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journal or publication title	Chemical Engineering Science
volume	55
number	17
page range	3429-3436
URL	http://hdl.handle.net/10232/00006789

doi: 10.1016/S0009-2509(00)00014-2

Kinetic model for simultaneous leaching of zinc sulfide and manganese dioxide in the presence of iron-oxidizing bacteria

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Abstract

The effect of iron-oxidizing bacteria on the simultaneous leaching of zinc sulfide and manganese dioxide was studied. Some researchers have reported the enhancement of the leaching rate during the simultaneous leaching of metal oxides and metal sulfides. In the present study, we examined the effect of the presence of *Thiobacillus ferrooxidans* in the simultaneous leaching. We also examined the reaction rates during the simultaneous leaching in the presence of the bacteria in order to study the reaction kinetics. The rate equation was obtained for each reaction: the oxidation of zinc sulfide by ferric iron, the oxidation of zinc sulfide by ferric iron and by the bacteria, the reductive dissolution of manganese dioxide by ferrous iron, and the simultaneous dissolution of zinc sulfide and manganese dioxide. A kinetic model based on these equations was proposed and the extent of leaching during the simultaneous dissolution with *T. ferrooxidans* was determined.

Keywords: *Thiobacillus ferrooxidans*; Kinetics; Leaching; Reaction engineering; Simulation; Bioleaching

1. Introduction

During simultaneous leaching of metal oxides and metal sulfides, the consumption of oxidizing and reducing agents can be reduced. Therefore, simultaneous leaching is suitable for the process aimed at the decrease in emissions. For the ZnS–MnO₂ system, since the process does not require the roasting step of zinc sulfide, the environmental impact of this step can be eliminated. The sulfur contained in zinc sulfide is removed as elemental sulfur. In addition to this advantage, both Zn and MnO₂ can be simultaneously electrowon in one electrowining operation (Rath & Paramguru, 1994; Srinivasa Rao & Paramguru, 1998).

Some researchers previously investigated the simultaneous leaching of metal oxides and sulfides. Ghosh and Imai (1985) have reported that an iron-oxidizing bacterium, *Thiobacillus ferrooxidans*, leached manganese from manganese dioxide in the presence of the sulfide ores of copper. They proposed overall reactions catalyzed by *T. ferrooxidans*, but the detailed mechanism was not mentioned. Iwai, Okui, Izaki, Awakura and Majima (1987) have investigated the feasibility of the hydrometallurgical treatment of mixed ores of manganese nodules and nickel sulfide based on the leaching rate, the stoichiometry of the leaching reaction and the determination of the rest potentials of the samples. Kai, Taniguchi, Ikeda and Takahashi (1996) have reported the enhancement effect of *T. ferrooxidans* on the redox leaching of manganese nodules and nickel sulfide, but they did not carry out the kinetic study. Li (1996) has studied the mechanism of the simultaneous leaching of zinc sulfide concentrate and manganese ores. He studied the effect of leaching temperature on leaching rate and obtained the activation energy for this process. Chen and Fu (1995) have described the leaching kinetics of manganese nodules using the

shrinking core model in the presence of zinc sulfide concentrate. They examined the rate controlling steps. The galvanic interactions of manganese dioxide with sphalerite (Rath & Paramguru, 1994) and pyrite (Paramguru & Nayak, 1996) have been investigated by polarization and leaching studies. Rath and Paramguru (1994) have examined two mechanisms: the cyclic action of the Fe³⁺/Fe²⁺ redox couple and galvanic interaction between zinc sulfide and manganese dioxide. They concluded that a galvanic interaction did not play an important role in their case.

Generally a kinetic model is available for the design of a leaching process and for the prediction of optimum operating conditions. However, there have been few studies concerning the method to predict the extent of leaching in the simultaneous dissolution system. In the present study, we studied the simultaneous leaching of zinc sulfide and manganese oxide. The leaching was carried out in the presence of the iron-oxidizing bacterium *Thiobacillus ferrooxidans* to improve the metal recovery. We obtained the reaction rate equations and kinetic parameters for the reactions involved in the simultaneous dissolution system to propose a reaction model.

