KINETIC ELEMENTS IN THERMOPHILIC-MICROBIAL LEACHING OF SULFUR FROM COAL

Charles C. Y. Chen and Duane R. Skidmore

Department of Chemical Engineering
Columbus, Ohio 43210

ABSTRACT

A mechanism found suitable for pyritic sulfur removal from coal by mesophilic organisms has been modified and evaluated for the same reaction by the thermophile: Sulfolobus acidocaldarius. The mechanism as modified includes direct and indirect mechanistic elements whose magnitudes were determined experimentally at leaching conditions with and without microbes. Chemical leaching of pyrite by Fe(III) ions and the chemical oxidation of Fe(II) to Fe(III) were found to contribute significantly to overall conversions at thermophilic temperature (72 °C) but not at mesophilic temperature (25-37 °C). The model thus constructed fit overall sulfur leaching data well after suitable assumptions had been made for extent of cell attachment; gas (oxygen) transfer rates, sulfur accessibility, and sulfate reprecipitation rates. The resulting equation is useful for process sumulation, control and design. Further work is needed to define additional sulfur leaching effects.

INTRODUCTION

The Sulfolobus acidocaldarius microbe is thermophilic and acidophilic with optimum growth at temperatures between 70-75 °C and a pH 2-3[1]. The microorganism can grow autotrophically on elemental sulfur, mineral sulfides, and ferrous ions, while it can also grow on glucose and yeast extract[1,2]. Recent reports claimed the oxidation of dibenzothiophene (DBT) and organic sulfur in coal by this organism[3,4].

The thermophilic organism S. acidocaldarius has some advantages over the widely used mesophile Thiobacillus ferrooxidans for microbial coal desulfurization[5-7]. Its extremely thermophilic, acidophilic, aerobic and autotrophic character make it resistant to contamination. The rates of chemical reaction between ferric iron ions and pyrite are higher at high temperature, which benefits the process of sulfur removal. The solubility of some mineral sulfates is higher at low pH and high temperature, which reduces reprecipitation in a process for sulfur reduction. Finally, microbial ability to remove organic sulfur is very important.

Mathematical models have been proposed to describe the kinetics of microbial coal desulfurization[8,9]. The model designed for mesophiles neglected chemical reactions which occurred in parallel with biological reactions in coal-water slurry system. The model proposed in this report considers both chemical and biological reactions, as more realistic for sulfur bioleaching at elevated temperatures. Microbial oxidation of ferrous ions and of sulfur in coal were studied to provide particular values for the model parameters.

MATERIALS AND METHODS

Culture methods

The medium for microbial growth was a basal salts solution and an energy source with or without supplements. The basal salts solution had the

following composition (g/l): $(NH_4)_2SO_4$, 1.3; KH_2PO_4, 0.28; $MgSO_4 \cdot 7H_2O$, 0.25; $CaCl_2 \cdot 2H_2O$, 0.07; in 1 liter of tap water. The energy source can be elemental sulfur, ferrous ions or sulfur in coal. Sometimes yeast extract was a supplement. The pH of the medium was adjusted to 2.0 with 3.0 N H_2SO_4.

The original culture of S. acidocaldarius (ATCC 53230) from Dr. Brierley at the New Mexico Institute of Mining and Technology and transfers from Dr. Kargi at Lehigh University were used throughout the investigation.

Eight hundred ml. of the medium were placed in a three necked, round bottomed flask equipped with a condenser. The system was autoclaved at 121 °C for 15 min and then inoculated with a culture of S. acidocaldarius. Microbial cells were grown and harvested from a medium where elemental sulfur was the energy source 3-5 days after inoculation. The culture was first centrifuged at 1000x g for 5 min to remove the sulfur particles. Then, the cell solution was centrifuged at 4000x g for 20 min to separate the cells. The cells were resuspended in basal salts solution without an energy source. These cells were used as inoculum for ferrous ion oxidation and sulfur leaching from coal.

Accurate cell counts were achieved for experimental runs from protein analyses calibrated with visual cell counts under a phase contrast microscope equipped with a Petroff-Hausser counting chamber. The total protein was assayed by the modified Bradford Method suggested by Peterson[10].

Medium with ferrous sulfate as the energy source was prepared by adding 9 g/l or 3.18 g/l of $FeSO_4 \cdot 7H_2O$ to the basal salts medium to yield an initial iron concentration of 2000 or 700 ppm. Experiments were conducted with and without yeast extract supplement. An uninoculated control flask was run in parallel to show the rate of chemical oxidation of ferrous iron by oxygen from the air. Samples were taken every 12-24 hours for the assay of ferrous and ferric iron concentrations. The analysis followed a procedure using 1,10 phenanthroline hydrochloride as the indicator for iron concentration. Details of the analytical procedures are available in the literature[11].

