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Correlation Study of Magnetite Dissolution in HyBRID Decontamination Process

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1. Introduction

In nuclear reactor system especially the reactor coolant system, inner surface corrosion products are often troublesome in the efficiency of power generation and maintenance of the system. In the operating plants, the localized corrosion on SG tubes which are transporters of thermal energy to the secondary side lowers the reduction heat transfer efficiency as well as degrades the lifetime of SG [1]. Moreover, the accumulated corrosion products containing radioactive materials inside corrosion layers bring about the difficulty of periodic maintenance or life-end decommissioning work due to the increased background radioactive field. Therefore the corrosion products are considered unfavorable and to be removed.

Magnetite, Fe_3O_4, is a commonly found corrosion product on the inner surface of reactor coolant system. Simply magnetite can be reduced to hematite, Fe_2O_3, and further to iron when oxygen is limited or ample reducing agents are supplied. Along this line, number of decontamination processes has been developed since 1970s and most of them contain organic acid and additive chelating agents. However, many reports have pointed out the negative environmental effect of those chemicals, and currently there are new approaches to overcome the limited decontamination efficiency and large volume of secondary waste from other alternate processes without using such those organic chemicals.

In the present study, we investigate HyBRID (Hydrazine-Based Reductive metal Ion Decontamination) solution as a new decontamination process, and applied statistical correlation approaches as a preliminary study toward the empirical modeling of the magnetite dissolution in HyBRID solution. Correlation study is one of the most used techniques for investigating the relationship between variables. It quantifies the strength of the linear relationship of a pair of variables even though correlation does not identify the causation between variables. In this study, we investigated the correlation of magnetite dissolution and some independent variables in terms of chemical concentration, pH, temperature, or amount of catalysts. Some experimental results previsouly published were reprocessed for this correlation studies in which we also highlight the effect of added copper(II) ion as a catalyst of redox mechanism [2, 3].

2. Methods and Results

2.1. Reductive Dissolution Mechanisms of Magnetite

A unit cell of magnetite, $(Fe^{3+}Fe^{2+}Fe^{3+})O_4$, has oxygen ions in a perfect cubic close-packed array. The tetrahedral sites are occupied by half of the Fe^{3+} ions and octahedral sites are occupied by the Fe^{2+} and the remaining half of the trivalent iron. The reductive dissolution of magnetite in HYBRID solution is initialized by the protonation of oxygen on the magnetite surface (eq. (1)) resulting positive charge and relaxed bond between metal and oxygen. This relaxed bond later takes non-reductive dissolution to form soluble Fe^{2+} and H_2O by taking metal hydrazine complexes as eq. (2). This type of bridging or chelating reaction retains a basic site of $N_2H_5^+$ to be capable of coordination which is reducing reaction in the oxidizing solution.

$$\text{Fe(III)-O} + \text{H}^+ \longleftrightarrow \text{Fe(III)-O}\cdots\text{H}^+ \tag{1}$$

$$\begin{aligned} &2[\text{Cu}^+ - \text{N}_2\text{H}_5^+] + 8\text{H}^+ + (\text{Fe}^{3+})_2\text{Fe}^{2+}\text{O}_4 \\ &\longrightarrow 2[\text{Cu}^{2+} - \text{N}_2\text{H}_5^+] + 3\text{Fe}^{2+} + 4\text{H}_2\text{O} \end{aligned} \tag{2}$$

2.2. Correlation study of Magnetite Dissolution

As a preliminary study for empirical modeling of dissolution magnetite, correlation study was used to investigate the relationship between related variables and dissolution ratio. In magnetite dissolution, the general aspects of the model are the acidic strength, concentration of reducing agents, and other operating variables such as temperature and reaction time. Chelate formation and precipitation of added chemicals are expected implicitly, variables on those mechanisms were not considered in this study.

2.2.1. Correlation between two variables

Pearson's correlation coefficient was used to measure the dependence of each variable and dissolution ratio and the formulation is given in eq. (3),

$$\begin{aligned} \rho_{X,Y} &= \text{corr}(X,Y) = \frac{\text{cov}(X,Y)}{\sigma_X \sigma_Y} \\ &= \frac{E[(X-\mu_X)(Y-\mu_Y)]}{\sigma_X \sigma_Y} \end{aligned} \tag{3}$$

where E(X) is the expected value of X variable, μX a mean value of a set of X variables, σX a standard deviation of a set of X variables, and cov and corr are alternative formula notation of covariance and correlation respectively.

2.3. Correlation of pH and magnetite dissolution without copper(II) ion

As described earlier, magnetite dissolution is known to be enhanced as the solution acidity is getting stronger due to the protonation of oxygen. Additionally lower pH prevents the precipitation of dissolved magnetite in the form of other Fe salts. The dissolution fraction in terms of pH is shown in Table I.

Table I: Experimental condition of magnetite dissolution.

pH	Dissolved fraction of Fe_3O_4
1	0.54
2	0.46
3	0.44
4	0.02

Mean values of pH and dissolved fractions are respectively 2.5 and 0.365 and sample standard deviations are 1.291 for pH and 0.234 for dissolved fraction with Bessel's correction [4]. Calculating expected values from eq. (4), the correlation coefficient is obtained as -0.872.

2.4. Correlation of temperature and magnetite dissolution without copper(II) ion

Increasing the temperature makes the particles move faster to increase the chance of collision. It does not make equilibrium shift but definitely speed up the dissolution rate. Table II shows the increased magnetite dissolution in 2 hours as the temperature increased.