2. Materials and methods

The zinc sulfide and manganese oxide used for the experiments were commercially available reagents (Wako Pure Chemical Industries, Ltd.). Leaching was carried out using 100 ml of the leaching solution in a 300 ml Erlenmeyer flask that was constantly shaken at 70 rev/min in a water bath. The flasks were plugged with porous plastic closures. The temperature of the water bath was maintained at 303 K. Zinc sulfide, manganese oxide, ferrous sulfate and ferric sulfate were

contained in the liquid according to the experimental conditions. In the case of bio-leaching, an active culture of an iron-oxidizing bacterium was added to the leaching solution and the initial cell concentration was adjusted to the prescribed value. The pH of the leaching solution was controlled to 2.0 with 10 N sulfuric acid during the leaching. Normal losses due to evaporation were periodically compensated for by the addition of distilled water. A small amount of solution was periodically removed for analysis. After filtration and the required dilution, the samples were analyzed for manganese and zinc using atomic absorption spectrophotometry.

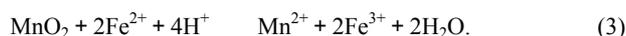
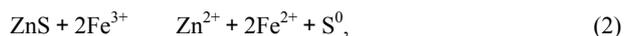
The organism used was the acidophilic iron-oxidizing bacterium, *Thiobacillus ferrooxidans*, which was isolated from the acid mine water of the Yanahara Mine, Japan. The bacterium was aerobically cultured in a shake flask with a 9 K liquid medium of Silverman and Lundgren (1959) using ferrous iron and adapted to zinc ion by repeated sub-culturing. The liquid medium contained the following components (in kg/m³ water): (NH₄)₂SO₄, 3.0; KCl, 0.1; K₂HPO₄, 0.5; MgSO₄·7H₂O, 0.5; Ca(NO₃)₂, 0.01 and FeSO₄·H₂O. In our case, the initial concentration of ferrous iron was adjusted to be 8.0 kg/m³. Cell numbers were directly counted using a microscope at ×400 magnification.

3. Systems of reactions

The overall reaction of the simultaneous dissolution of zinc sulfide and manganese dioxide is

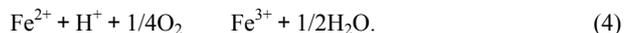


Both the zinc sulfide and manganese dioxide are insoluble in the dilute H₂SO₄ solution of pH=2, but they dissolve when they coexist in the system. This is due to a galvanic interaction between the two solids (Rath & Paramguru, 1994). When ferrous and ferric irons are presented in this system, the dissolution rates of zinc sulfide and manganese dioxide are both increased. This is because of the oxidation of zinc sulfide by ferric iron and the reduction of manganese dioxide by ferrous iron



In this case, leaching is promoted by the cyclic action of the Fe³⁺/Fe²⁺ redox couple.

It is well known that the iron oxidizing bacterium, *Thiobacillus ferrooxidans*, oxidizes ferrous iron in a liquid medium



When zinc is leached from zinc sulfide by the solution containing irons, ferrous iron oxidized by *T. ferrooxidans* promotes the dissolution of ZnS according to Eq. (2). This mechanism is called indirect mechanism and has been studied by many researchers (Boon, Snijder, Hansford & Heijnen, 1998) and used in many industrial leaching processes.

This bacterium is capable of chemoautotrophic growth using energy obtained from the oxidation of inorganic sulfur compounds as well as ferrous iron oxidation. Zinc sulfide is dissolved by the bacteria and produces sulfate ion



Nakazawa, Kudo, Chen and Sato (1989) have reported that sulfite, which was produced in the bio-oxidation process of elemental sulfur by *T. ferrooxidans* and *T. thiooxidans*, plays a significant role in the dissolution of manganese nodules. In the system of the present study, elemental sulfur is produced by (1) and (2). Therefore, the enhancement of MnO₂ dissolution was also expected by the addition of *T. ferrooxidans*.

