Empirical Modeling of Metal Oxides Dissolution

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1. Introduction

There have been tons of studies to examine the dissolution of metal oxides in terms of dissolution kinetics, type of reactants, geometry, etc. [1-4]. However, most of previous studies is the observation of macroscopic dissolution characteristics and might not provide the atomic scale characteristics of dissolution reactions. Even the analysis of microscopic structure of metal oxide with SEM, XRD, etc. during the dissolution does not observe the microscopic characteristics of dissolution mechanism. Computational analysis with well-established dissolution model is one of the best approaches to understand indirectly the microscopic dissolution behaviour. Therefore, the authors utilized the computational modelling of metal oxide, specifically for magnetite, Fe_3O_4, and the interpretation of the dissolution characteristics is proposed in the present study. The relevant reaction path ways are postulated with the reaction rate constants obtained by batch experiments and provided with the plausible pretexts.

The approximated dissolution model and its computation are expected to alternate the time-consuming experimental dissolution tests and sophisticated interpretation of dissolution mechanism with limited experimental data. Even though the model discrimination is not included in this study, the proposed deterministic model representations could be a useful tool for the systematic understanding of metal oxide dissolution. In addition, metal oxide was assumed stationary during the acidic and reductive dissolution and the spatial information by the effect of diffusion was not considered in the present study. Though the dissolution experiment could not be a homogenous system, we assumed it as a well-stirred system.

The dissolving solution we used in the present study is composed of hydrazine as a strong reducing agent and sulphuric acid as a hydrogen donator. This solution is prepared in lieu of oxalic acid or EDTA based organic acid solution to prevent the further treatment problems by the use of those chemical agents. Furthermore the dissolution study could be applied especially for the development of decontamination agents to remove radioactive material formed in the vicinity of nuclear reactors.
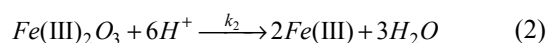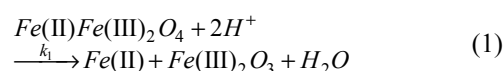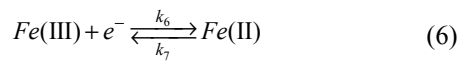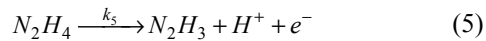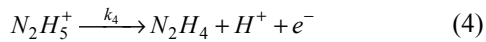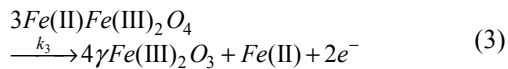
2. Methods and Results

2.1 Interpretation of metal oxides dissolution characteristics

Iron oxide dissolution is occurred by three different pathways simultaneously or competitively; i) acidic dissolution, ii) reductive dissolution, and iii) chelation activated surface complexation with the presence of chelating ligands. An acidic dissolution that is equivalent to a non-reductive dissolution is a simple desorption process of metal ions at higher activation energy. Therefore the more active sites on the reacting surface could be released into the solution and the temperature increase could raise the probability of this reaction due to the increased active sites. On the other hand, the reductive dissolution is characterized by induction and autocatalytic dissolution. During the induction period, the release of readily soluble ions such as ferrous ions can take place. Unless the soluble ions exist in the lattice of oxide, electron transfer to the metal ion to be soluble in reductive fashion must precede the release to the solution.

2.2 Dissolution mechanism

As described earlier, both acidic and reductive dissolution may occur in N_2H_4/H^+ solution. Ample hydrogen ion is offered in acidic mood initially and may be additionally provided during the dissolution by oxidation of $N_2H_5^+$ since N_2H_4 is known mostly existed as $N_2H_5^+$ in acidic condition. The overall mechanism is described as follows.

