The role of orientation of crystal lattice on the development of bacterial leaching patterns on pyrite single crystals

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Synopsis

To investigate the influence of orientation of crystal lattice on the bacterial leaching of pyrite crystals, single crystals of 100, 111 and 110 plane orientations were used for the study. Experiments were carried out in the presence of a *Thiobacillus ferrooxidans* culture. The different corrosion patterns observed on the surfaces of the bioleached samples suggests a variation in cell-surface interaction from one crystal plane to the other. The surface corrosion patterns generally reflected the influence of the symmetrical arrangement of the atomic planes in the lattice on which they formed. The results indicate that the surface properties of mineral sulphides may control the evolution of corrosion patterns and consequently the initial oxidation process in acid bacterial leaching.

Introduction

Due to its abundance and ready availability in most industrial processes, an understanding of the reactivity of pyrite is important, especially for such applications as ore processing by flotation, coal desulphurization, as well as for geochemical processes like the production of acid mine waste waters. All of these processes involve reactions at pyrite surfaces and, as a result, there is a need to understand the nature of these surface reactions. Consequently, one area of attention is the effect of crystal structure and crystallographic orientations on the oxidation kinetics of pyrite. A few studies, albeit on the non-bio approach, have been carried out on the most common occurring FeS_2 surfaces. A significant number of these have been on the FeS_2 (100) surfaces, including a comparison of the oxidation rate with the (111) surfaces[1-4]. However, in recent years, the importance of microbial activity in the oxidative dissolution of sulphides, especially pyretic minerals, has become well established[5-9]. While a significant amount of research has been directed towards the type of mechanism involved in the bioleaching process[10–16], the effect of surface structure has also received some attention[17–23].

Although the bioleaching behaviour of the sulphide minerals has been suggested to involve specificity with respect to crystallographic orientation[24–26], there are relatively few studies which try to explain the aspects involved, especially the possible association, if any, among the crystallographic orientation of the surfaces, the observed dissolution pits and evolution of the leaching process. The objectives of the work described in this paper are to investigate the correlation between the crystallographic orientation of pyrite single crystals and the bacterial leaching patterns that develop on the surfaces during the early stages of leaching, mostly within the first few weeks. It is hoped that a deeper appreciation of the influence and role of crystal orientation on the bioleaching process of the mineral sulphide will help understanding of whether it is possible to enhance or inhibit sulphide oxidation processes.

Crystallographic planes of pyrite

The arrangement of atoms at a surface is the single most important factor affecting its physical and chemical behaviour. In considering an ideal periodic lattice, it is clear that the abrupt termination of the lattice must result in a unique crystalline configuration of atoms whose behaviour must also reflect the presence of unaccomodated chemical bonds. It is, however, simpler to consider the surface atoms as individual entities bonded to the lattice, but with fewer neighbour bonds than atoms in the interior of the crystal. It is also important to remember that in reality the crystallographic planes are not necessarily atomically flat, but instead have steps and other surface imperfections that will contribute to the initial surface reactivity.

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The 100 plane

The planar (100) surface (Figure 1a) exposes the face of the face-centred cube of bulk FeS_2 and is known to be the most stable surface[2]. The surface is close to ideal, and has a bulk termination of Fe and S species with a fivefold coordination of the Fe sites and threefold coordination of the S sites, these being the respective bonding environments for the uppermost surface of Fe and S sites on a flat terrace.

The 110 plane

The (110) surface unit cell is rectangular, with repeat vectors with lengths of a = 5.431 and b = 7.680 (Figure 1b). The surface structure has a fourfold co-ordination of the Fe site and there are four surface Fe atoms contained within the surface cell, two of each of equivalent symmetry. In the <110> direction, the Fe sites are separated by one sulphur atom.

The 111 plane

According to Guevremont *et al.*[1], the 111 surface can either be sulphur or iron terminated (Figure 2a and 2b). The surface Fe atoms or S_2 groups are threefold coordinated, each bonded to three species (S_2 or Fe respectively) in the layer below. The unit cell of the ideal termination is hexagonal with a cell edge of approximately 7.68.