4. Results and discussion

4.1. Oxidation of zinc sulfide

We obtained a simplified kinetic equation for the oxidative dissolution of zinc sulfide based on the models proposed by Verbaan and Huberts (1988) and Konishi, Kubo and Asai (1992)

$$r_{ZF} = k_{ZF} [\text{ZS}]_0 (1 - X_{\text{ZS}})^{2/3} [\text{Fe}^{3+}] \quad (6)$$

where [ZS]₀ is the initial concentration of zinc sulfide and X_{ZS} is the fraction of dissolved zinc sulfide. This equation considers particle shrinkage by dissolution. Therefore, the oxidation rate of zinc sulfide is proportional to the term (1 - X_{ZS})^{2/3} and was proportional to the concentration of ferric iron (Konishi et al., 1992). Fig. 1 shows the change in ZnS dissolution with leaching time for some initial concentrations of ferric iron. Zinc sulfide did not dissolve when [Fe³⁺] = 0. The lines in Fig. 1 were the results of the calculation from Eq. (6) when the value of the rate constant k_{ZF} = 1.66 × 10⁻³ 1/h. The experimental results could be well predicted by Eq. (6). Under all the conditions in which ferric iron is initially present, ferric iron was almost completely reduced to ferrous iron after 120 h. The stoichiometric relation between the produced ferrous iron and leached zinc followed Eq. (1).

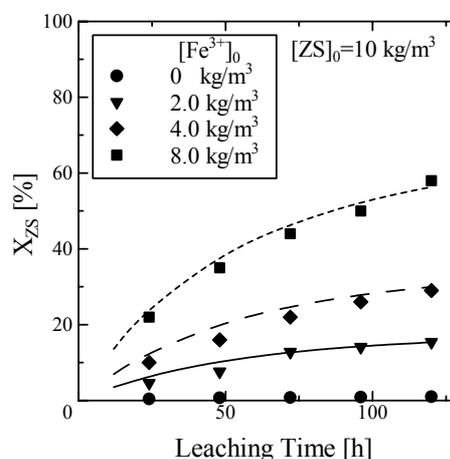


Fig. 1. Dissolution of zinc sulfide by ferric iron.

4.2. Dissolution of manganese dioxide by ferrous iron

Manganese dioxide only slightly dissolves in sulfuric acid solution, but it dissolved easily by adding ferrous iron in the solution. This reaction was much faster than the reaction of ZnS dissolution. The reaction was almost finished in 20 min. Fig. 2 shows that the fraction of dissolved manganese dioxide did not change with leaching time after the initial leaching stage. The final extent of leaching was dominated by the initial ferrous iron concentration. The concentration of ferrous iron was

negligible after 20 min and the ratio of the molar concentration of leached manganese ion and produced ferric iron was about 1 : 2. Therefore, it was confirmed that the dissolution of manganese dioxide proceeded via Eq. (3). Since, the rate of this reaction was much greater than that of the other reaction in the system, this reaction was not considered to control the overall reaction rate. The ferrous iron formed by ZnS dissolution would be immediately oxidized by the manganese dioxide. For this reason we did not determine the reaction rate equation for the dissolution of manganese dioxide by ferrous iron. For calculation, we assumed that the consumption rate of ferrous iron is equal to the formation rate of ferrous iron.

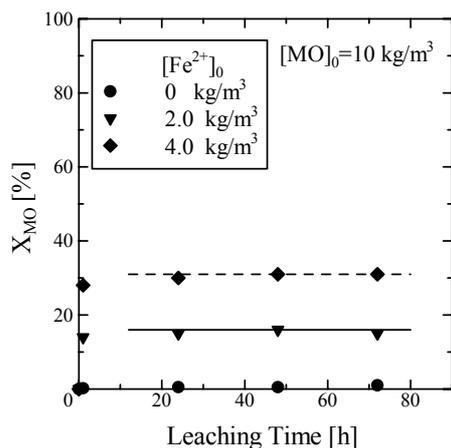


Fig. 2. Dissolution of manganese dioxide by ferrous iron.

