

## Empirical Modeling of Metal Oxides Dissolution

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### 1. Introduction

Redox reaction is the main function of the metal component dissolution from the oxides. Insoluble Fe(III) existing in magnetite, for an example, can be reduced in the form of Fe(II) ion by reduction of electron and thus soluble into the solution. On the other way, insoluble Cr(III) could be released by the oxidation from chromite as Cr(VI) which is the most soluble chromium compound in water.

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 the 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,  $\text{Fe}_3\text{O}_4$ , and the interpretation of the dissolution characteristics is proposed in the present study. The relevant reaction pathways 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

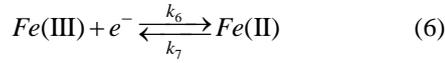
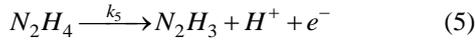
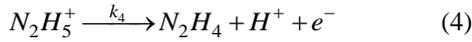
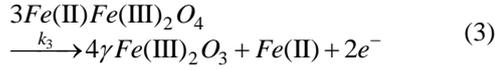
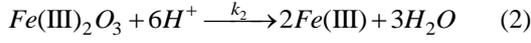
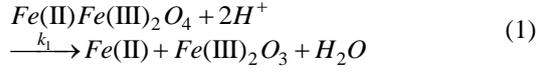
Magnetite contains both bivalent iron (Fe(II),  $\text{Fe}^{2+}$ , or ferrous ion) and trivalent iron (Fe(III),  $\text{Fe}^{3+}$ , or ferric iron) and relatively faster dissolution rate because instable ferrous ions existing in the lattice of oxide could be released easily to the solution requiring short induction period. Next the ferric ions is reduced to ferrous ions with an electron provided from other oxidation reaction such as hydrazinium to hydrazine [5], or autocatalytic effect by the absorbed ferrous ion on the surface of magnetite.

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. When a sufficient amount of soluble ions are generated, the second reduction step of autocatalytic dissolution follows. The autocatalytic dissolution is initiated by the adsorption of aqueous ferrous complexes onto the surface of metal oxide and electron transfer occurs on the interface. Then the desorption of the reduced soluble ions follows. It is the reason why the addition of ferrous ions at the beginning of metal oxide dissolution facilitate the initial reaction rate reported in many literatures [6-7].

#### 2.2. Dissolution mechanism

As described earlier, both acidic and reductive dissolution may occur in  $\text{N}_2\text{H}_4/\text{H}^+$  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.



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 shown 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.

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

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

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

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

The overall dissolved iron oxide expressed with the  $Fe(II)$  concentration contains the cathodic reaction of magnetite and reduction of ferric ion to soluble ferrous ion by electron transfer. In the presence of a strong reducing agent such as hydrazine, the overall dissolution is governed by reductive dissolution and it will be demonstrated in next section.

### 2.2. 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.

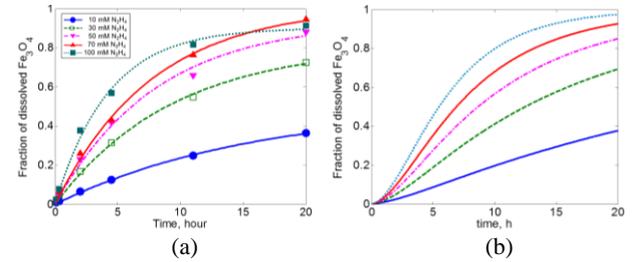


Figure 1. Comparison of magnetite dissolution between experiment (a) and model prediction (b).

The dissolution of magnetite in this experiment showed the exponential decay expressed in eqn. (11), and the coefficient,  $\lambda$ , is highly dependent on the experimental condition of hydrazine concentration, pH, temperature, etc. and empirically obtained. Therefore the solution of the lumped dissolution does not provide information enough to understand the effect of each influencing factor.

$$C_t = C_o(1 - e^{-\lambda t}) \quad (11)$$

In addition the model expectation is pretty similar to the dissolution characteristics observed from experiments. Rather the reaction model solution properly shows the characteristics of rate increase by autocatalytic effect of dissolved ferrous ions during the dissolution which is not predictable by homogenous

model used for interpolation of experimentation results in Fig. 1 (a).

The other information mostly hard to tract in real experiment is shown in Fig. 2. Magnetite was almost disappeared after 20 hours for all cases, but the remaining hematite or maghemite might affect the less existence of soluble ferrous ion in the solution. Besides, concentration of hydrogen ions was increased during the dissolution adjusting the pH from 3 down to 1.4 in Fig. 2 (c). pH changes experimentally recorded were around 2.1-2.5 after dissolution due to the consumption of a certain amount hydrogen ions by oxygen in solution.

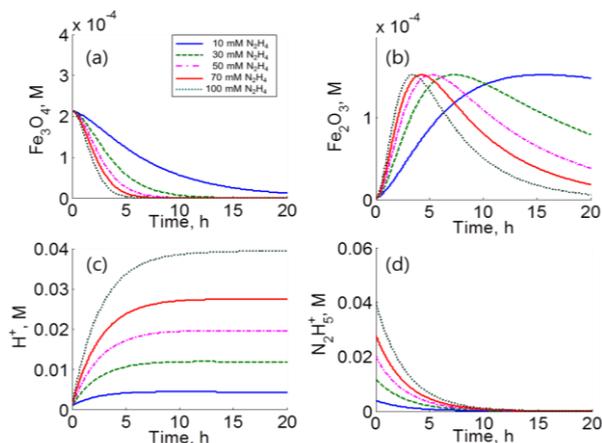


Figure 2. Concentration changes of key players in magnetite dissolution.

To quantify the reductive dissolution accommodated by hydrazine, we solved the reaction equations assuming the dissolution with the absence of hydrazine in solution and showed result in Fig. 3. The magnetite was totally disappeared but the concentration of Fe(II) ions in solution was saturated just right after 60% dissolution for 50 days as in Fig. 3 (a) and the hematite was generated instead with no further changes by only acidic dissolution as shown in Fig. 3 (b).

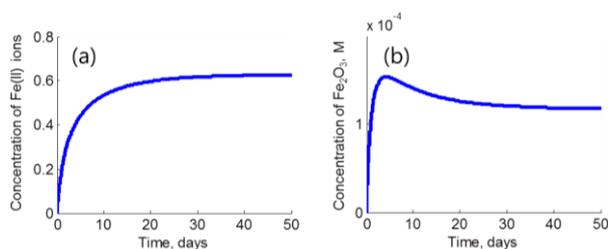


Figure 3. Total dissolved magnetite (a) and generated hematite (b) for the dissolution with the absence of reductive component.

### 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.

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