Effect of Raw Amount of CuSO4 on Precipitation of Cu2O in the HyBRID Decontamination of Magnetite

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1. Introduction

The removal of radioisotopes from the primary coolant system of a nuclear power plant takes place with the dissolution of corrosion metal oxide layers deposited with the radioisotopes. Chemical decontamination by oxidative and reductive dissolution is considered to be the most effective method to date. KAERI has developed the HyBRID process without using any organic acids or organic chelating agents [1]. The solution containing sulfuric acid (H2SO4), hydrazine (N2H4), and copper sulfate (CuSO4) provided the acidic and reductive dissolution of transition metal ions from the corrosion metal oxides. Since the HyBRID decontamination process does not use any organic chelates, precipitates of metal ions can be formed as the solution pH changes. Under a reducing condition, Cu2+ ions may form precipitates of Cu2O or be hydrolyzed into Cu(OH)2 precipitates. Thus it is important to find the conditions at which no precipitation of Cu2O or Cu(OH)2 is formed.

In this work we studied the effect of the concentration of copper ions in the HyBRID aqueous solution on the formation of Cu2O or Cu(OH)2 precipitates for the HyBRID dissolution of magnetite. Raw amount of CuSO4 was changed in order to control the concentration of copper ions.

2. Reaction Scheme and Calculation Method

The key reactions of the HyBRID dissolution of magnetite are as follows:

\[
\begin{align*}
    3Fe_2O_3 + 4H_2SO_4 & \rightarrow 3Fe^{2+} + 2Fe^{3+} + 4SO_4^{2-} + 4H_2O \\
    2CuSO_4 + \frac{1}{2}N_2H_4 & \rightarrow 2Cu^{2+} + 2SO_4^{2-} + \frac{1}{2}N_2 + 2H^+ \\
    Fe^{2+} + Cu^{+} & \rightarrow Fe^{2+} + Cu^{2+} \\
    3Fe_2O_4 + 2CuSO_4 + \frac{1}{2}N_2H_4 + 4H_2SO_4 & \rightarrow 3Fe^{2+} + 2Cu^{2+} + 6SO_4^{2-} + \frac{1}{2}N_2 + 2H^+ + 4H_2O
\end{align*}
\]

Cu2+ are reduced by N2H4 to produce Cu+. The resulting Cu+ are oxidized to Cu2+ after reducing the Fe3O4 layer, and the Cu2+ are rapidly reduced to Cu+ by N2H4, thereby completing redox cycling. N2H4 participates in the reaction pathway of reducing Fe3+ to Fe2+ and simultaneously regenerating oxidized Cu2+ into Cu+. During the cycle of Cu+ ions to Cu2+ ions, the released electrons promote the reduction of Fe3+.

To determine the effect of the concentration of copper ions in the HyBRID dissolution of magnetite, the E-pH (Pourbaix) diagram for Cu was first constructed and then compared with the equilibrium composition and pH of the solution. The E-pH diagram shows the thermodynamic stability areas of different species as functions of pH and potential scales in an aqueous solution. Thus, the E-pH diagram for Cu shows the stability areas where species and ions such as Cu+, Cu2+, Cu2O, Cu(OH)2 are present depending on the pH and the redox potential. The E-pH module in the HSC Chemistry® version 9 [2] was used to construct the E-pH diagram. The module is based on STABCAL (Stability Calculations for Aqueous Systems) developed by Huang [3].

Calculation of the multicomponent equilibrium compositions in heterogeneous systems like the HyBRID dissolution of magnetite was conducted using the GEM module of the HSC Chemistry® 9. The equilibrium composition was calculated using the GIBBS solver, which used the Gibbs energy minimization method. In aqueous solution, the Pitzer model was used to calculate mean activity coefficients of the aqueous species [4]. Gas is assumed to behave as ideal mixture. The Pitzer parameters were obtained from the HSC AQUA Pitzer database [2].