4.3. Bacterial leaching of ZnS

The leaching of zinc sulfide by *T. ferrooxidans* has been studied by many investigators (Choi, Torma, Ohline & Ghali, 1993). Boon et al. (1998) have pointed out that this direct mechanism is negligible based on their redox-stat experiment. Konishi et al. (1992) have showed that the direct leaching could not be ignored when the concentration of irons was low, and studied the kinetics of the reactions. In the present study, we used their models for the biological dissolution of ZnS to analyze the data for the simultaneous leaching. We also used the Langmuir isotherm to evaluate the adsorbed bacteria on the surface of a solid

$$X_a = K_A X_{am} X_L / (1 + K_A X_L), \quad (7)$$

where X_{am} is the maximum adsorption capacity and X_L is the cell concentration in the liquid phase. In the present study, *T. ferrooxidans* will adsorb on zinc sulfide and manganese dioxide. The adsorbed cells on zinc sulfide catalyze the dissolution of zinc sulfide, but the cells on manganese dioxide are inactive toward the dissolution of manganese dioxide. According to the model of Konishi et al. (1992), the growth rate of bacteria adsorbed on zinc sulfide is represented by the following equation:

$$R_A = \mu_A X_a [(X_{am} - X_a) / X_{am}] (A / V). \quad (8)$$

The dissolution rate of zinc sulfide by the bacteria was calculated from R_A

$$r_{ZB} = R_A / Y_A, \quad (9)$$

where Y_A is the growth yield of adsorbed bacteria which is

defined as the ratio of the total number of cells formed by bacterial growth on the surface of zinc sulfide to the mass of ZnS utilized by the cells.

Since the system contained ferrous iron in the liquid phase, this effect was considered in the analysis. The growth rate of bacteria by ferrous iron in the liquid phase has been obtained by Lacey and Lawson (1970)

$$R_L = \mu_m X_L [Fe^{2+}] / (K_s + [Fe^{2+}]). \quad (10)$$

This equation is based on the Michaelis–Menten mechanism. The reaction rate was well correlated by this equation when the initial concentration of ferrous iron was smaller than 10 kg/m³. The rate of oxidation of ferrous iron by the bacteria in the liquid phase was obtained using the growth yield Y_L of bacteria on ferrous iron

$$r_{FB} = R_L / Y_L. \quad (11)$$

We used the experimental result of Lacey and Lawson for the value of K_s i.e., $K_s = 0.048$ kg/m³. We obtained the values of μ_m and Y_L from the experimental data of the cultivation of *T. ferrooxidans* by ferrous iron.

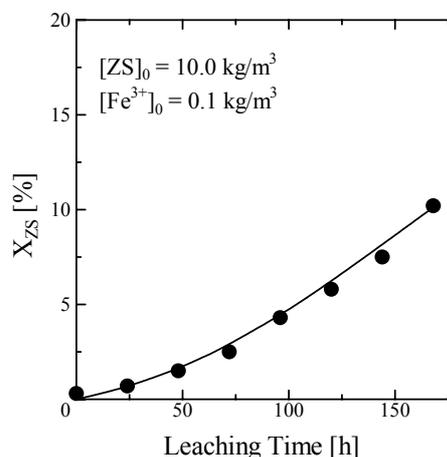


Fig. 3. Dissolution of zinc sulfide by *T. ferrooxidans*.

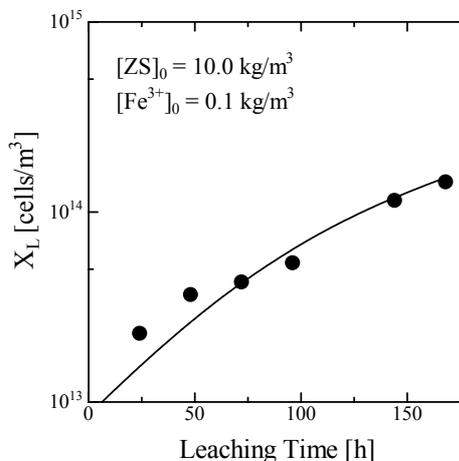


Fig. 4. Growth of *T. ferrooxidans* by zinc sulfide.

