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STUDIES ON THE MECHANISM AND KINETICS OF BIOLEACHING

In the past five years significant advances have been made in understanding the mechanism by which the bioleaching of sulphide minerals occurs. Kinetic models based on the proposed mechanism are being used successfully to predict the performance of continuous bioleach reactors. The measurement of oxygen and carbon dioxide consumption rates together with the measurement of redox potentials, has led to this further elucidation of the mechanism of bioleaching of sulphide minerals and enabled the kinetics of the sub-processes involved to be determined separately. It has been shown that bioleaching involves at least three important sub-processes. The primary attack of the sulphide mineral is a chemical ferric leach producing ferrous iron.

The first two sub-processes of chemical ferric reaction with the mineral and bacterial oxidation of the ferrous iron are linked by the redox potential. The sub-processes are in equilibrium when the rate of iron turnover between the mineral and the bacteria is balanced. Rate equations based on redox potential or ferric/ferrous-iron ratio have been used to describe the kinetics of these sub-processes.

The kinetics of bacterial ferrous iron oxidation by *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* have been determined over a range of expected operating conditions. Also the chemical ferric leach kinetics of pyrite have been measured under conditions similar to those in bioleach systems. The kinetics have been described as functions of the ferric/ferrous-iron ratio or redox potential which enables the interactions of the two sub-processes to be linked at a particular redox potential through the rate of ferrous iron turn-over. The use of these models in predicting bioleach behaviour for pyrite presented and discussed. The model is able to predict which bacterial species will predominate at a particular redox potential in the presence of a particular mineral, and which mineral will be preferentially leached. The leach rate and steady state redox potential can be predicted from the bacterial to mineral ratio. The implications of this model on bioleach reactor design and operation are discussed.

Using these rate equations it is possible to predict the steady state redox potential and sulphide mineral conversion in a continuous bioleach reactor. The model successfully predicts laboratory data and is being tested against data from pilot-plant and full-scale bioleach systems.

Using 16S rDNA techniques, it has been shown that in pyrite–arsenopyrite bioleach reactors, the iron oxidizer, *Leptospirillum ferrooxidans* and the sulphur oxidizer, *Thiobacillus caldus* predominate. No *Thiobacillus ferrooxidans* could be detected. These observations are in agreement with the predictions from the kinetics and the electrochemical mechanism of ferric leaching of sulfide minerals.

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INTRODUCTION

The bioleaching of copper has been practiced for some time from copper bearing sulfide ore and waste in dumps (Murr, 1980). More recently heap leaching has been used for copper bioleaching and the pretreatment of arsenical refractory gold ores (Schnell, 1997, Brierley, 1997). The biooxidation of arsenical gold-bearing concentrates in large stirred tank bioreactors has been practiced since 1984 with several large plants in different parts of the world (Dew et al., 1997; and Miller, 1997). The design of these has been based on the use of the empirical logistic equation to describe the kinetics of bioleaching (Pinches et al., 1988; Hansford and Miller, 1993; Dew, 1995). However recent work by Boon (1996) has led to the development of a mechanistically based model for bioleaching (Boon et al., 1995; Hansford, 1997). This model predicts the kinetics of bioleaching, explains the microbial selection which takes place in bioleach systems and is the basis for the derivation of a performance equation for continuous bioleach reactors. The predictions of the model are in accordance with microbial identification using 16S rDNA techniques and the electrochemistry of the ferric leaching of sulfide minerals (Rawlings et al., 1998). This paper will review these recent developments.

BACKGROUND

The use of degree-of-reduction balances (Roels, 1983) coupled with off-gas analysis for the measurement of oxygen and carbon dioxide utilisation rate has been developed by Boon (1996) in order to measure bacterial concentration (mole $C \cdot l^{-1}$) and pyrite concentration in bioleach systems. These measurements have proved difficult in the past. The activity of the bacteria was determined as the specific rate of oxygen utilisation (mole $O_2 \cdot (\text{mole C})^{-1} \cdot h^{-1}$) and was measured either from off-gas analysis in the bioreactors or off-line in a biological oxygen monitor.