Other experiments were conducted with 5% coal slurry comprised of Kentucky #9 coal and basal salts solution. The slurry was either inoculated or uninoculated with the cells. Every 12-24 hours, 3 ml of slurry were taken from each flask and filtered through Whatman #1 filter paper. Concentrations of sulfate, ferrous, and ferric iron in the solution and total sulfur content in the coal were measured. Concentration of sulfate was determined by the turbidimetric method specified in ASTM[12]. The sulfur content in coal was measured by combustion and titration using a LECO sulfur analyzer.

KINETIC ELEMENTS

The mechanism for pyritic sulfur oxidation was first proposed by Silverman[13] for Thiobacillus species as comprised of direct and indirect oxidative components. The direct mechanism requires direct contact between bacteria and pyrite since no extracellular enzymes are involved. In the indirect mechanism, the ferric iron chemically reacts with pyrite to give ferrous iron and elemental sulfur. The bacteria then oxidize ferrous iron to ferric iron and oxidize elemental sulfur to sulfate. In the absence of bacteria, the regeneration of ferric iron is the rate limiting step for pyrite oxidation. Bacteria increase the pyrite oxidation rate by oxidizing ferrous iron to ferric iron. Precipitation of iron-sulphate was observed when ferric iron was present at high concentration.

To model the system, kinetics of the following reactions were considered:

1. Chemical oxidation of ferrous ions to ferric ions by dissolved oxygen without bacteria
2. Biological oxidation of ferrous ions by suspended microorganisms with bacteria
3. Chemical oxidation of pyrite to iron and sulfate
4. Biological oxidation of pyrite by attached microbes
5. Precipitation of sulfate and ferric ions

Microbial oxidation of pyrite by Thiobacillus ferrooxidans has been studied and Monod type models were proposed[8]. The basic concept is that the adsorbed cells grow on pyrite surfaces and the suspended cells grow on ferrous ions. An equilibrium exists between the free cells and the adsorbed cells according to the Langmuir isotherm. However, Kargi and Robinson pointed out that in their study of pyrite leaching with S. acidocaldarius, that the number of free cells remained unchanged while the attached cells grew in number[9]. Recent reports showed that in the short term, the cells attached to coal particles following the Langmuir isotherm and that selective adsorption on pyrite surfaces was evident, but irreversiblity was developed through long term cell-coal contact[14,15].

The attached cells are assumed to have a maximum specific growth rate of $\mu_{M,S6}$ which is independent of the amount of pyrite. As suggested by Huber et al.[6], the Monod type of model was not appropriate here since pyrite is not a soluble substrate. The value, X_A is the density of attached cells, defined as cells/mM pyrite, and Y_S is the yield factor for microbial oxidation of pyrite defined as cells/mM FeS_2 oxidized. The microbial growth is considered as occurring in two ways. One is the growth on pyrite surface, the other term is the growth on ferrous iron in solution. For the growth on pyrite surface, the number of attached cells is limited by a saturation cell density designated as X_A^*. For the growth on ferrous iron, the Monod expression can be applied. The density of the cells which did not attach to the pyrite surface (could be free suspended or attached to surfaces other than pyrite) is designated as X_F. Based on the assumptions, the rate equation for each kinetic element is proposed as follow:

$$\text{Rate of chemical oxidation of } Fe^{2+} = k_1 [Fe^{2+}] - k_{-1}[Fe^{3+}] \quad \text{.....(1)}$$

$$\text{Rate of microbial oxidation of } Fe^{2+} = \frac{\mu_{M,Fe}^* [Fe^{2+}]}{K_{Fe} + [Fe^{2+}]} * \frac{X_F}{Y_{Fe}} \quad \text{....(2)}$$

$$\text{Rate of chemical oxidation of } FeS_2 = k_s[Fe^{3+}]\left(\frac{[Fe^{2+}]_{eq}}{[FeS_2]_{eq}} - \frac{[Fe^{2+}]}{[FeS_2]}\right) \quad \text{..(3)}$$

$$\text{Rate of biological oxidation of } FeS_2 = \frac{\mu_{M,S}^* X_A^* [FeS_2]}{Y_S} \quad \text{.....(4)}$$

$$\text{Rate of } Fe^{3+} \text{ precipitation} = k_p [Fe^{3+}] \quad \text{.....(5)}$$