Materials and method

Bacteria culture and leaching media

The strain of *Thiobacillus ferrooxidans* used was originally obtained from the University College, Cardiff, and was propagated in 9K nutrient medium[27]. The number of bacterial cells was estimated by direct counting using the improved Helber counting chamber. The final cell concentration used for experimental inoculation was approximately 1×10^8cells/ml. The leaching experiments were carried out in 9K basal medium at a pH of 1.8 adjusted with sulphuric acid. At the beginning a small amount of Fe^{2+} was added as an energy source for the microorganisms and a cell suspension (10% v/v.) was added to the leaching solution.

Pyrite samples

The pyrite samples were identified and characterized by X-

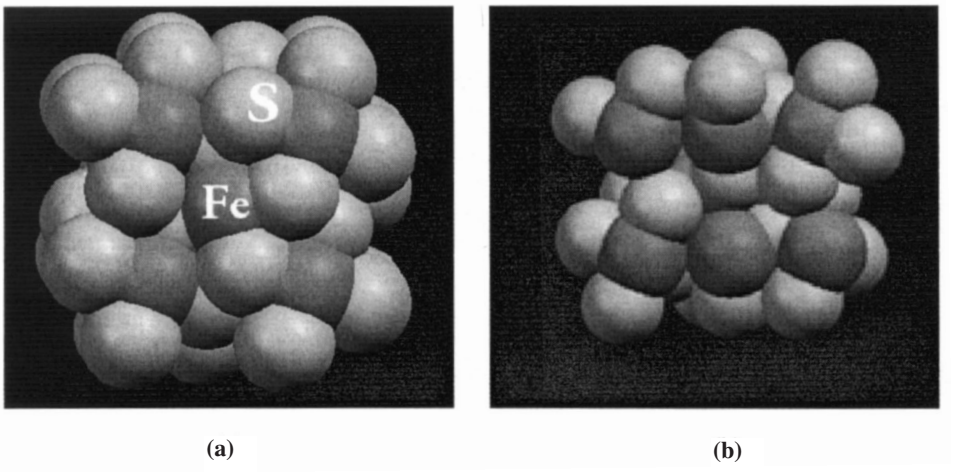


Figure 1—Pyrite (a) (100) and (b) (110) surfaces (simulations done by Mercury 1.0 from Hyperchem)

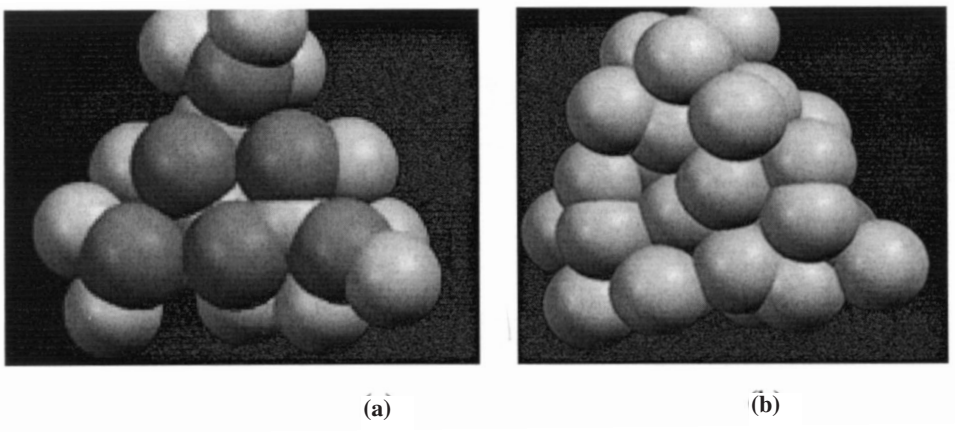


Figure 2—(a) The Fe (111A) and (b) S_2 terminated (111B) surfaces (simulations done by Mercury 1.0 from Hyperchem)

ray diffraction method. Chemical analysis of the pyrite samples by inductively coupled plasma atomic absorption spectroscopy identified the chemical composition of the mineral as typical pyrite, with 46.1% Fe and 53.1% S. This does not deviate much from, theoretical composition of 46.6% Fe and 53.4% S. The main impurities were found to be Ca, Al, Ti, Sr, Zn, Na, K, Mg and Co, all in trace amounts. The samples were prepared and leached in duplicate as described in detail in an earlier paper[28].

