by reductive dissolution of magnetite in oxalic acid as in the Eq (1) ;

$$Fe_3O_4 + 4\ H_2C_2O_4 \rightarrow 3\ Fe^{2+} + 3\ C_2O_4^{2-} + 2\ CO_2 + 4\ H_2O \ldots\ldots(1)$$

The chemical equilibrium of reductive dissolution of magnetite in oxalic acid of 20[mM/L] at 25℃ was simulated by Visual Minteq code and the result is shown in Figure 1. The concentration of total ferrous ions is 3 times of magnetite as in the Eq(1). The equilibrium showed that an increase of ferrous concentration decreases in the residual oxalate due to ferric ion reduction and at the maximum of aqueous ferrous oxalate concentration, the ferrous concentration is 15[mM/L] which is the same with the residual oxalate as in Eq(1). Therefore the maximum ferrous concentration, $Cmax\_Fe^{2+}$ in Co_Ox is as in the Eq(2)

$$Cmax\_Fe^{2+} = C\_Ox,$$
$$\text{where } C\_Ox = Co\_Ox - Cmax\_Fe^{2+}/3 \ldots\ldots(2)$$

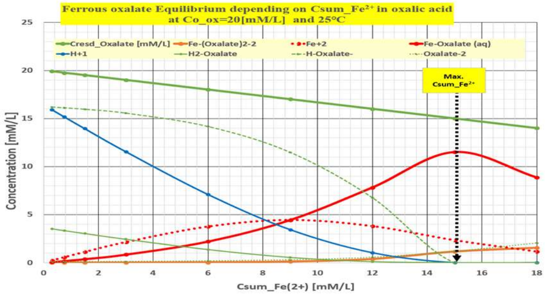


Fig. 1. Chemical equilibrium depending on magnetite concentration in oxalic acid of 0.02 [M/L] at 25, before precipitation by Visual Minteq.

In general, the precipitation behavior of a supersaturated solution is determined by the solubility of the precipitate according to the solution concentration and temperature. For the precipitation behaviour of this ferrous oxalate system, not only the solubility but also the maximum soluble ferrous concentration in oxalic acid were considered as important precipitation variables. Therefor a new pseudo saturation parameter, $S = Co\_Fe^{2+}/C\_Ox$ was proposed as an indicator of precipitation parameter.

The fast and slow fraction crystal growth model was proposed as follows;

- dX/dt = (1-w)*kf *X + w*ks*X
  IC: X(0) = 1

X(t) = (1-w)* exp(-kf*t) + w* exp(-ks*t),
where X = (C_Fe-C*_Fe)/(Co_Fe-C*_Fe),
Co_Fe, C*_Fe is initial and solubility conc,
w is slow precipitation fraction,
kf, ks is fast and slow precipitation rate constant, respectively……………………………………(3)

2.2 Concentration dependency of ferrous oxalate precipitation kinetics

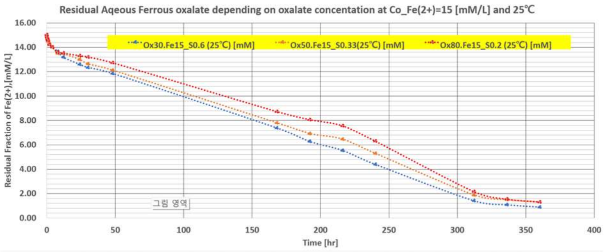
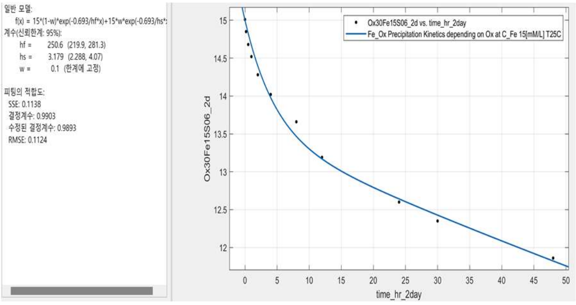


Fig. 2. the residual ferrous concentration depending on oxalate at C_Fe=15[mM/L] and 25℃ for 15 days.

Fig. 2 shows that the solubility of C_Fe(2+) at C_Ox of 30 to 80 [mM/L] and 25℃ is around 1[mM/L] which is far less than that in water. The figure 2 also shows that the precipitation of ferrous oxalate proceeds rapidly in the beginning and then precipitates slowly.

The precipitation behavior depending on pseudo saturation, S at Co_Fe of 15[mM/L] and 25℃ shows that the greater pseudo saturability, the faster precipitation.



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일반 모델:
    f(x) = 15*(1-w)*exp(-0.693/hf*x)+15*w*exp(-0.693/hs*:
계수(신뢰한계: 95%):
      hf =       250.6  (219.9, 281.3)
      hs =       3.179  (2.288, 4.07)
      w =          0.1  (한계에 고정)

피팅의 적합도:
  SSE: 0.1138
  결정계수: 0.9903
  수정된 결정계수: 0.9893
  RMSE: 0.1124
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Fig. 3. Comparison of experimental and model results for ferrous oxalate precipitation at C_ox=30, C_Fe=15 and 25℃ for 2days.

Fig. 3 is an example of simulation of ferrous oxalate precipitation which shows that the proposed model agrees well with the experimental results.

2.3 Temperature dependency of ferrous oxalate precipitation kinetics

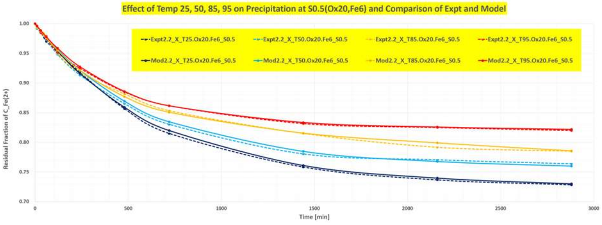

Fig. 4. Comparison of experimental and model results for ferrous oxalate precipitation behaviour depending on temperature at C_ox =20 and C_Fe=6 [mM/L].

The above figure shows that the proposed model agrees well with the experimental results and the experimental results were in good agreement with the precipitation behavior according to the temperature of the supersaturated solution.

3. Conclusions

As part of the chemical decontamination of PWR system, the ferrous oxalate precipitation kinetics were studied by reductive dissolution of magnetite oxide in oxalic acid. Within the scope of the experiment, the following conclusions were drawn:

1. The more pseudo saturability of ferrous ions in oxalic acid, the faster precipitation at a constant ferrous ion concentration.
2. The proposed fast and slow growth crystallization model agrees well with the experimental results.

ACKNOWLEDGEMENT

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