By staged additions of pyrite at four hourly intervals to a batch bioleach, Boon et al. (1995) were able to measure the specific rate of oxygen utilisation, q_{O_2}, as a function of ferric/ferrous-iron ratio or redox potential. The oxygen rate was also related to the amount of pyrite present as the pyrite specific rate, ν_{O2}. The results of a typical run are shown in Fig. 1, where it can be seen that q_{O2} decreases with increasing ferric/ferrous-iron ratio or redox potential while ν_{O2} increases. Samples of the bacteria were taken from the batch and the pyrite removed by centrifugation and the specific rate of oxygen utilisation measured in the off-line respirometer, BOM, using ferrous iron medium. The specific rate of oxygen utilisation, q_{O_2}, could be measured over a wider range of ferric/ferrous-iron ratios than for the pyrite batch, but over the region where ranges overlapped, the data for the pyrite- and ferrous iron-grown bacteria coincided, as shown in Fig. 2. From this it was concluded that in both cases ferrous

iron was the primary substrate, and that the bioleaching of pyrite occurs as a two-step mechanism involving the chemical ferric leaching of the pyrite and the bacterial oxidation of the ferrous iron produced, back to the ferric form.

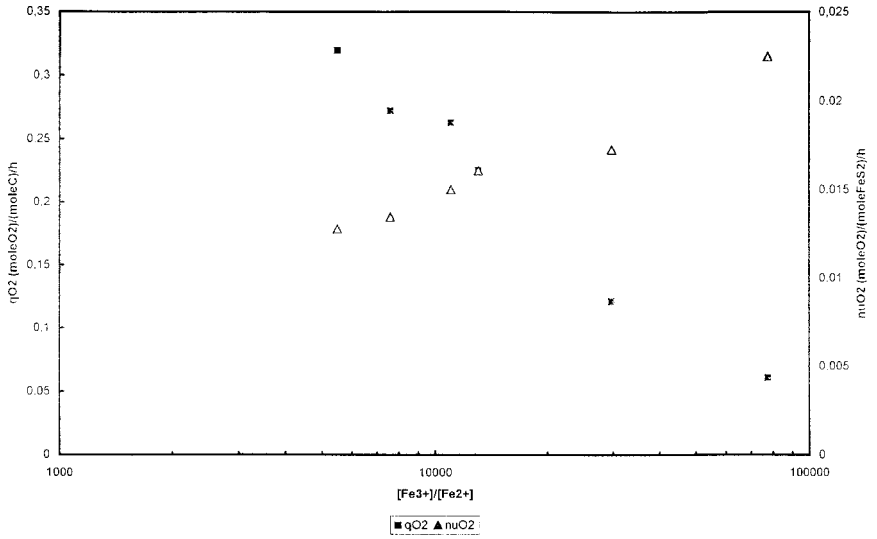

Fig. 1. Bacterial and pyrite specific oxygen utilisation rates as functions of the ferric/ferrous-iron ratio for the bioleaching of pyrite (2–20 g·l^{-1}) by *Leptospirillum ferrooxidans* (25–100 g·l^{-1}) and total iron 2.4–5.0 g·l^{-1} pH = 1.6, T = 30 °C