Table II: Experimental result of magnetite dissolution by the change of temperature

Temperature, $^\circ$C	Dissolved fraction of Fe_3O_4
75	0.01
85	0.07
95	0.54

During the calculation of the correlation coefficient, mean values of temperatures and dissolved fractions are 85 and 0.207 respectively and sample standard deviations are 10 and 0.290 for each. Correlation coefficient is obtained as 0.913.

2.5. Correlation of hydrazine concentration and magnetite dissolution without copper(II) ion

Hydrazine is one of strong reducing agents and used in many field of chemical reactions. Hydrazine was added in sulfuric acid solution under fixed pH of 3±0.05. The experimental results are shown in Table III.

Table III: Experimental result of magnetite dissolution by the change of hydrazine, N_2H_4.

Hydrazine, M	Dissolved fraction of Fe_3O_4
0.005	0.045
0.01	0.109
0.02	0.172
0.04	0.537
0.05	0.607
0.06	0.619
0.07	0.663
0.1	0.536

Mean values of hydrazine concentration and dissolved fractions are 0.044 and 0.411 respectively and sample standard deviations are 0.036 and 0.526 for each and σhydrazine, dissolution is obtained as 0.822.

2.6. Correlation of copper concentration and magnetite dissolution.

To enhance the dissolution ratio, the effect of metal ions such as Mn^{2+}, Zn^{2+}, Cu^{2+}, and etc. on the dissolution of magnetite in sulfuric acid solution. Among those metal ions, copper(II) ion was reported to have notable positive effect on dissolution efficiency due to the potentially formation of bridging ligands with hydrazine and sulfate. To evaluate the correlation coefficient between copper ions and dissolution fraction, we used previous experimental results as shown in Table IV. As a result, magnetite had a relatively faster dissolution comparing to other variables.

Table IV. Experimental result of magnetite dissolution by the change of hydrazine, N_2H_4.

Copper(II) ion, M	Dissolved fraction of Fe_3O_4	
	at pH 2	at pH 3
5e-4	0.11	0.73
1e-3	0.15	0.74
1.5e-3	0.22	0.75
2e-3	0.28	0.76
2.5e-3	0.27	0.78

In this experiment, correlation coefficients between added copper(II) ion and both dissolved fraction of magnetite at pH 2 and at pH 3 were calculated as 0.957 and 0.986 respectively. The scattered plots of experimental results and correlation are shown in Fig. 1.

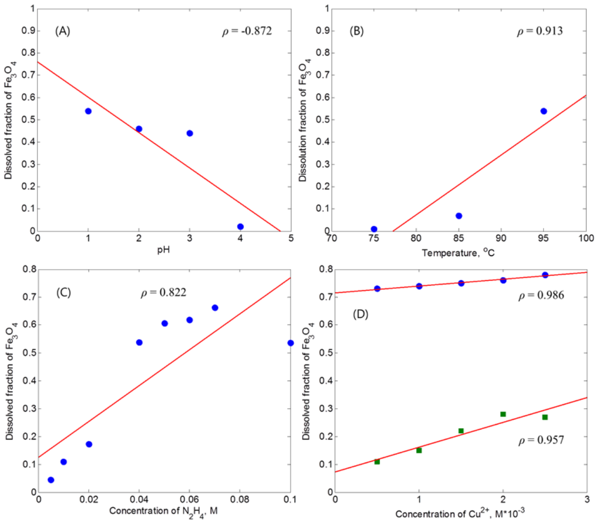

Fig 1. scattered plots of experimental results and correlation between magnetite dissolution and (A) pH, (B) temperature, (C) N_2H_4 concentration, and Cu(II) ion concentration.

3. Discussion

From this correlation study, we can infer that pH and dissolution have a strong negative correlation as -0.872 in the acidic solution without copper(II) ion. At relatively week acidic solution of pH 4, the initiation of dissolution by oxygen and hydrogen bond is harder so that the dissolution was much slower than under stronger acidic solution. So can we say that both variables are correlated with such that coefficient? When we have ρ is -0.872, p-value of null-hypothesis is 0.128 for two-tailed probability indicating that both variables cannot be said linearly correlated because null-hypothesis is significantly considered with the acceptable confidence level. On the other hand, the correlation between concentration of hydrazine and magnetite dissolution has p-value 0.012 and this is within the confidence interval (95%), we can say hydrazine and dissolution are correlated.

In addition, correlation between hydrazine concentration and dissolution was positively moderate because the reaction between hydrazine and magnetite is limited by less concentrated magnetite. Among all independent variables, the concentration of copper(II) ion has a strongest correlation (ρ=0.986) to magnetite dissolution in moderate acidic solution of pH 3. However, this statistical analysis was not intended to determine the accuracy of the experimental results, nor to estimate the causative effect of variables. Instead, such strong correlation gives us strong belief of the formation of $[Cu^+(N_2H_5^+)]$ chelate which decreases oxidation state of the protonated magnetite to make it soluble ferric ion and can be further treated in the empirical modeling.

4. Conclusion

In present study, we investigated the magnetite dissolution in HyBRID solution as newly developing decontamination process. As a preliminary study for empirical modeling of decontamination by HyBRID solution, simply correlation study between variable and magnetite dissolution was introduced with studied mechanism and experimental results. Although methods used in this study is too general, knowing correlations between variables is beneficial to understand the dissolution mechanism and supportive for future empirical modeling.

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