Fig. 3 shows the relationship between the fraction of leached zinc and leaching time. Fig. 4 shows the change in concentration of free bacteria in the liquid phase. In the

experiment, the initial concentration of bacteria in the liquid phase was adjusted to about 1.0×10^{13} cells/m³. The initial concentration of zinc sulfide and ferric iron was 10.0 and 0.1 kg/m³, respectively. In this system, at least four processes are involved: dissolution of zinc sulfide by ferric iron, bacterial oxidation of ferrous iron, and bacterial oxidation of elemental and zinc sulfide. The lines in these figures represent the calculated values from (7), (8), (9), (10) and (11). We used the values obtained by Konishi et al. (1992) for the parameters in Eq. (7): $K_A = 5.90 \times 10^{-15}$ m³/cells, $X_{am} = 3.57 \times 10^{11}$ cells/m². The values obtained for μ_A and Y_A fit our experimental data shown in Fig. 3 and Fig. 4. These values were approximate to those obtained by Konishi et al. (1992). Their values were 0.075 1/h and 2.8×10^{14} cells/kg ZnS for μ_A and Y_A , respectively. The parameters experimentally obtained in the present study were: $\mu_m = 0.054$ 1/h, $\mu_A = 0.087$ 1/h, $Y_L = 1.4 \times 10^{13}$ cells/kg Fe²⁺, and $Y_A = 2.0 \times 10^{14}$ cells/kg ZnS.

4.4. Simultaneous dissolution of ZnS and MnO₂ without iron

In the simultaneous dissolution of ZnS and MnO₂ in the absence of iron ions, the dissolution rates of both solids were significantly enhanced by the galvanic interaction between the two solids (Rath & Paramguru, 1994). We considered that the dissolution rates of these solids depended on the concentrations of the solids in the liquid phase. Fig. 5 shows the relationship between the dissolution rate and the concentration of each solid. In this experiment, the sum of the initial concentration of solids was adjusted to 20.0 kg/m³. Therefore, when the concentration of one of the solids increased, that of the other decreased, and the dissolution rate had a maximal value around 10 kg/m³. By assuming that the dissolution rate depended on the solid concentrations, we determined the dependence of the rate on the concentrations from an analysis of the experimental data. Fig. 6 shows the linear relationship between the dissolution rate and the parameter $[ZS]^{0.5}[MO]^{0.65}$. Consequently, the rate equations of the dissolution caused by the galvanic interaction were

$$r_{ZG} = k_{ZG}[ZS]^{0.5}[MO]^{0.65}, \quad (12)$$

$$r_{MG} = r_{ZG}(M_{MO} / M_{ZS}), \quad (13)$$

where r_{ZG} and r_{MG} are the dissolution rate of ZnS and MnO₂ by the galvanic interaction.

Since there was an initial rise in the dissolution during the first several hours, we studied the concentration dependence of the dissolution rate in the first 4 h. The initial dissolution rates were correlated by the following equations:

$$r_{ZGi} = k_{ZGi}[ZS]^{0.6}[MO]^{0.4}, \quad (14)$$

$$r_{MGi} = r_{ZGi}(M_{MO} / M_{ZS}). \quad (15)$$

(14) and (15) were used in the calculation when the fraction of dissolved solid was below 0.25 and 0.05 for zinc sulfide and manganese dioxide, respectively. Fig. 7 and Fig. 8 show the comparison between the experimental data and the predictions from these equations. The rate constants were found to be $k_{ZG} = 0.0013$ m^{0.45} / h kg^{0.15} and $k_{ZGi} = 0.0075$ 1/h. Including the improvement in the rise in the initial dissolution of the MnO₂, it was proven that these equations well correlated with the experimental data.

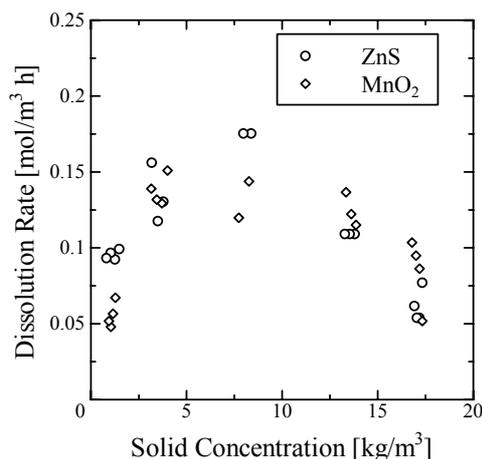


Fig. 5. Effect of solid concentration of dissolution rate on the solids.