Surface and solution analysis

A scanning electron microscope, JEOL JSM T220, was used to monitor bacterial adhesion and surface changes occurring on the samples during leaching. The samples were observed at weekly intervals. The total iron released during the leaching period was measured at a 2-day interval using a Perkin-Elmer 1100B atomic absorption spectrophotometer with an air /acetylene flame.

Results and discussion

Dissolution rates

The analysis of total iron dissolved during the leaching period for the three crystallographic orientations investigated indicates different trends of dissolution. Figure 3 shows the total dissolved iron for bioleaching solutions. While the matching cut faces of the (100) and (110) planes behaved similarly, those of the (111) surfaces did not. Since the dissolution rate was measured in terms of released iron, it can be assumed that the plane with a higher overall released iron is the iron-terminated surface (hereafter referred to as A), and the other corresponding matching surface is taken as the sulphide terminated surface (B plane)[28]. The (100) plane gave the least overall amount of total dissolved iron.

The solution analysis also presents evidence signifying that although microbial dissolution of the mineral was visible from the dissolution of the mineral in the early stages of leaching, microbial oxidation of ferrous to ferric iron, as observed from the redox potential in Figure 3, was slight. This seems to suggest that the dissolution of the mineral occurs mostly through direct cell-mineral interaction during the early stages of leaching.

Bacterial leaching patterns

The proximity of attached bacteria to observed corrosion patterns on the sample surfaces was initially used as an approximation for the study of the evolution of corrosion patterns. This was done by determining whether pits were established at locations on the mineral surface defined by attached bacteria. For instance, if the cells are found close to or lying inside pits that conform to the shape or size of the bacterial cells, it could be concluded that these pits are cell induced. However, surface observation of leached samples after seven days or more of leaching failed to show any substrate colonization, although corrosion pits were noted. Thus any specific relationship between the pits and bacteria as observed by other researchers was difficult to detect[17,24,26]. However, when the surfaces were observed in the early stages of leaching, e.g. 4 or 5 days, before heavy precipitates gathered on the substrates, bacteria were observed randomly distributed on the (111B), (110) and (100) surfaces. No significant colonization was observed on the (111A) surfaces.

The most striking feature detected in this study was the surface films observed mostly on the (111B) and (110) surfaces (Figure 4) in the early stages and after about a week of leaching. No bacteria were observed in close vicinity to these films. The fact that the film was sometimes observed

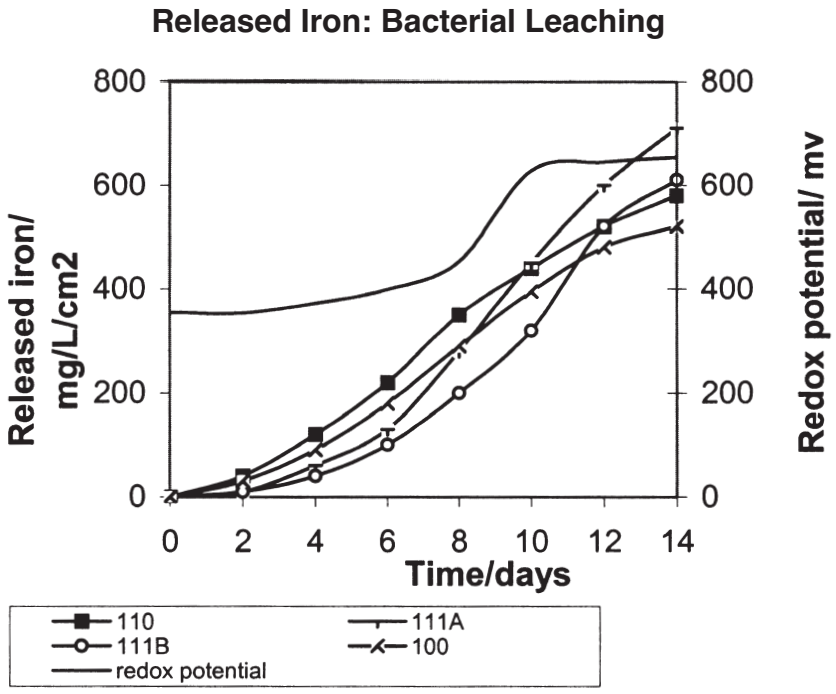


Figure 3—Leaching trends of given surfaces in bioleaching solution: 9K basal medium, 10 vol.% bacteria inoculumn, 0.05 M Fe2+ solution concentration, pH 1.8