Based on the rate equations proposed above, balance equations for Fe(II), Fe(III), attached cells, free-floating cells and pyritic sulfur can be writen as:

$$\frac{d[Fe^{2+}]}{dt} = -k_1([Fe^{2+}] - K_e\,[Fe^{3+}]) + \frac{\mu_{M,Fe} * [Fe^{2+}]}{K_{Fe} + [Fe^{2+}]}$$

$$+ 3\,k_s[Fe^{3+}]\left(\frac{[Fe^{2+}]_{eq}}{[FeS_2]_{eq}} - \frac{[Fe^{2+}]}{[FeS_2]}\right) + 3\,\frac{\mu_{M,S}\,X_A[FeS_2]}{Y_S} \quad \ldots\ldots\ldots(6)$$

$$\frac{d[Fe^{3+}]}{dt} = k_1([Fe^{2+}] - K_e\,[Fe^{3+}]) + \frac{\mu_{M,Fe}*[Fe^{2+}]}{K_{Fe} + [Fe^{2+}]}\,\frac{X_F}{Y_{Fe}} - k_p[Fe^{3+}] \quad \ldots\ldots(7)$$

$$\frac{d\,X_A}{dt} = L_{M,S}\,X_A \qquad \text{when } X_A < X_A^* \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

$$= 0 \qquad \text{when } X_A = X_A^*$$

$$\frac{d\,X_F}{dt} = \frac{\mu_{M,Fe}[Fe^{2+}]}{K_{Fe} + [Fe^{2+}]} + X_A * \left(\frac{d[FeS_2]}{dt}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

$$-\frac{d[FeS_2]}{dt} = k_s[Fe^{3+}]\left(\frac{[Fe^{2+}]_{eq}}{[FeS_2]_{eq}} - \frac{[Fe^{2+}]}{[FeS_2]}\right) + \frac{\mu_{M,S} * X_A*[FeS_2]}{Y_S} \quad ..(10)$$

$$= 2\,\frac{d[SO_4^{=}]}{dt}$$

The factor 3 came from the assumption that 3 moles of ferrous iron were released when one mole of FeS_2 was oxidized with 2 moles of ferr iron.

RESULTS AND DISCUSSIONS

Oxidation of ferrous ions in aqueous solution:

In the absence of microorganism and pyrite, the equations to describe the pure chemical oxidation of ferrous ions can be derived simply by dropping the biological terms and sulfur turms in the balance equations for a general bioleahing system. Equilibrium was reached in a few days and no more oxudation occurred. A drop of total iron concentration signified precipitation of ferric ions.

Microbial oxidation of ferrous ions

Figure 1 demonstrates the data from a run with inoculated ferrous sulfate medium. In the presence of microbes, the balance equation can be derived by dropping the sulfur terms in the general equations. The results of simulation are given in Figure 1. The experimental data indicate that ferrous ions were completed oxidized to ferric ions with the help of microorganisms. Ferric ion concentrations in the medium increased rapidly at first and then dropped due to precipitation of ferric-sulfate complex. The drop of ferrous ions was associated with growth of the microorganism.

Oxidation of pyrite in aqueous solution

Experimental results with uninoculated 5% coal slurry are shown in Figure 2. An equilibrium was detected beyond which no more oxidation occurred. Model prediction and data are shown in Figure 2. The model fits the data to a satisfactory degree.

Microbial oxidation of pyrite

The data from batch leaching of -270+325 mesh Kentucky #9 coal was fitted with this model. As Case I, it is assumed that cells preferentially adsorbed on the pyrite surface. In other words, all the attached cells were on pyrite sites in the coal. Case II has only part of the attached cells on the pyrite surface while others were on coal surfaces.

Figure 3 shows the simulation for case I. The predicted ferrous iron concentration was higher than the experimental data. Figure 4 shows the simulation results with the assumption of case II. The predicted ferrous iron concentration in the first two days of leaching was lower than the experimental data, which means that fewer cells were utilizing ferrous iron as energy. In Figure 4 the number of cells which were attached to pyrite surface was assumed to be 10% of the the cells attached to coal particles. The model predicted the general trend, or the dynamics of the leaching system, but more information is required to develop further the model for a better fit to the experimental data.

CONCLUSION

Kinetic elements were proposed to describe the bacterial leaching system. The cells attached to pyrite sites grew on pyrite and yielded ferrous iron and sulfate as the products. The cells which were not on the pyrite sites, either attached to the coal surface or freely suspended utilized ferrous iron as an energy source. Chemical oxidation of pyrite by ferric iron and chemical oxidation of ferrous iron were also considered. The model gave a good description of the dynamics of the leaching system.

There are limitations in applying this model since assumptions were made to simplify the rate equations. Also, cells counts in the coal slurry were not accurately followed due to interference from the materials leached from coal. However, the model predicts the trends of concentration profiles of Fe(II), Fe(III) and sulfate ions in solution. More experiments with accurate cell counts is necessary to make the model more generally applicable.