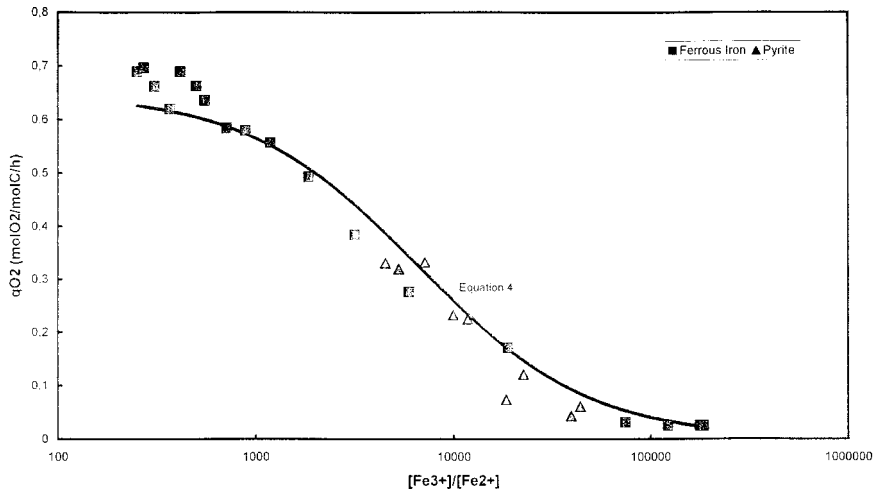

Fig. 2. Specific oxygen utilisation rates of pyrite and ferrous iron grown *Leptospirillum ferrooxidans* as a function of ferric/ferrous-iron ratio together with the prediction of Eq. (5)

The reactions involved are:

$$FeS_2 + 14Fe^{3+} + 8H_2O \quad = \quad 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{1}$$

and

$$4Fe^{2+} + O_2 + 4H^+ \quad = \quad 4Fe^{3+} + 2H_2O \tag{2}$$

Boon (1996) has described the kinetics of the overall process

$$4FeS_2 + 15O_2 + 2H_2O \quad = \quad 4Fe^{3+} + 8SO_4^{2-} + 4H^+ \tag{3}$$

in terms of the pyrite specific oxygen utilisation rate as a function of the ferrous/ferric-iron ratio of the form:

$$v_{O2} \quad = \quad \frac{-r_{O_2}}{[FeS_2]} \quad = \quad \frac{v_{O_2}^{max}}{1 \; + \; B\dfrac{[Fe^{2+}]}{[Fe^{3+}]}} \tag{4}$$

and the specific oxygen utilization rate of the bacterial ferrous oxidation sub-process can be expressed as a simplified form of that previously used for inhibited Michaelis–Menten kinetics (Jones and Kelly, 1983):

$$q_{O_2} \quad = \quad \frac{-r_{O_2}}{c_X} \quad = \quad \frac{q_{O_2}^{max}}{1 \; + \; K\dfrac{[Fe^{3+}]}{[Fe^{2+}]}} \tag{5}$$

Boon (1996) has reported the following values for the kinetic constants: $v_{O2}{}^{max}$ = 0.025 h^{-1}, B = 0.00045 and $q_{O_2}^{max}$ = 1.7 h^{-1}, K = 0.0005 for the bioleaching of pyrite by *Leptospirillum*-like bacteria and $q_{O_2}^{max}$ = 2.2 h^{-1}, K = 0.05 for ferrous iron oxidation for a pure culture of *Thiobacillus ferrooxidans*.

THE MECHANISM AND KINETICS OF SULFIDE MINERAL BIOLEACHING

The two sub-processes are linked at pseudo steady state by equating the rate of ferrous iron production from the chemical ferric leach reaction to the rate of consumption of ferrous iron by the bacteria. In order to do this, the kinetics of the two sub-processes must be rewritten for ferrous iron production and utilization in terms of the rate of ferrous iron production per unit surface area of the pyrite particles as:

$$\nu_{Fe^{2+}} = \frac{-r_{Fe^{2+}}}{[FeS_2]} = \frac{\nu^{max}_{Fe^{2+}}}{1 + B\dfrac{[Fe^{2+}]}{[Fe^{3+}]}} \tag{6}$$

and the specific rate of bacterial ferrous iron oxidation:

$$q_{Fe^{2+}} = \frac{-r_{Fe^{2+}}}{c_X} = \frac{q^{max}_{Fe^{2+}}}{1 + K\dfrac{[Fe^{3+}]}{[Fe^{2+}]}} \tag{7}$$

so that at a particular pyrite and bacterial concentration the pseudo steady state will be defined by:

$$\frac{\nu^{max}_{Fe^{2+}}[FeS_2]}{1 + B\dfrac{[Fe^{2+}]}{[Fe^{3+}]}} = r_{Fe^{2+},\,chem} = -r_{Fe^{2+},\,bact} = \frac{q^{max}_{Fe^{2+}}}{1 + K\dfrac{[Fe^{3+}]}{[Fe^{2+}]}} \tag{8}$$

where it is possible to express the ferric/ferrous-iron ratio in terms of the redox potential using the Nernst equation as:

$$\frac{[Fe^{3+}]}{[Fe^{2+}]} = \exp\left(\frac{E_h - E_0}{\dfrac{RT}{nF}}\right) \tag{9}$$

