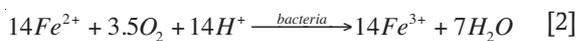




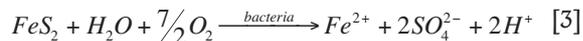
# How do bacteria interact with minerals?

by F.K. Crundwell\*, P.R. Holmes†, and T.A. Fowler‡

Sulphide minerals, such as pyrite and sphalerite, are leached by ferric sulphate. This reaction produces ferrous sulphate and other dissolved products. The ferrous sulphate is re-oxidized to ferric sulphate by bacteria. These reactions can be written as:



However, in 1964 Silverman and Ehrlich proposed that this is not the only role that is played by bacteria. These researchers proposed that *T. ferrooxidans* enhances the rate of oxidation of pyrite above that achieved by chemical reaction with ferric sulphate at the same solution conditions. This enhancement in the rate of dissolution was proposed to occur by direct microbiological action, possibly by the extracellular secretion of an enzymatic oxidant. Since the Silverman and Ehrlich proposal, different authors have made opposing claims concerning the action of *T. ferrooxidans* on pyrite. This 'direct mechanism' of bacterial dissolution of pyrite can be given by the following reaction:



Thus, the distinguishing feature between the two proposals is the role played by ferric ions in the dissolution of the mineral. In the 'indirect mechanism' represented by reactions [1] and [2], the mineral is leached only by the ferric ions, whereas in the 'direct mechanism', the mineral is not leached by ferric ions, but by some biological agent. Because bacteria readily attach to surfaces, Silverman refined the classification in 1967 to include three categories: the indirect mechanism, the indirect contact mechanism and the direct contact mechanism. The indirect contact mechanism is that in which bacteria are attached to the mineral surface, but the leaching of the mineral is by ferric ions rather than by biological action (that is, by reaction [2]), and not by reaction [3]). This is illustrated in Figure 1. Thus, bacterial attachment to the surface of the mineral particles is a necessary but not a sufficient condition for the occurrence of the direct mechanism.

In spite of much research and debate, the question central to the proposal of a direct mechanism remained unanswered. This question is 'does *T. ferrooxidans* enhance the rate of dissolution above that achieved by chemical reaction under the same conditions in solution?'. It is this question we have addressed in our studies.

In all previous work, the same conditions in solution were never achieved. This makes a comparison of the rate of leaching in the presence and absence of bacteria very

difficult. In this work, we invented a new apparatus that controlled the conditions in solution, so that we were able to accurately determine the rates of biotic and abiotic leaching at the same solution conditions. This is the only work that