Nomenclature

k_s: Rate constant for chemical oxidation of pyrite, (mM/day ppm^2)
k_1 : Rate constant for chemical oxidation of ferrous iron, (1/day)
k_{-1} : Rate constant for reduction of ferric ions, (1/day)
$\mu_{M,F}$: Maximum specific growth rate of cells on ferrous iron, 1/day)
K_{Fe}: Saturation constant in the Monod model, (mg Fe/l)
Y_{Fe}: Yield factor for cell growth on ferrous iron, (cells/nM Fe)
$\mu_{M,S}$: Specific growth rate on pyrite (1/day)
Y_S: Yield factor for growth on pyrite, (cells/mM FeS_2)
X_F : Free-floating cell density, (cells/ml solution)
X_A : Attached cell density, (cells/gm coal)

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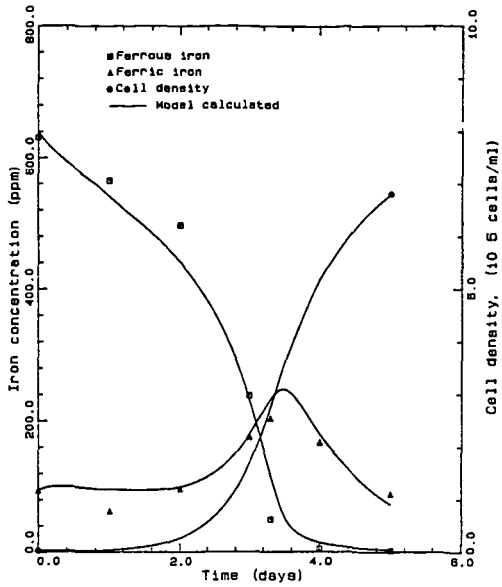

Figure 1 Curve-fitting of experimental data on microbial oxidation of ferrous iron, run #4

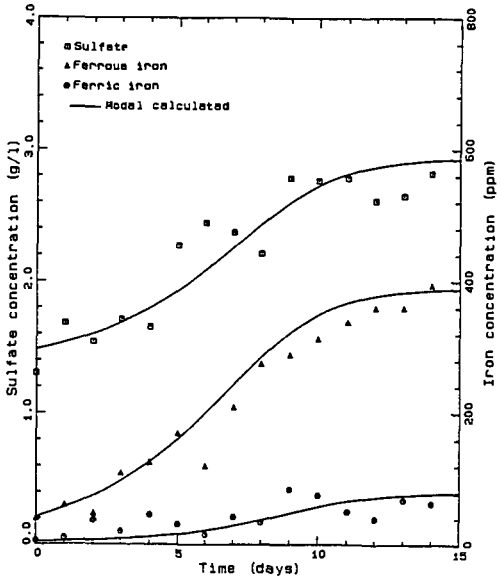

Figure 2 Curve-fitting of experimental data on an uninoculated control of 10% slurry of Kentucky #9 coal with a single dose of basal salts.

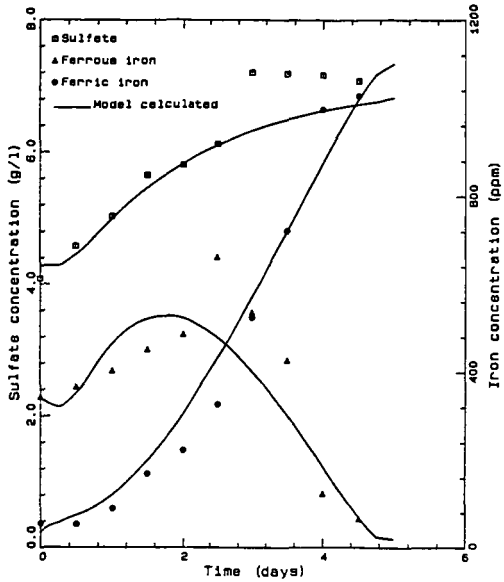

Figure 3. Curve-fitting of experimental data on batch leaching of -270 +325 mesh Kentucky #9 coal, case I.

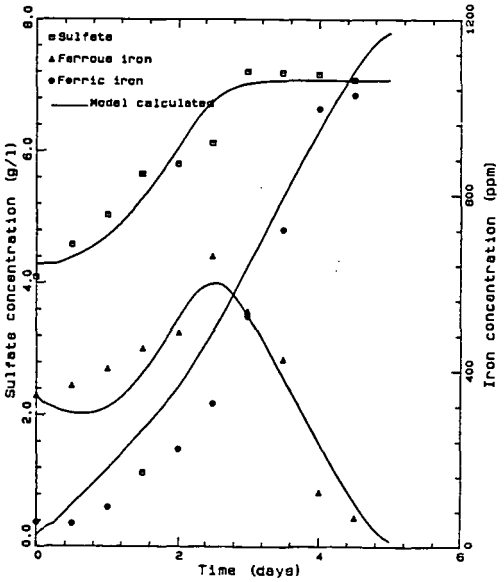

Figure 4. Curve-fitting of experimental data on batch leaching of -270 +325 mesh Kentucky #9 coal, case II.