Using the stoichiometry of Eqs. (1) and (2), the following values for the ferrous iron based kinetic constants can be obtained from Boon's oxygen based values $\xi^{max}_{Fe^{2+}} = 0.0067\ h^{-1}$, $B = 0.00045$, $q^{max}_{Fe^{2+}} = 6.8\ h^{-1}$, $K = 0.0005$ for the bioleaching of pyrite by *Leptospirillum*-like bacteria and $q^{max}_{Fe^{2+}} = 8.8\ h^{-1}$, $K = 0.05$ for ferrous iron oxidation for a pure culture of *Thiobacillus ferrooxidans*. Although it is known that *Thiobacillus ferrooxidans* can also oxidize sulphur and sulphur moieties for the purpose of simulation, it is assumed that this is not the rate controlling sub-process in this system.

Figure 3 shows the rates of ferrous iron generation by ferric leaching of pyrite and ferrous consumption by *Leptospirillum ferrooxidans* and *Thiobacillus ferrooxidans*. The curves are plotted for a concentration of 10 $g \cdot l^{-1}$ of +53 –75 μm pyrite and for bacterial concentrations of 150 mg $C \cdot l^{-1}$ at a total iron concentration of 12 $g \cdot l^{-1}$. The point of intersection of the curves represents the pseudo-steady state giving the rate of ferrous iron turn-over and the redox potential. It can be seen that for the bioleaching of pyrite that the ferric leach curve intersects the bacterial ferrous oxidation curve of

Leptospirillum ferrooxidans at a higher rate of ferrous turnover than *Thiobacillus ferrooxidans* and therefore *Leptospirillum ferrooxidans* will be dominant species. This has been confirmed by Rawlings (1995) who has found that *Leptospirillum ferrooxidans* predominates in the bioreactors of the GENCOR BIOX® process treating an arsenopyrite-pyrite concentrate.

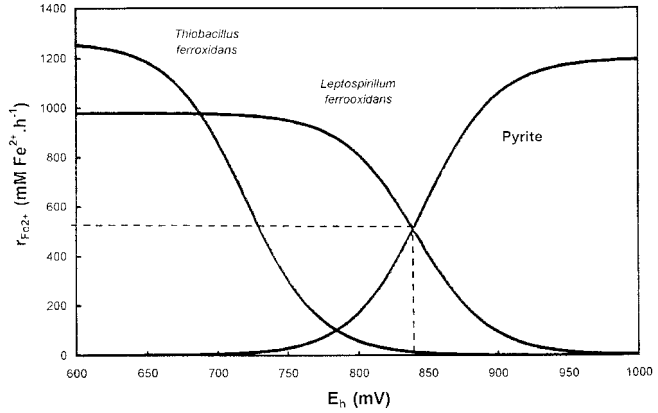

Fig. 3. Predicted rate of ferrous iron production by ferric leaching of –53 +75 μm pyrite at 10 $g \cdot l^{-1}$ together with the predicted rate of ferrous iron oxidation by *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* at 150 mg $C \cdot l^{-1}$ as functions of the redox potential. The predictions are made using Eq. (8) with the kinetic constants found by May et al. (1997), Boon (1996), van Scherpenzeel (1997)

The point of intersection of the chemical and bacterial curves, defines the pseudo-steady state redox potential and the rate of ferrous iron turn-over, which can be related stoichiometrically to the rate of pyrite bioleaching. The intersection point depends on both the concentration of bacteria and active surface area concentration of the pyrite. In this way the model presented here can be related to those which are based on a bacteria-to-mineral ratio, $c_X/[FeS_2]$ (Boon, 1996). As the bacterial concentration and/or the surface area concentration change the redox potential and overall pyrite bioleaching rate will change accordingly.

