Journal of Industrial Microbiology, (1995) 14, 420–423

Microbial desulfurization of coal and oxidation of pure pyrite by *Thiobacillus ferrooxidans* and *Acidianus brierleyi*

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(Received 6 June 1993; accepted 21 December 1994)

Key words: Pyrite oxidation; Coal desulfurization; *Thiobacillus ferrooxidans*; *Acidianus brierleyi*; Kinetics

SUMMARY

Thiobacillus ferrooxidans and *Acidianus brierleyi* were capable of oxidizing pure pyrite as well as oxidizing sulfur in coal. First order reactions were assumed in the kinetic analysis performed. For oxidation of pure pyrite the rate constant was higher for *A. brierleyi* than for *T. ferrooxidans*. For sulfur removal from coal the values of the rate constants were comparable for the two microorganisms.

INTRODUCTION

When using coal combustion for energy production, microbial desulfurization of coal is one alternative for the control of sulfur emission [6]. Investigations of coal desulfurization have been performed using the mesophilic, acidophilic eubacterium *Thiobacillus ferrooxidans* [3–4,8], which removes pyritic sulfur from coal. The thermophilic and acidophilic archaea *Acidianus brierleyi* has also been used in coal desulfurization investigations [1,13]. This latter species was formerly called *Sulfolobus brierleyi* [17].

Inorganic sulfur in coal consists mainly of pyrite, FeS_2. The percentage of pyrite in coal varies from almost nothing to over 10%, depending on the grade of the coal [10]. The forms of the pyrite in different coal types differ. The pyrite in coal may occur in particulate form, in bands or it may be finely scattered [2].

The reaction for microbial pyrite oxidation is:

$$2\ FeS_2 + 7.5\ O_2 + H_2O \rightarrow 2\ Fe^{3+} + 4\ SO_4^{2-} + 2\ H^+$$

In microbial pyrite oxidation two mechanisms are distinguished, the indirect mechanism and the direct contact mechanism, respectively. In the indirect mechanism, the bacteria oxidize Fe^{2+} to Fe^{3+}; the regenerated Fe^{3+} ions are then used for chemical oxidation of pyrite. In the direct contact mechanism the pyrite is oxidized biologically and it requires physical contact between the bacteria and the pyrite particles. It is possible that both the direct and the indirect contact mechanisms may occur simultaneously [18].

Some of the ferric and sulfate ions may precipitate as jarosite according to the following reaction [11]:

$$3\ Fe^{3+} + M^+ + 6\ H_2O + 2\ SO_4^{2-} \rightarrow MFe_3(SO_4)_2(OH)_6 + 6\ H^+$$

where M^+ may be potassium or hydrogen. Sodium and ammonium jarosites may also be produced, but not as fast as potassium jarosite [5].

Pure pyrite is often used as a model substance for the pyrite contained in coal during investigations of microbial coal desulfurization. However, all pyrites are not identical and the behaviour of the pyrite depends on the source. Pyrite in coal differs from pyrite found in ore [12]. Pyrite in coal is more reactive than ore pyrite. The lower reactivity with Fe^{3+} and acid of ore pyrite compared with coal pyrite may depend on the formation of a passivating surface layer of iron hydroxides, elemental sulfur and/or unidentified sulfur species [12]. These findings might be of significance when selecting the type of coal for microbial desulfurization. The grade of the coals investigated by several research groups vary from lignite to bituminous coal. However, there is no indication that one coal type is better suited for microbial treatment than another.

We have shown that coal types with high content of pyrite are desulfurized better by *Thiobacillus ferrooxidans* and *Acidianus brierleyi* than coal types containing less pyrite [16]. Because of Swedish legislation, most of our work has been done with low sulfur coals.