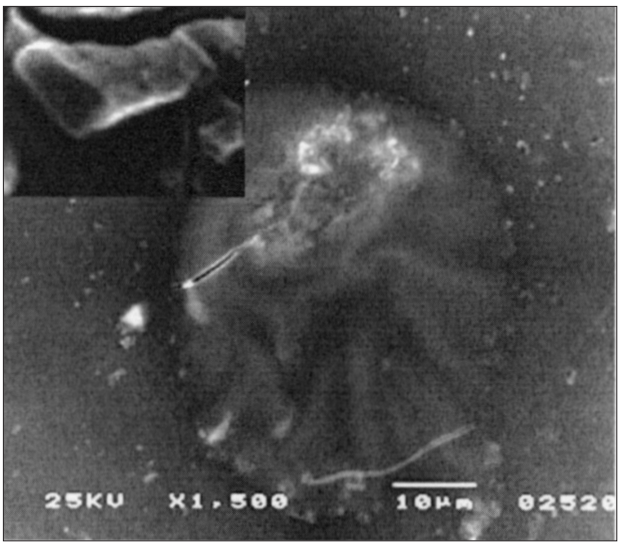


Figure 4—Surface films observed on (110), (100) and 111B surfaces: inset shows how some of the surface films appeared on enlargement

after a week of leaching, when the samples were washed prior to surface observation, indicates that this film can form a strong attachment to the surface.

It was further observed that the surface planes associated with a high ratio of sulphur/iron atoms on the immediate outer layer e.g. the (110) and (111B) planes (Figure 1 and Figure 2b) in general, generated elliptical/elongated pits (Figures 5 and 7 respectively) similar to those observed by Bennet and Tributsch[17], and Edwards *et al.*[26]. These pits were, however, much larger than the bacterial cell dimensions. On the other hand, the layers of organic films observed mostly on these planes exceeded the actual amount of surface covered by the cells, indicating that the film spreads beyond the area of bacterial contact. Since the elongated pits were observed mainly on surfaces covered with organic films, it might be suggested that the extension of the film beyond the area of direct bacteria contact extends the zone/compartment of interaction with the surface, subsequently generating larger pits. This zone of bacteria-surface interaction has also been suggested by the work done by Sand *et al.*[13]. Furthermore, since not all the planes developed this film (the 111A did not) it is possible that the initial colonization of the pyrite surface by the bacteria depends on the outer exposed layers. A quantitative and qualitative analysis reported in an earlier paper indicates a significant support of this concept[28].

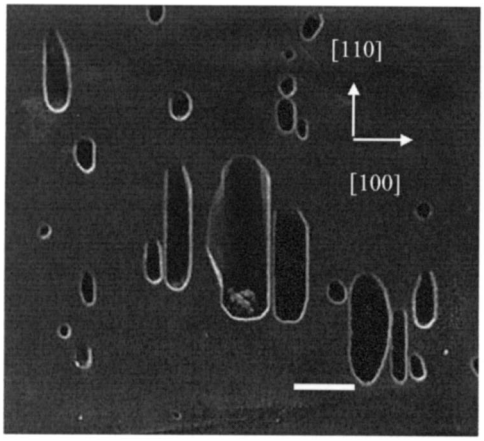
Given that bacteria were not observed in the vicinity of the surface films, it may be that the bacteria reside long enough to produce some surface film before detaching or moving to a new location on the surface. It is possible then that the film contains some constituent that enhances leaching, thus reducing the necessity for bacteria to remain in close proximity to the films for corrosion patterns to develop. This organic film layer has been estimated to be sufficiently thick, about 3–7nm[29], for it to be taken into consideration in the interfacial chemical mechanism[12,13].