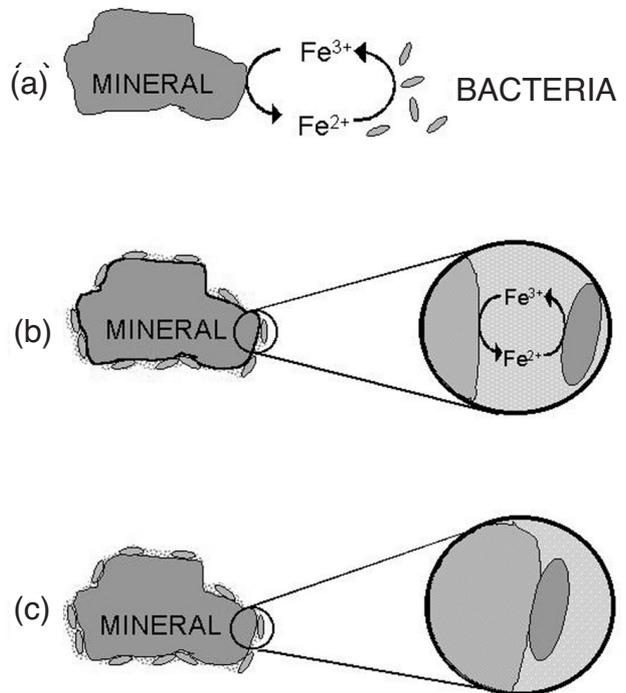


Figure 1—The three proposed mechanisms for the action of *Thiobacillus ferrooxidans* on sulphide minerals. (a) The indirect mechanism, in which bacteria oxidize ferrous ions in the bulk solution to ferric ions and ferric ions leach the mineral. (b) The indirect contact mechanism, in which attached bacteria oxidize ferrous ions to ferric ions within layer of bacteria and exopolymer material, and the ferric ions within this layer leach the mineral. (c) The direct contact mechanism, in which the bacteria directly oxidise the mineral by biological means, without any requirement for ferric or ferrous ions. Thus, the distinguishing feature between the direct and the indirect mechanism is the participation of ferric ions in leaching the mineral. In the indirect mechanism, ferric ions leach the mineral, whereas in the direct mechanism ferric ions do not leach the mineral. The qualifier 'contact' refers to either the direct or the indirect mechanism occurring by attached bacteria.

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has achieved this.

The results of a study of the leaching of pyrite and sphalerite in the presence and absence of bacteria at the same solution conditions are summarized here.

The leaching of pyrite occurs at a higher rate in the presence of bacteria than in the absence of bacteria. Analysis of the rate of reaction as a function of concentration indicates that the order of reaction with respect to ferric ions is the same in the presence and the absence of bacteria. The reaction order is 0.5. However, the order of reaction with respect to  $H^+$  is  $-0.5$  in the absence of bacteria, and  $-0.39$  in the presence of bacteria. This suggests that the presence of bacteria does not change the mechanism of leaching, but in some manner affects the pH at the mineral surface.

These results are shown in Figures 2 and 3.

An electrochemical study of pyrite showed that the mixed potential decreases in the presence of bacteria, while it is constant in the absence of bacteria. A detailed mechanism of the leaching of pyrite in ferric sulphate solutions was used to interpret the results. It is shown that both the leaching results and the mixed potential results can be explained by

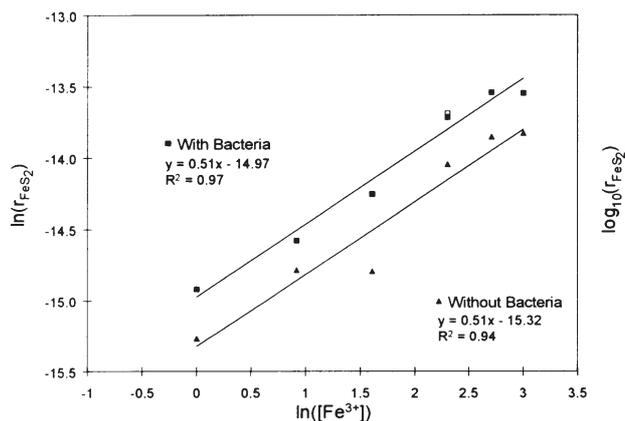


Figure 2—Plot of the natural logarithm of the rate of dissolution of pyrite against the natural logarithm of ferric ion concentration to determine the order of reaction with respect to  $Fe^{3+}$

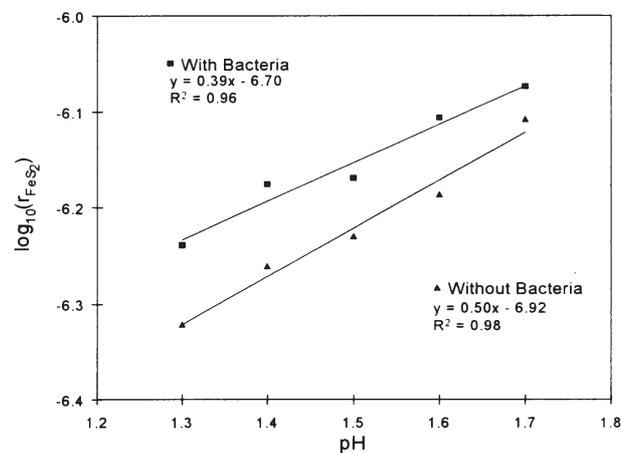


Figure 3—Plot of the logarithm ( $\log_{10}$ ) of the rate of dissolution of pyrite against the pH of the solution to determine the order of reaction with respect to  $H^+$ . (Note that  $pH = -\log_{10}[H^+]$ )

an increase in the pH at the mineral surface as a result of bacterial activity. This means that the increase in the leaching rate of pyrite is a result of the indirect contact mechanism. The mechanism that explains our results is shown in Figure 4.