In the present investigation, desulfurization of coal and the oxidation of pure pyrite were studied using the thermophilic archaea *Acidianus brierleyi* and the mesophilic eubacterium *Thiobacillus ferrooxidans*. One purpose of the investigation is to outline if pure pyrite and pyrite in coal are desulfurized differently. In the data evaluation, the rate constants of pure pyrite oxidation/desulfurization of coal for the two microorganisms are investigated assuming first order kinetics [15]:

$$S = S_\infty + (S_0 - S_\infty)e^{-kt} \quad (1)$$

where t is the time for exposure to microorganisms, k is the

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first order rate constant, S is total sulfur content in coal or pyrite (mg S L^{-1}) at time t, S_0 is the starting value of S and S_∞ is S of infinite time.

MATERIALS AND METHODS

Acidianus brierleyi DSM 1651 and *Thiobacillus ferroxidans* DSM 583 were obtained from DSM (Deutsche Sammlung von Mikroorganismen), Braunschweig, Germany. *A. brierleyi* and *T. ferrooxidans* were reinoculated every fourth week. *A. brierleyi* was maintained on yeast extract and *T. ferrooxidans* on ferrous iron. Pyrite was obtained from Boliden Kemi AB, Helsingborg, Sweden. The coal investigated was obtained from the European Centre for Coal Specimens (SBN), Eijgelshoven, The Netherlands. The study was done on coal 177US41 (sulfate S 0.05%, pyrite S 0.87%, organic S 0.46%). The sulfur values presented are on a dry weight basis. The coal was prepared by wet grinding prior to the experiments; this treatment leads to the dissolution of a small amount of sulfur. The median particle size for pyrite and coal in the experiments was <88 μm and <100 μm, respectively. The medium used was 'Leathen's' medium (K_2HPO_4 0.05 g L^{-1}, $(NH_4)_2SO_4$ 0.15 g L^{-1}, $MgSO_4 \cdot 7H_2O$ 0.50 g L^{-1}, $Ca(NO_3)_2$ 0.01 g L^{-1}, KCl 0.05 g L^{-1}). In the experiment with *A. brierleyi* and coal 177US41, 1 g L^{-1} yeast extract was added to the medium.

Experiments with coal were performed in air lift reactors of bench scale size (reactor diameter 80 mm, reactor height 400 mm, diameter of draught tube 45 mm) [9] filled to a volume of 1.8 L. The air flow was 1000 ml min^{-1} during the coal experiments. The pH during the tests was 2. The coal concentration in the reactors was 7.7% and 6.0% by weight for *A. brierleyi* and *T. ferrooxidans*, respectively. For the oxidation of pure pyrite, the experiments were performed in 500-ml shake flasks filled to a volume of 150 ml. The concentration of pyrite in the shake flask experiments was 2% (w/w). The temperature during the tests was 70 °C and 30 °C for *A. brierleyi* and *T. ferrooxidans*, respectively.

Samples of slurry were intermittently withdrawn from the reactors for analysis. The pyrite slurry was filtered. The coal slurry was filtered, washed and dried. Jarosite precipitated on the coal surfaces was removed in boiling 5 M hydrochloric acid.

Oxidation of pure pyrite was followed by measuring the sulfate concentration in the liquid, turbidimetrically after precipitation with $BaCl_2$ (ASTM D516-68). The total sulfur content of the coal was determined after removal of jarosite using a Leco sulfur analyzer SC132 (Leco Corporation, St Joseph, MI, USA).

RESULTS

T. ferrooxidans and *A. brierleyi* oxidized pure pyrite as well as sulfur in coal as seen in Figs 1 and 2. In the experiment with pure pyrite and *A. brierleyi*, the microorganisms had to adapt from yeast extract to pyrite. Therefore a lag period was observed. The lag period has not been included in Fig. 1 because the purpose of the present investigation was to study the kinetics of the oxidation. During experiments involving pure pyrite (Fig. 1), the rate of pyrite oxidation was higher for *A. brierleyi* than for *T. ferrooxidans*. However, during experiments with coal, the two microorganisms removed sulfur at comparable rates (Fig. 2). First order rate constants for the oxidation of pure pyrite and for the desulfurization of coal were evaluated by fitting expression (1) to the data in Figs 1 and 2.