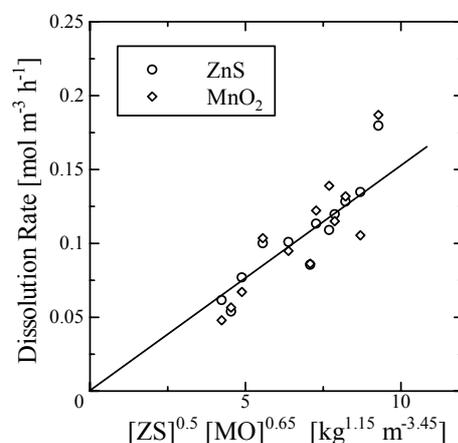


Fig. 6. Relationship between dissolution rate and the parameter $[ZS]^{0.5}[MO]^{0.65}$.

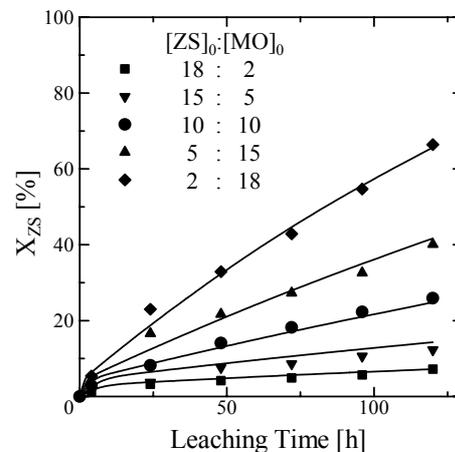


Fig. 7. Dissolution of zinc sulfide during simultaneous leaching.

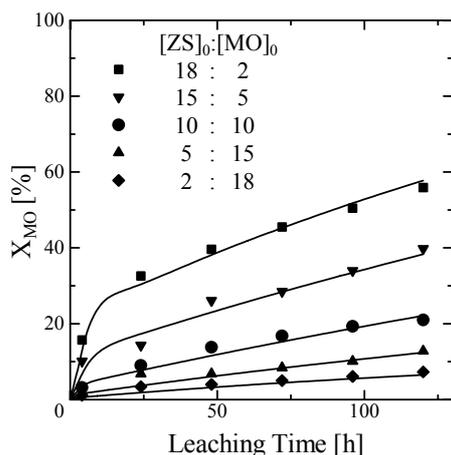


Fig. 8. Dissolution of manganese dioxide during simultaneous leaching.

4.5. Simultaneous dissolution of ZnS and MnO₂ in the presence of irons

The dissolution rates of both solids were enhanced when ferric and ferrous irons were present in the system for simultaneous leaching. In this case, the dissolution was produced by the cyclic action of the redox couple $\text{Fe}^{2+} / \text{Fe}^{3+}$ besides the galvanic interaction. Fig. 9 and Fig. 10 show the dissolution of ZnS and MnO₂ when the initial concentration of ferric iron was 1.0 kg/m³. It is clearly seen that the dissolution was much larger for the system containing iron ions than for the system without iron ions shown in Fig. 7 and Fig. 8. We compared the experimental results with the calculation from the rate equations obtained for the galvanic interaction and redox reaction. However, the experimental data were much larger than the calculations. We then considered that the reaction rate of the galvanic reaction or redox reaction was enhanced. Fig. 11 shows the relationship between the initial concentration of zinc sulfide and the fraction of dissolved solids after 48 h. This figure also shows the calculation from the three models: (A) The solid lines represent the calculation based on the model which did not take into account the enhancement factor, (B) the broken lines were the calculation from the model in which the reaction rate of the galvanic interaction increased, and (C) the dotted lines are the prediction when the reaction rate of ZnS dissolution by ferric iron was increased. The enhancement factors of the latter two models were adjusted so that the calculated MnO₂ dissolution agreed with the experimental value at 10 kg/m³ for the initial concentration of zinc sulfide. Model B (broken lines) could successfully predict the experimental data for the other initial concentration. On the other hand, model C tended to overestimate the solid dissolution when X_{ZS} and X_{MO} were larger than 30%. The lines in Fig. 9 and Fig. 10 show the predictions from model B. The enhancement factor was 2.6 in this case.