3. Results and Discussion

Fig. 1 shows the E-pH diagrams for Cu constructed at a constant temperature of 95°C and at different concentrations of Cu. It gives the pH values at the boundaries between the region where Cu exists in the form of Cu+ ion exist and the region where Cu exists in the form of Cu2O solid. The pH values vary depending on the total concentration of Cu. Fig. 2 illustrates the relationship between the pH value and the Cu concentration at two boundaries between stability areas. The pH value decreased linearly with increasing the Cu concentration. Since the species affecting the magnetite dissolution is Cu+ ions, it is important to adjust so that the Cu+ ions do not change to Cu2+, Cu2O(s), or Cu(OH)2(s). To prevent the Cu+ ions from being oxidized to the Cu2+ ions, the redox potential should be lower than 0.2 V by adding N2H4. In order to prevent precipitation of Cu+ ions into Cu2O(s), the pH of the solution should be made sufficiently low.

The equilibrium calculations were conducted at the experimental conditions given in Table 1. Raw amount of CuSO4 changed from 5 × 10−4 to 1 × 10−1 mol. Raw amounts of Fe2O3, N2H4, and H2SO4 in the feed were kept constant. Fig. 3 shows the effect of the raw amount of CuSO4 on the amount of Cu2O precipitates produced in the HyBRID dissolution of magnetite. At very low amounts of CuSO4, no precipitation of Cu2O
occurred. However, precipitation of Cu$_2$O was apparent at higher amounts of CuSO$_4$. The amount of Cu$_2$O produced increased with the increase of the raw amount of CuSO$_4$ and decreased with the increase of the temperature.

Table 2 shows the equilibrium amounts of Cu$_2$O and Cu(OH)$_2$ and the solution pH values calculated at different raw amounts of CuSO$_4$ at 95°C. The pH values at the boundaries between the areas of Cu$^+$ and Cu$_2$O obtained from the E-pH diagrams (Fig. 1) are also listed in Table 2. Precipitation of Cu(OH)$_2$ did not occur at any CuSO$_4$ amounts. The solution pH decreased with the increase of the raw amount of CuSO$_4$. When the raw amount of CuSO$_4$ was less than $1 \times 10^{-2}$, there was no precipitation of Cu$_2$O because the solution pH was lower than the pH value obtained from the E-pH diagram. However, at the raw amounts of CuSO$_4$ higher than about $1.6 \times 10^{-2}$, the solution pH was higher than the pH value from the E-pH diagram, causing the precipitation of Cu$_2$O.

![Fig. 1. E-pH diagrams for Cu at 95°C.](image)

![Fig. 2. The pH values at the boundaries between stability area as a function of Cu concentration at 95°C.](image)

Table 2. Recipe of experiments for the HyBRID dissolution of magnetite

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Phase</th>
<th>Raw amount [mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$</td>
<td>solid</td>
<td>$2.16 \times 10^{-4}$ (0.05 gram)</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>aqueous</td>
<td>0.03377</td>
</tr>
<tr>
<td>N$_2$H$_4$</td>
<td>aqueous</td>
<td>0.05791</td>
</tr>
<tr>
<td>CuSO$_4$</td>
<td>solid</td>
<td>$5 \times 10^{-4} - 1 \times 10^{-1}$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>aqueous</td>
<td>55.5 (1 liter)</td>
</tr>
</tbody>
</table>

4. Conclusion

The effect of the concentration of copper ions in the HyBRID solution on the formation of Cu$_2$O or Cu(OH)$_2$ precipitates was studied in the HyBRID dissolution of magnetite. The pH values at which the coexistence of Cu$^+$ and Cu$_2$O(s) occurred were found by preparing the E-pH diagram with varying Cu concentration at a constant temperature (95°C). According to the results of the equilibrium calculations for the aqueous system of the HyBRID dissolution of magnetite, precipitation of Cu$_2$O occurred at a high amount of CuSO$_4$ added into the solution and there was no precipitation of Cu(OH)$_2$ at any raw amounts of CuSO$_4$. To prevent precipitation of Cu$^+$ ions into Cu$_2$O(s), the amount of CuSO$_4$ added into the HyBRID solution should be adjusted so that the pH of the solution is less than the pH value found in the E-pH diagram.

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REFERENCES