Table 1 summarizes kinetic data for pyrite and sulfur in coal expressed as the rate constant (k) and the global initial reaction rate ($-r_0$). The latter reflects the concentration of leachable sulfur in the reactor as well as the value of the rate constant. The initial reaction rate can be estimated from Eqn 2:

$$-r_0 = k\,(S_0 - S_\infty) \qquad (2)$$

The efficiency of a microorganism is reflected by the rate constant, which is a direct measure of the retention time required for reaching a certain conversion. *A. brierleyi* was superior to *T. ferrooxidans* with pure pyrite as a substrate (Table 1), but for coal sulfur the two microorganisms were comparable. For both microorganisms, the rate constant for oxidation of pure pyrite was lower than the rate constant for desulfurization of coal.

DISCUSSION AND CONCLUSIONS

Acidianus brierleyi and *Thiobacillus ferrooxidans* oxidized pure pyrite and removed sulfur from coal. The two microorganisms removed the same amount of sulfur from the coal studied. They also removed sulfur from the coal at similar rates. However, the rate for oxidation of pure pyrite was higher for *A. brierleyi* than for *T. ferrooxidans*. Consequently, the rate constant for oxidation of pure pyrite was higher for *A. brierleyi* than for *T. ferrooxidans*. On the other hand, the two microorganisms had similar rate constants during desulfurization of coal. Furthermore, in earlier experiments with *A. brierleyi* in air-lift reactors [7,9] the pyrite oxidation rate was similar to the rate obtained in the present study.

The two microorganisms showed lower rate constants for oxidation of pure pyrite than for removing sulfur from the investigated coal. The rate constant is a lumped constant which depends on several of the prevailing conditions. Several such conditions have been suggested. For instance, pure pyrite is less reactive than pyrite in coal [12]. This phenomenon is suggested to be due to passivation of the pyrite surface and leads to a higher rate constant for coal as a pyrite source. Furthermore, the pyrite particles used in the present experiments had a median diameter of <88 μm, while coal particles had a mass median diameter of <100 μm. Thus, the pyrite particles in coal had a smaller diameter than the pure pyrite; hence, the specific surface area (m^2 g^{-1}) of the former particles was much greater. It is expected that oxidation of pyrite is directly related to the surface area. Thus a much higher rate constant for the coal was anticipated. Also, the growth conditions may be more beneficial for coal because coal may act as a source for energy and/or nutrition for cell growth [14]. This leads to a larger rate constant for the coal. Finally, mass transfer limitations within coal particles may lower the value of the lumped rate constant.