The rate of leaching of sphalerite with bacteria is the same as that without bacteria at low concentrations of ferrous ions. However, the rate is significantly higher than that without bacteria at high concentrations of ferrous ions. A porous layer of elemental sulphur is present on the surface of the chemically leached particles, while no sulphur is present on the surface of the bacterially leached particles. The analysis of the data using the shrinking-core model shows that the chemical leaching of sphalerite is limited by the diffusion of ferrous ions through the sulphur product layer at high concentrations of ferrous ions. The analysis of the data shows that diffusion through the product layer does not limit the rate of dissolution when bacteria are present. This suggests that the action of the bacteria in oxidizing the sulphur formed on the particle surface is to remove the barrier to diffusion by ferrous ions. This is illustrated in

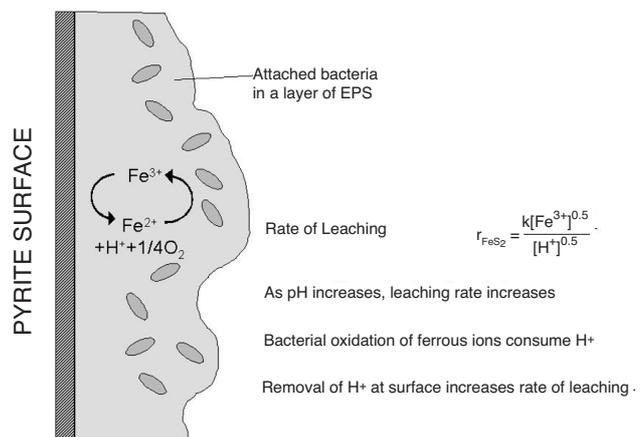


Figure 4—Bacteria consume  $H^+$  at the mineral surface, which increases the pH at the surface. If the rate of leaching is dependent on the pH, then this will result in an increase in the rate of leaching

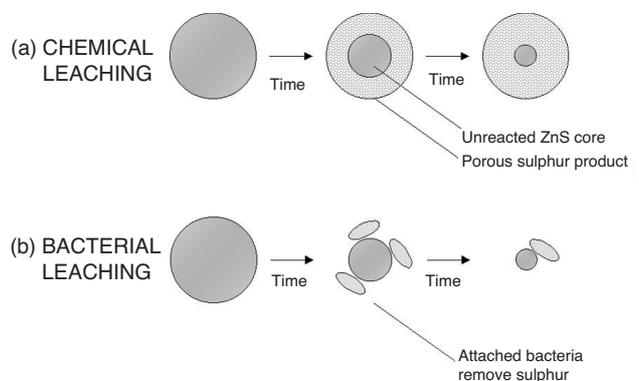


Figure 5—A schematic diagram of a reacting sphalerite particle (a) The chemical leaching mechanism, showing the formation of a porous layer of sulphur on the core of unreacted sphalerite. The reaction given by Equation [1] occurs at the surface of the unreacted core of zinc sulphide. Diffusion of soluble reactant and products through the sulphur may control the rate of dissolution under some conditions. (b) The leaching mechanism in the presence of bacteria. *T. ferrooxidans* oxidizes sulphur, removing any barrier to diffusion

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Figure 5.

Thus, we have shown that attached bacteria may increase the rate of dissolution above the chemical rate of dissolution at the same solution conditions in two cases: (i) if the rate of dissolution of the mineral is affected by the formation of a porous layer of sulphur by a phenomenon known as product layer diffusion, then the removal of the sulphur by the bacteria will result in an increase in the rate of leaching and (ii) if the dissolution of the mineral increases with increasing pH at the mineral surface, then the attachment of bacteria to the surface may result in an increase in the pH at the surface, which increases the rate of reaction. In both cases, it was shown that even though attached bacteria increased the rate of dissolution under some conditions, the mechanism of leaching was the chemical dissolution by ferric ions.

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