4.6. Simultaneous dissolution of ZnS and MnO₂ in the presence of *T. ferrooxidans*

Finally, we carried out the simultaneous leaching in the presence of *T. ferrooxidans*. The initial cell concentration in the liquid phase was about 10×10^{13} cells/m³. The concentration of each solid was 10 kg/m³. The initial concentration of ferric iron was 0.1 kg/m³. Fig. 12 shows the experimental result. The dissolution of zinc sulfide was enhanced by the presence of the bacteria, while the dissolution of manganese dioxide was only

slightly influenced by the bacteria. From these results, *T. ferrooxidans* seems to promote the dissolution of zinc sulfide. Beside the biological oxidation of zinc sulfide, the removal of sulfur yielded from the oxidation of zinc sulfide by ferric iron improved the dissolution rate of ZnS and galvanic reaction rate.

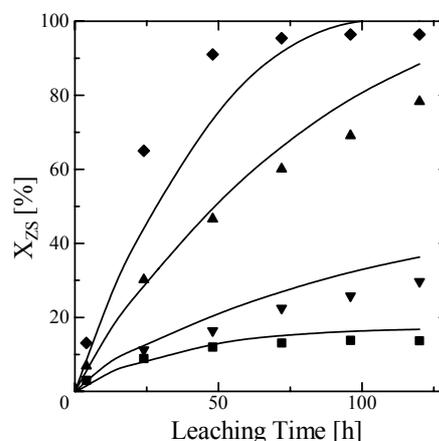


Fig. 9. Dissolution of zinc sulfide during simultaneous leaching with iron.

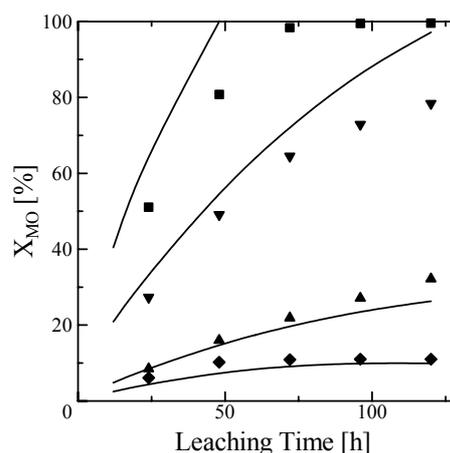


Fig. 10. Dissolution of manganese dioxide during simultaneous leaching with iron.

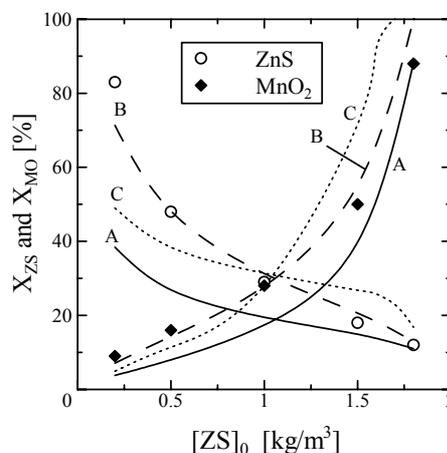


Fig. 11. Comparison of experimental dissolution with predictions from three models.

We examined the kinetics of the simultaneous leaching in the presence of *T. ferrooxidans* by the model based on the rate equations obtained for each reaction previously. Both *T. ferrooxidans* and manganese dioxide competitively oxidize ferrous iron. As described above, the dissolution rate of manganese dioxide by ferrous iron was very large. Therefore, a large part of ferrous iron was oxidized to ferric iron by manganese oxide. The result of the calculation based on Model B almost agreed with the experimental result as shown in Fig. 12.

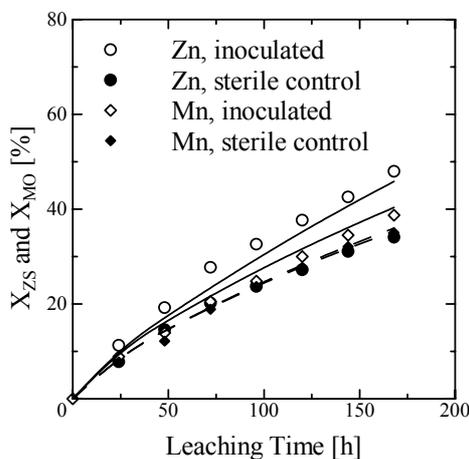


Fig. 12. Metal dissolution during simultaneous leaching in the presence of *T. ferrooxidans*.

