

Computational Model of Copper Catalyzed Metal Oxide Dissolution in Reducing Acidic Solution

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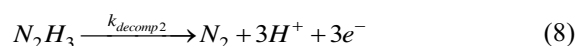
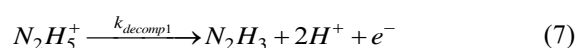
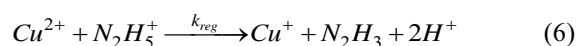
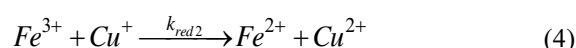
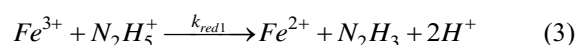
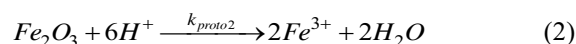
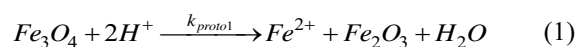
1. Introduction

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 [1-3]. However, most of previous studies is the observation of macroscopic dissolution characteristics and might not provide the atomic scale characteristics of dissolution reactions. In this study, computational models of dissolution mechanisms for metal oxides, specifically for magnetite and nickel-ferrite 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. 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. In addition, the dissolving ability of the solution is catalyzed by the addition of copper ions.

2. Dissolution mechanisms of metal oxides

Metal oxides undergo both acidic and reductive dissolutions 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 $N_2H_5^+$. Also copper ions lead more favorable reduction process by reducing ferric ion to ferrous ion. The lower activation energy of the $N_2H_4/H^+/Cu^{2+}$ system could dissolve metal oxides faster than systems with no copper ions. The overall mechanism is described as follows.



In deterministic model, interpreting the microscopic behavior 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. Using MATLAB non-stiff ODE solver, all reaction rate equations were solved simultaneously and shown in Fig. 1.

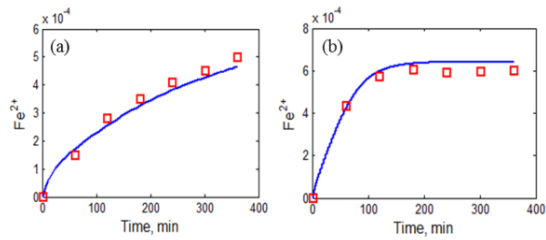


Fig. 1. Profiles of chemical reagents in Fe_3O_4 dissolution w/ N_2H_4 and H_2SO_4 solution for (a) w/o Cu^{2+} and (b) w/ Cu^{2+} .

3. Effects of Concentrations of Hydrazine and Copper Ions

In acidic solution, the dominant existence of hydrazine is hydrazinium ion, N_2H_5^+ , after the protonation in ample hydrogen condition. The oxidation of hydrazine to N_2H_4^+ ion and further to nitrogen in the solution where a reduction half-cell reaction presents is described in equations (7) and (8). For the dissolution of magnetite, a favorable reduction process takes place by reducing ferric ion to ferrous ion. However, the paths of hydrazine oxidation could differ when the solution is added by cupric ions. This was depicted in both Figs. 2 and 3.

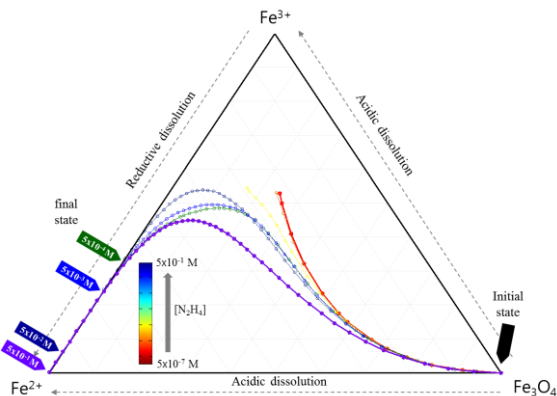


Fig. 2. Composition triangle of Fe_3O_4 , Fe^{3+} , Fe^{2+} after 6 h of the magnetite dissolution model by the increase of N_2H_4 , but $[\text{Cu}^{2+}]$ is 50 mM for everywhere.

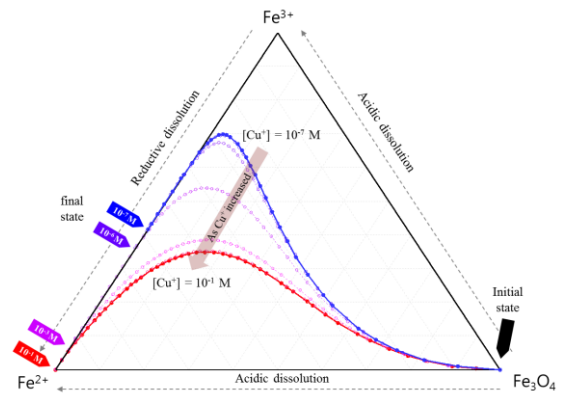


Fig. 3. Composition triangle of Fe_3O_4 , Fe^{3+} , Fe^{2+} after 6 h of the magnetite dissolution model by the increase of Cu^+ , but $[\text{N}_2\text{H}_4]$ is 0.05M for everywhere.

4. Conclusion

From this study, it was suggested that hydrazine as a reducing agent facilitated the dissolution of magnetite to a certain degree. The addition of cupric ion in hydrazine-based acidic solution was suggested to make the dissolution more effective, and accordingly gave rise to significantly enhanced dissolution rate. This study also shows that a well-established computational model can be a useful tool to cope with the detailed estimation of performance for the decontamination of large facility.

REFERENCES

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