In the bioleaching of sulphide minerals which have lower rest potentials, the ferric leach curve will intersect the bacterial curves at a lower redox potential where the ferrous iron oxidation rate of *Thiobacillus ferrooxidans* may be higher than that of *Leptospirillum ferrooxidans* and then it may dominant.

According to this two-step mechanism for sulphide mineral bioleaching it is possible to determine the kinetics of the chemical and bacterial sub-processes independently and then use the kinetic constants so derived to predict both the steady state and dynamic performance of bioleach systems. Recent work on the purely chemical ferric leaching of pyrite by May et al. (1997) has shown that the values for ξ_{Fe2+}^{max} and B agree with those obtained from the data of Boon et al. (1995), for the bioleaching of pyrite. The dependence of the bacterial kinetics on redox potential is

consistent with the chemiosmotic theory of Ingledew (1982), while the dependence of the ferric leach kinetics on redox potential is in accord with electrochemical theory. The existence of a two-step mechanism for the bioleaching of sulphide minerals has a number of important implications for the modelling of bioleaching, viz.,

i) the overall process can be reduced to a number of independent sequential and/or parallel sub-processes,

ii) each of these sub-processes can be studied separately,

iii) the results of the above can be used to predict the performance of bioleaching operations for a variety of different minerals, bacteria and operating conditions.

MODELING THE PERFORMANCE OF CONTINUOUS BIOLEACH REACTORS

In a continuous bioreactor at steady state it can be shown that the growth rate of the micro-organisms is equal to the dilution rate, D, or reciprocal of the residence time, $1/\tau$.

$$\mu = D = \frac{1}{\tau} \tag{10}$$

If it is assumed that the specific growth rate of the bacteria is directly related to the specific rate of ferrous iron oxidation via a yield constant, $Y^{\max}_{Fe^{2+}EX}$, then:

$$q_{Fe^{2+}} = \frac{\mu}{Y^{\max}_{Fe^{2+}X}} = \frac{D}{Y^{\max}_{Fe^{2+}X}} \tag{11}$$

Substituting for q_{Fe2+} from Eq. (7) and solving for the ferric/ferrous iron-ratio gives:

$$\frac{[Fe^{3+}]}{[Fe^{2+}]} = \frac{Y^{\max}_{Fe^{2+}} q^{\max}_{Fe^{2+}} \tau - 1}{K} \tag{12}$$

and using the Nernst equation this can be expressed as redox potential.

This applies to completely mixed bioreactor at steady state provided there is no retention of biomass in the bioreactor. It therefore applies to a bioreactor being fed with pyrite and it can be seen that the steady state ferric/ferrous-iron ratio or redox potential is not dependent on the concentration of pyrite in the feed but only on the residence time. This is analogous to the behaviour of a chemostat (Schuler and Kargi, 1992).

From the stoichiometry of Eq. (1), the rate of pyrite leaching is related to the rate of ferrous iron production rate by that reaction as:

$$r_{FeS_2} = \frac{1}{15} r_{Fe^{2+}} = -\frac{1}{15} \xi_{Fe^{2+}} \alpha\, [FeS_2] \tag{13}$$

A steady state pyrite balance over the bioreactor gives:

$$F([FeS_2]_{in} - [FeS_2]) = Vr_{FeS_2} \tag{14}$$

so that the pyrite concentration leaving the bioreactor is given by:

$$[FeS_2] = \frac{15[FeS_2]}{15 + 15B\dfrac{[Fe^{2+}]}{[Fe^{3+}]} - \alpha\tau\xi^{max}_{Fe^{2+}}} \tag{15}$$

and the pyrite conversion by

$$X_{FeS_2} = \frac{[FeS_2]_{in} - [FeS_2]}{[FeS_2]_{in}} = \frac{15B\dfrac{[Fe^{2+}]}{[Fe^{3+}]} - \alpha\tau\xi^{max}_{Fe^{2+}}}{15 + 15B\dfrac{[Fe^{2+}]}{[Fe^{3+}]} - \alpha\tau\xi^{max}_{Fe^{2+}}} \tag{16}$$