5. Conclusions

Dissolution rates were enhanced by the presence of the iron-oxidizing bacterium *T. ferrooxidans* in the simultaneous leaching system containing zinc sulfide and manganese dioxide. Especially the dissolution rate of zinc sulfide was improved. It is considered that the bacterial oxidation of zinc sulfide and elemental sulfur yielded on the surface of it might be effective for the enhancement. The removal of elemental sulfur might also improve the galvanic reaction rate.

In order to study the kinetics of the simultaneous leaching, we determined the reaction rate equation for each reaction. Consequently, the model obtained in this study could predict the dissolution of zinc sulfide and manganese dioxide during the simultaneous leaching. This model could predict the dissolution even in the presence of *T. ferrooxidans*. Our approach would be useful for the design of a leaching process and for the optimization of operating conditions of other simultaneous leaching systems.

Notation

A	surface area of solid particles, m^2
$[Fe^{2+}]$	ferrous iron concentration, kg/m^3
$[Fe^{3+}]$	ferric iron concentration, kg/m^3
$[Fe^{3+}]_0$	initial concentration of ferric iron, kg/m^3
K_A	equilibrium constant for cell adsorption, $m^3/cells$
K_s	saturation constant for substrate, kg/m^3
k_{MG}	rate constant of dissolution of MnO_2 by galvanic interaction, $1/h$
k_{ZF}	rate constant of dissolution of ZnS by Fe^{3+} , $1/h$
k_{ZG}	rate constant of dissolution of ZnS by galvanic interaction, $1/h$

$k_{ZG,i}$	rate constant of dissolution of ZnS by galvanic interaction in initial stage, $1/h$
M_{MO}	formula weight of manganese dioxide, mol/g
M_{ZS}	formula weight of zinc sulfide, mol/g
$[MO]$	concentration of manganese dioxide, kg/m^3
$[MO]_0$	initial concentration of manganese dioxide, kg/m^3
R_A	growth rate of bacteria adsorbed on solid particles, $cells/h\ m^3$
R_L	growth rate of bacteria in liquid phase, $cells/h\ m^3$
r_{FB}	oxidation rate of ferrous iron by liquid-phase bacteria, $kg/h\ m^3$
r_{MG}	dissolution rate of MnO_2 by galvanic interaction, $kg/h\ m^3$
$r_{MG,i}$	dissolution rate of MnO_2 by galvanic interaction in initial stage, $kg/h\ m^3$
r_{ZB}	dissolution rate of ZnS by bacteria, $kg/h\ m^3$
r_{ZF}	dissolution rate of ZnS by Fe^{3+} , $kg/h\ m^3$
r_{ZG}	dissolution rate of ZnS by galvanic interaction, $kg/h\ m^3$
$r_{ZG,i}$	dissolution rate of ZnS by galvanic interaction in initial stage, $kg/h\ m^3$
V	volume of solid-liquid mixture, m^3
X_a	concentration of adsorbed bacteria per unit surface area of solid particles, $cells/m^2$
X_{am}	maximum adsorption capacity per unit surface area of solid particles, $cells/m^2$
X_L	concentration of bacteria suspended in liquid phase, $cells/m^3$
X_{MO}	fraction of dissolved manganese dioxide
X_{ZS}	fraction of dissolved zinc sulfide
Y_A	growth yield of bacteria on zinc sulfide, $cells/kg$
Y_L	growth yield of bacteria on ferrous iron in liquid phase, $cells/kg$
$[ZS]$	concentration of zinc sulfide, kg/m^3
$[ZS]_0$	initial concentration of zinc sulfide, kg/m^3

Greek letters

μ_A	specific growth rate of bacteria on solid surface, $1/h$
μ_L	specific growth rate of bacteria in liquid phase, $1/h$
μ_m	maximum specific growth rate of bacteria in liquid phase, $1/h$

Acknowledgements

The authors are grateful to financial support by a Grant-in-Aid for Scientific Research (No.10141240) from the Ministry of Education, Science, Sports and Culture, Japan.

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