The observed bacterial leaching patterns on the surfaces were seen to favour the <110> and <100> directions. The crystal structure of pyrite indicates that these are the directions of high sulphide density[25]. This signifies that if the leaching patterns are a result of direct-cell mineral interaction, then the high density of the corrosion patterns along these sulphur-enriched zones implies that sulphur removal or surface attack occurs in a crystallographically controlled manner,

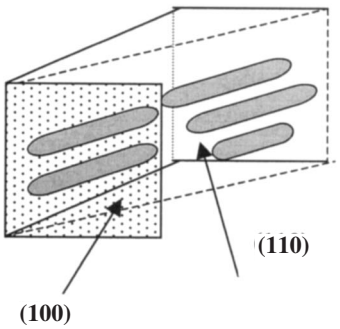
The bacterial leaching patterns observed on the (110) planes (Figure 5a) lie parallel to the <110> directions and penetrate into the plane.

The (110) surfaces were covered with elliptical/rod-like pores and quasi-circular pits. In general, the elliptical pits developed in pairs and had their axis oriented parallel to the plane direction (Figure 5b). The circular pits with a diameter of 1-2 µm were found mostly in close location with the developed elliptical ones.

On the 100 plane the leaching patterns appear as circular pores that tend to penetrate into the crystal face and elliptical pores (Figure 6) that penetrate into and grow along the plane, although not to the same extent in axial length as those observed on the (110) plane (<20 µm on (100) compared to up to 50 µm for (110) planes). If the elliptical



(a)



(b)

Figure 5—(a) elliptical/rod-like bacterial leaching patterns (110) plane, bar size 10 µm , (b) schematic projection on the (110) plane

pits arise as a result of the persistence of disulphide atoms along a crystallographic direction, by considering the checkerboard structure of alternate disulphide and Fe atoms existing on the (100) planes (Figure 6b) their development will be bounded/restricted by the Fe atoms. As a result, they will not develop to a large extent along the <100> directions resulting in a tendency to circular pit formation. The elongated pores wil,l however, develop with a preferred orientation along the <110> directions (note inset Figure 6a).

By considering the geometric positions of the atoms on the different surfaces, it can be pointed out that the presence of surface sites with different coordination affects the dissolution of the atoms from these specific sites. According to Bockris and Razumney[30], the activation barrier to detach an ion from a step edge or a kink site into solution is expected to be smaller than for ions from a flat terrace. Due to the stepped {110} structure (saw-tooth-pattern of Fe atoms,[3] compared to that of the {100}, which is more of a flat terrace (Figure 6b), oxidation propagation in the <110> direction should be enhanced. As a result, with the gradual generation of ferric iron by bacteria in solution, the pits initiated in the early stage of bacterial leaching will develop easily in this direction compared to the <100> directions.

The (111) plane is bounded by <110> directions, which, as indicated above, are high sulphur directions. On the (111B) plane corrosion patterns, thus, occur parallel to the edges of the plane, creating triangular enclosures (note the area labelled a, on Figure 7a and compare this to the schematic representation of the patterns on the crystal structure in Figure 7b).

The 111A surface did not reveal any corrosion pits during the first days of leaching and no bacteria were observed attached on the surface. With the gradual production of ferric iron, however, circular pits similar to those observed on the 100 plane appeared. Since elongated pits were observed on the (111B) from the beginning of leaching, which were later interspersed with quasi-circular pits, while the circular pits were observed on the(111A) plane after a few days of leaching, with the elongated ones developing at later stages, it might be assumed that the sulphur layer defines elongated pits, while the exposed iron layer creates quasi-circular pits.

By considering the low ferric iron in solution as observed in Figure 1, and the absence of bacteria colonization and elongated pits on the iron terminated (111A) surface, it can be concluded that it is probably the initial attachment and action of the bacteria to and on the active sites on the immediate surface layers that defines the initial process of leaching, pit formation and subsequent evolution of these corrosion pits on the surfaces during the early leaching stages.