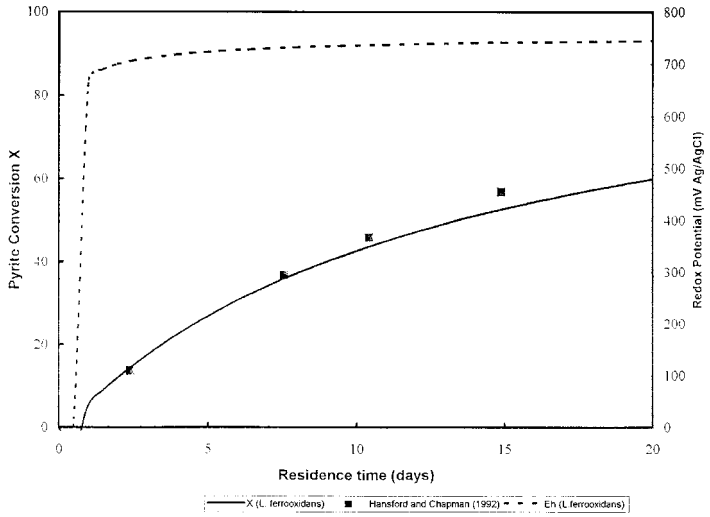

Fig. 4. Predicted (Eq. (16)) and measured conversions (Hansford and Chapman, 1992) of pyrite in a continuous bioleach reactor

Substituting the ferric/ferrous-iron ratio from Eq. (12) into Eq. (16) shows that the pyrite conversion is also a function of only the residence time in the bioreactor and the rate constants and particle size distribution of the pyrite.

Unfortunately at the time of writing there was only one set of continuous pyrite bioleaching data available (Hansford and Chapman, 1992). This was obtained in a laboratory-scale, 5-litre continuous bioleach reactor using a culture thought to be *Thiobacillus ferrooxidans* and a pyrite flotation concentrate from Crown Mines, South

Africa. For the 53–75 μm size fraction for steady state pyrite conversions were obtained. No redox potential data are available. The results are compared with the predictions of Equation (16) using kinetic constants obtained for the bioleaching of 53–75 μm size fraction pyrite flotation concentrate from Prieska Copper Mine, Copperton, South Africa by Boon (1996) and confirmed for the abiotic ferric leaching of the same concentrate by May (1997). The kinetic constants for the bacterial oxidation of ferrous iron oxidation used were those obtained for *Leptospirillum ferrooxidans* by van Scherpenzeel (1997). The predicted and actual conversions are shown in Fig. 4. The agreement between the prediction and the experimental data is remarkable particularly when considering that the pyrite concentrates are from different sources and that the bacteria used by Hansford and Chapman (1992) were unidentified and thought to be *Thiobacillus ferrooxidans*. However in retrospect it is reasonable to assume that the bacteria which would predominate in a continuous culture growing on pyrite would be *Leptospirillum ferrooxidans*.

CONCLUSIONS

The two-step mechanism for bioleaching provides a basis for predicting the overall rates of bioleaching from the rates of the controlling sub-processes of chemical ferric leaching and bacterial ferrous iron oxidation. These can be conveniently expressed in terms of the ferric/ferrous-iron ratio or redox potential. This approach also predicts which microbial species will predominate. It also suggests that the kinetics of the two sub-processes can be investigated separately. Further refinement of this approach is necessary to include changes in size and surface of the sulphide minerals, the formation of precipitates which could occlude the surface and the bacterial oxidation of the sulphur moiety.

SYMBOLS

$[Fe^{2+}]$ – ferrous iron concentration, mole·l^{-1}
$[Fe^{3+}]$ – ferric iron concentration, mole·l^{-1}
$[FeS_2]$ – pyrite concentration, mole·l^{-1}
c_X – bacterial concentration, (mole C)·l^{-1}
E – redox potential, mV
E_0 – standard redox potential, mV
F – Faraday constant, 96485 C·(mole)$^{-1}$
n – number of electrons in redox reaction,
q_{O_2} – bacterial specific oxygen utilisation rate, (mole O_2)·(mole C)$^{-1}$·h^{-1}
$q_{Fe^{2+}}$ – bacterial specific ferrous utilisation rate, (mole)·(mole C)$^{-1}$·h^{-1}
R – universal gas constant, 8.134 J·K^{-1}(mole)$^{-1}$
$r_{Fe^{2+}}$ – rate of ferrous iron production, mole·l^{-1}·h^{-1}
r_{O_2} – rate of oxygen production, mole·l^{-1}·h^{-1}