$$Fe(\text{II})Fe(\text{III})_2O_4 + 2H^+ \xrightarrow{k_1} Fe(\text{II}) + Fe(\text{III})_2O_3 + H_2O \tag{1}$$

$$Fe(\text{III})_2O_3 + 6H^+ \xrightarrow{k_2} 2Fe(\text{III}) + 3H_2O \tag{2}$$

$$3Fe(\text{II})Fe(\text{III})_2O_4 \xrightarrow{k_3} 4\gamma Fe(\text{III})_2O_3 + Fe(\text{II}) + 2e^- \qquad (3)$$

$$N_2H_5^+ \xrightarrow{k_4} N_2H_4 + H^+ + e^- \qquad (4)$$

$$N_2H_4 \xrightarrow{k_5} N_2H_3 + H^+ + e^- \qquad (5)$$

$$Fe(\text{III}) + e^- \underset{k_7}{\overset{k_6}{\rightleftarrows}} Fe(\text{II}) \qquad (6)$$

Regarding the slow acidic dissolution by protonation and relatively fast reductive dissolution, kinetic rate constants for reactions (1) to (6) were set. The further oxidation of hydrazine to N_2H_3 as own in eqn. (5) could be as low as it may not be significantly associated to the dissolution of magnetite. Also the conversion of magnetite to maghemite in eqn. (3) is negligible in the reductive dissolution due to the fast oxidation of hydrazinium to hydrazine in eqn. (4) accommodates the fast reductive dissolution of magnetite.

2.3 Deterministic model of dissolution

In deterministic model, interpreting the microscopic behaviour between solutes and reactants relying on the surface geometry is delegated by macroscopic ODE reaction rate equations derived by continuous concentration changes. The law of mass action as an empirical rule of thumb was used to determine the equations. The reaction rates of key players for the dissolution are listed below. Using MATLAB non-stiff ODE solver, all reaction rate equations was solved simultaneously.

$$\frac{d[Fe(\text{II})]}{dt} = k_1[Fe_3O_4][H^+] + k_3[Fe_3O_4] \\ + k_6[Fe(\text{III})][e^-] - k_7[Fe(\text{II})] \qquad (7)$$

$$\frac{d[Fe_2O_3]}{dt} = k_1[Fe_3O_4][H^+] - k_2[Fe_2O_3][H^+] \qquad (8)$$

$$\frac{d[Fe(\text{III})]}{dt} = k_2[Fe_2O_3][H^+] \\ - k_6[Fe(\text{III})][e^-] + k_7[Fe(\text{II})] \qquad (9)$$

$$\frac{d[N_2H_4]}{dt} = k_4[N_2H_5^+] - k_5[N_2H_4] \qquad (10)$$

2.4 Model Validation

To validate the model we proposed, experiments of magnetite were performed under the following experiment condition (see Table 1). Varied concentrations of hydrazine are set in experiments to account for the effect of hydrazine oxidation for the reductive dissolution. Other conditions such as pH and temperature were followed the typical dissolution experiment. Dissolved ferrous ions sampled at time by time were analyzed by Atomic Absorbance Spectroscopy.

Table 1. Experimental condition of magnetite dissolution

	$[N_2H_4]$,M	pH	Temp., °C	$[Fe_3O_4]$, M	Time, h
Value	$0 - 0.1$	3	95	2.15e-4	20

Fractions of dissolved magnetite at different hydrazine concentrations from experiments and ODE solutions are shown in Fig. 1 (a) and (b) respectively.
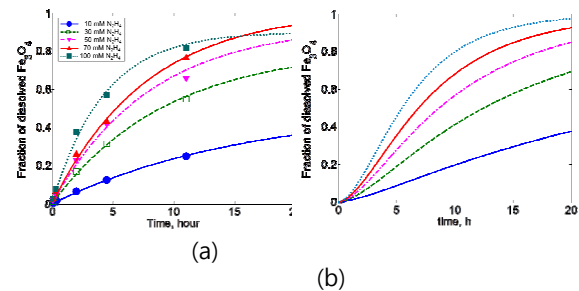

(a)

(b)

Fig. 1. Comparison of magnetite dissolution between experiment (a) and model prediction (b).

3. Conclusions

In-vitro dissolution profiles of magnetite were obtained by solving reaction equations and its validation was performed by comparison with experimental results in the present study. The empirical modeling by solving reaction rate equations could predict the dissolution profile well-matched to the experimental observations. Moreover, various designs of experimental conditions are applied to the in-vitro methods interpreting the dissolution characteristics controlled by each influencing parameter.

4. References

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