Conclusions

The work described in this paper has indicated that the formation of dissolution pits in the presence of bacteria is dependent upon the crystal surface on which they occur. The bacterial corrosion patterns were observed to favour the sulphide-enriched directions (110 and the 100). The qualitative analysis of the overall pitting morphology of the pyrite crystals indicates that the distribution of atoms on the outer surface layer, especially the presence of sulphur atoms, might have a strong influence on the initial bacterial activity on the pyrite surfaces.This indicates that the significant step in the early leaching process is probably the attachment of the bacteria to the active sites on the initial outer surface layers. These results have significant implications and ready application, especially in coal desulphurization operations where developing processes that are economic have become a dominating aspect.

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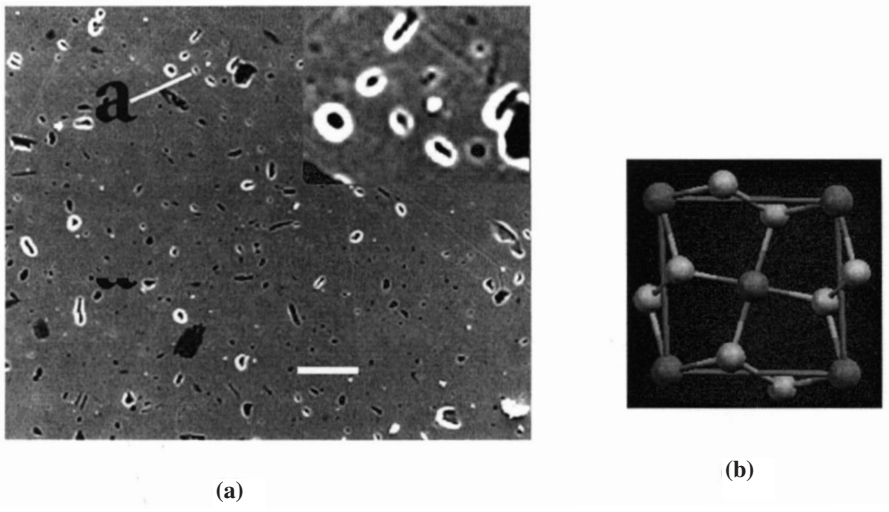


Figure 6—(a) elliptical and circular leaching patterns on (100) surfaces: bar size 10. Label a, and enlarged section upper right corner indicate the preferred orientation of the pits in the 110 direction. (b) indicates orientation of disulphide atoms on the (100) surface

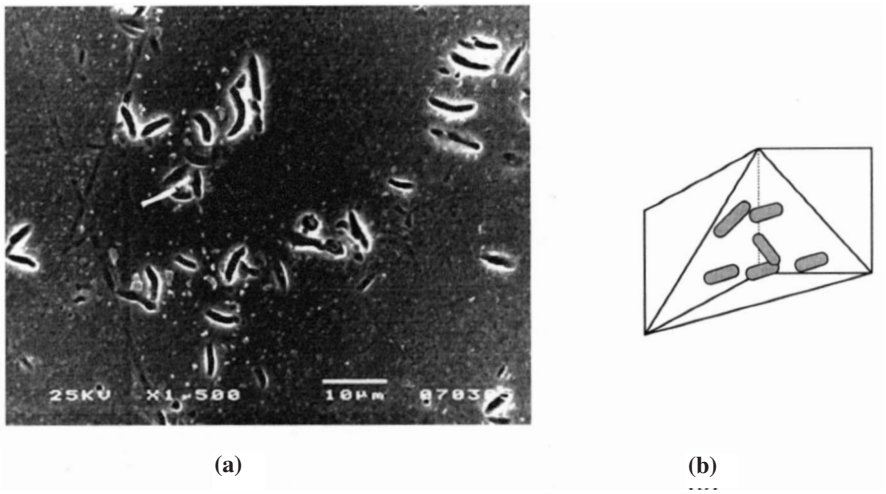


Figure 7 (a)—Dissolution pits on the (111B) surface. (b) schematic representation of the resulting pit morphology indicated by label a in (7a), as defined by the crystal structure of the (111) surface

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