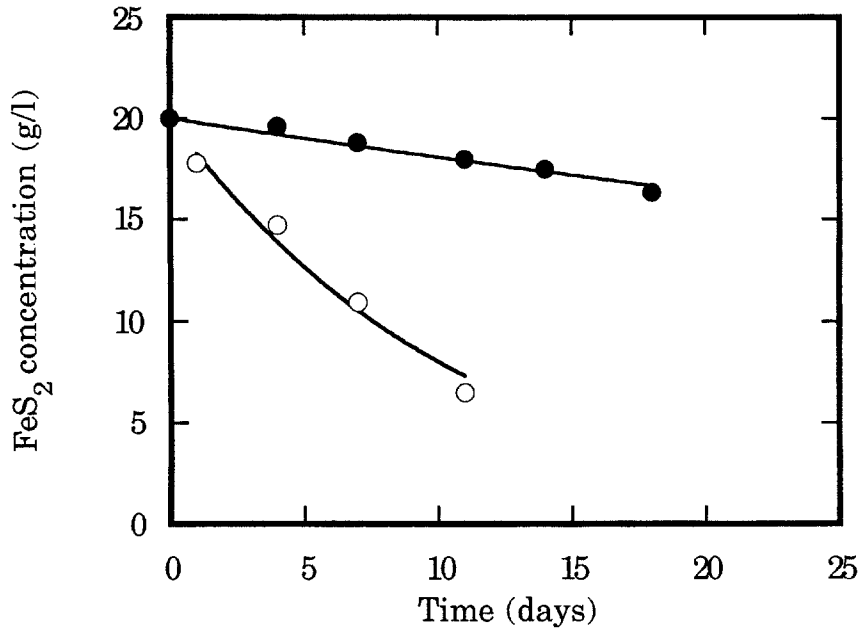

Fig. 1. Concentration of pyrite as a function of depyritization time during oxidation of pure pyrite by (●) *Thiobacillus ferrooxidans* and (○) *Acidianus brierleyi* (lag phase not included). Curves were obtained by a least-squares fit of Eqn 1.

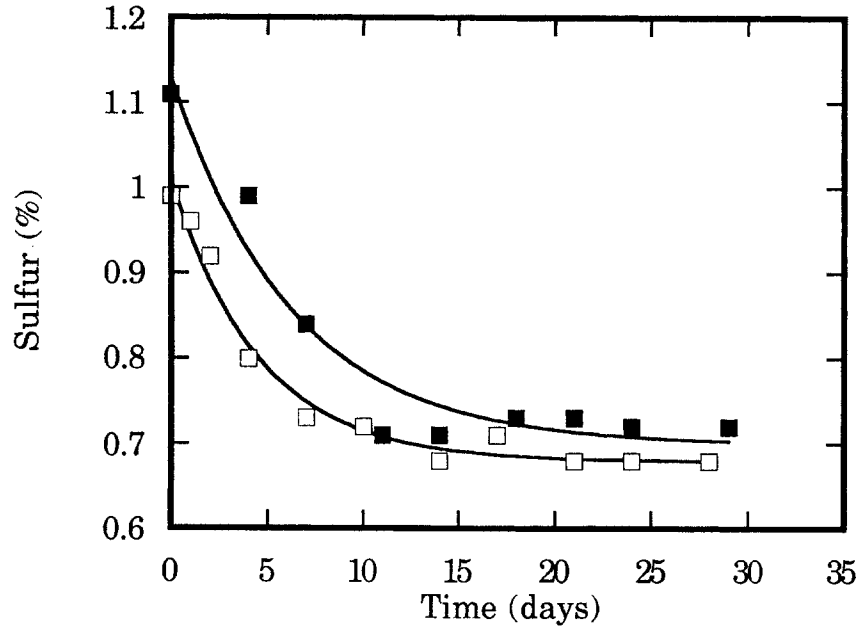

Fig. 2. Total sulfur content of coal 177US41 adjusted for jarosite formation as a function of desulfurization time; (■) *T. ferrooxidans*, (□) *A. brierleyi*. Curves were obtained by a least-squares fit of Eqn 1.

Especially the direct mechanism for oxidation of pyrite in coal may be limited because the microorganisms are too large to enter most of the coal pores. This suggests that pyrite oxidation in coal to a large extent must rely on the indirect mechanism in which pyrite is oxidized by ferric ion.

In conclusion, three conditions are suggested which may lead to a rate constant for oxidation of pyritic sulfur in coal higher than that for oxidation of pure pyrite. Thus, passivation of pure pyrite, higher surface area for pyritic sulfur in coal and beneficial growth conditions for coal may give a higher rate constant for coal than for pure pyrite. Consequently, results from studies of pure pyrite may not necessarily be directly used in the development of a process for microbial removal of pyrite from coal.

ACKNOWLEDGEMENTS

Financial support was provided by the Swedish National Board for Industrial and Technical Development.

TABLE 1

Comparison of rate constants and global initial rates for *Acidianus brierleyi* and *Thiobacillus ferrooxidans* during desulfurization of coal and oxidation of pure pyrite

Substrate	*Acidianus brierleyi*		*Thiobacillus ferrooxidans*	
	k (day^{-1})	$-r_0$ (mg S L^{-1} h^{-1})	k (day^{-1})	$-r_0$ (mg S L^{-1} h^{-1})
Coal	0.22	2.3	0.16	1.7
Pyrite	0.09	40	0.01	4.4

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