T – temperature, K
X_{FeS_2} – pyrite conversion
ν_{O_2} – pyrite specific oxygen utilisation rate, (mole O_2)·(mole FeS_2)·h^{-1}
$\nu_{O_2}^{max}$ – maximum pyrite specific oxygen utilisation rate, (mole O_2)·(mole FeS_2)·h^{-1}
$\xi_{Fe^{2+}}$ – pyrite specific ferrous utilisation rate, (mole Fe^{2+})·(mole FeS_2)·h^{-1s}
$\xi_{Fe^{2+}}^{max}$ – maximum pyrite specific ferrous utilisation rate, (mole Fe^{2+})·(mole FeS_2)·h^{-1}

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Hansford G.S., Badania mechanizmu i kinetyki bio³ugowania, *Fizykochemiczne Problemy Mineralurgii*, 32, 281–291 (w jêzyku angielskim)

W ostanich pięciu latach nastąpił znaczny postęp w rozumieniu mechanizmów ługowania siarczków. Obecnie z powodzeniem używane są modele kinetyczne oparte o mechanizm procesu, które pozwalają na przewidywanie wyników bio-ługowania w reaktorach. Pomiary szybkości zużycia tlenu i dwutlenku węgla wraz z pomiarami potencjału redoks pozwoliły na lepsze poznanie mechanizmu procesu i jego składowych. Podstawą procesu jest reakcja pomiędzy minerałem siarczkowym a jonami żelaza (III) z utworzeniem jonów żelaza (II) a subprocesy polegają na reakcji chemicznej jonów żelaza z minerałem oraz bakteryjnym utlenianiem jonów żelaza (II) i są one związane z potencjałem redoks. Oba subprocesy są w równowadze, gdy szybkość wędrówki jonów żelaza pomiędzy minerałem i bakteriami są w równowadze. Kinetyki wspomnianych subprocesów są oparte o potencjał redoks i stosunek jonów stężeń żelaza (III) do żelaza (II).

W pracy przebadano kinetykę bakteryjnego utleniania jonów żelaza (II) przez *Thiobacillus ferrooxidans* i *Leptospirillum ferrooxidans*. Mierzono także kinetykę chemicznego ługownia jonami żelaza (II) pirytu w warunkach zbliżonych do bioługowania. Kinetykę procesu opisano jako funkcję stosunku stężeń jonów żelaza (III) do żelaza (II) i potencjału redoks, co pozwoliło na połączenie oddziaływań obu subprocesów przy odpowiednim potencjale redoks poprzez szybkość transportu jonów żelaza (II). Zaproponowany model pozwala na przewidywanie wyników bioługownia pirytu, w tym określenie która bakteria będzie dominowała przy odpowiednich potencjałach redoks w obecności wybranego minerału i który minerał będzie preferencyjnie ulegał ługowaniu. W pracy przedyskutowano również implikacje modelu dla ważniejszych parametrów bioreaktora i zmienne procesu. Wykorzystując równanie szybkości reakcji jest możliwe przewidywanie potencjału redoks stany stacjonarnego i wyników ługowania w biorektorach o działaniu ciągłym. Model pozwala przewidywać wyniki badań laboratoryjnych i jest obecnie testowany dla wyników uzyskanych dla bioługowania na pełna skalę. Wykorzystując technikę 16S rDNA pokazano, że w reaktorach podczas bioługowania pirytu–arsenopirytu dominuje żelazowy utleniacz, *Leptospirillum ferrooxidans* i utleniacz siarkowy oraz *Thiobacillus caldus*. Nie stwierdzono obecności bakterii *Thiobacillus ferrooxidans*. Obserwacje te są zgodne z przewidywaniami z kinetyki procesu i elektrochemicznego mechanizmu ługownia minerałów siarczkowych za pomocą jonów żelaza (II).