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Solid-Phase Products of Bacterial Oxidation of Arsenical Pyrite

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Bacterial leaching of an As-containing pyrite concentrate produced acidic (pH < 1) leachates. During the leaching, the bacteria solubilized both As and Fe, and these two elements were distributed in solution-phase and solid-phase products. Jarosite and scorodite were the exclusive crystalline products in precipitate samples from the bacterial leaching of the sulfide concentrate.

The microbiological oxidation of auriferous pyrite and arsenopyrite materials has considerable industrial potential owing to improved gold recovery following the bacterial oxidation step (3, 4). The process involves stirred-tank reactors to provide controlled conditions and to confine the various products of the treatment. The bacterial oxidation of pyrite can be presented by the following half-cell equations:

$$FeS_2(s) + 8H_2O \rightarrow Fe^{3+} + 2HSO_4^- + 14H^+ + 15e^-$$

$$FeS_2(s) + 8H_2O \rightarrow Fe^{2+} + 2HSO_4^- + 14H^+ + 14e^-$$

$$4Fe^{2+} \rightarrow 4Fe^{3+} + 4e^-$$

Cathodic half-cell reactions are based on either oxygen or ferric iron reduction:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$4Fe^{3+} + 4e^- \rightarrow 4Fe^{2+}$$

The bacterial oxidation of pyrite and ferrous iron produces Fe(III) hydroxysulfates with a unit cell formula of $X_3Fe(SO_4)_2(OH)_6$ where X = K^+, Na^+, NH_4^+, or H_3O^+. With ferric iron and arsenate, poorly soluble arsenical precipitates are formed, but these have not been characterized for bacterial leaching systems. In the present work, precipitates were collected from two bacterial leaching systems which contained pyrite and arsenical pyrite as the parent substrate. The precipitates were analyzed by X-ray diffraction (XRD) and partial elemental composition with a view to characterizing the solid-phase products of this bioleaching system.

The auriferous pyrite ore in this work was from Olympia, Greece, and was used as a finely ground (particle size, <0.5-mm) concentrate. A partial elemental analysis of a bulk sample yielded the following composition (wt/wt): 38.7% Fe, 40.5% S, and 11.3% As. XRD analysis showed that the Olympia concentrate sample used in these experiments contained pyrite as the only sulfide mineral. Other peaks indicated that minor amounts of quartz and gypsum were also present. The lack of arsenopyrite indicates that As was associated with pyrite as arsenical pyrite.

The mixed culture used in experiments A and B was pooled from various moderately thermophilic bacteria from Kingsbury coal spoil (6) and strain BC13, which were initially obtained from P. R. Norris, University of Warwick, Coventry, England. This test culture also included strain KU, which was isolated at the University of Umeå from the Kingsbury source culture. The mixed culture was grown in 9K mineral salts solution which contained either 1.5 or 10% (wt/vol) Olympia concentrate as the sole source of energy. The cultures were incubated in stirred-tank reactors which were maintained at 45°C. Strains KU and BC13 were also grown in pure culture in shake flasks with 1.5% (wt/vol) Olympia concentrate.

The leaching was monitored by measuring pH and redox potential (Ag/AgCl reference), total Fe (Fe_{total}), Fe in solution (Fe_d), total As (As_{total}), and As in solution (As_d). The redox potentials are standardized to the hydrogen scale. Fe and As were analyzed by atomic absorption spectrometry. Fe_{total} and As_{total} were analyzed after acid digestion (0.2 ml of sample plus 1.8 ml of 5 M HCl for 30 min at 65°C). Fe_d and As_d were determined in supernatants of centrifuged samples (no acid digestion). Ferrous iron was determined titrimetrically with ceric sulfate, by using 1,10-phenanthroline-Fe(II) as indicator. The amounts of iron (Fe_{ppt}) and arsenic (As_{ppt}) precipitated in leach solutions were calculated as the difference (in grams per liter) between Fe_{total} and Fe_d and between As_{total} and As_d, respectively.

For XRD, samples were centrifuged to recover the suspended solids. The dried samples were gently ground in an agate mortar before XRD analysis. XRD analysis of topfill powder mounts was conducted by using CuKα radiation with a Philips PW 1316/90 vertical wide-angle goniometer equipped with a diffracted-beam monochromator and a θ compensating slit. All specimens were scanned from 10 to 70°2θ in increments of 0.1°2θ with a 10-s counting time. Although XRD is not a quantitative method, the peak area or height can be used as a measure of the changes in relative amounts of two or three minerals in a mixture. Because of good crystallinity, the intensities (number of counts at peak top) of the 4.46-Å (0.446-nm) scorodite peak at 19.9°2θ, the 3.09-Å (0.309-nm) jarosite peak at 28.9°2θ, and the 1.64-Å (0.164-nm) pyrite peak at 56.2°2θ were selected to represent these three minerals.

Energy-dispersive elemental X-ray spectroscopic analysis was conducted under an atmosphere of air by using an X-ray fluorescence spectrometer (Tracor X-ray Spectrace 4050). The tube voltage was 10 keV, the tube current was 0.01 mA, no filter was used, and counts were collected for 100 s.

Two experiments were performed in which solid-phase products were sampled and characterized. In experiment A (1.5% [wt/vol] pulp density), the test culture reached 800 mV after 4 days of leaching (Fig. 1), demonstrating that oxidized conditions were achieved for mineral dissolution. Ceric sulfate titration indicated the absence of ferrous iron in

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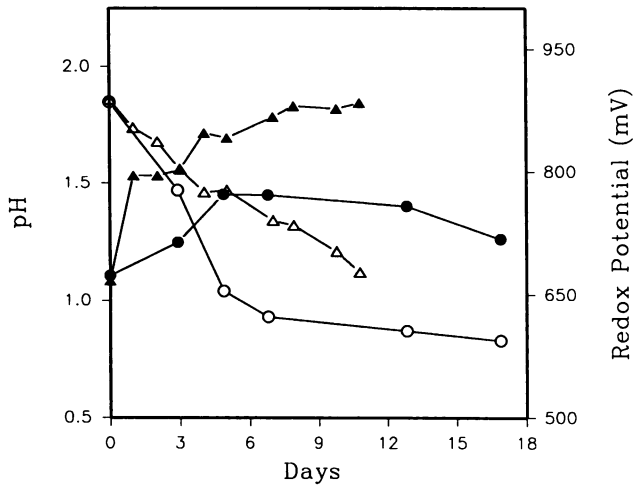

FIG. 1. Changes in the redox potential and pH during the bacterial leaching of arsenical pyrite. Symbols at 1.5% (wt/vol) pulp density: △, pH; ▲, redox potential. Symbols at 10% (wt/vol) pulp density: ○, pH; ●, redox potential.

solution. The main redox components in solution phase were the Fe(III)/Fe(II), As(V)/As(III), and sulfur couples, all originating from the concentrate sample as a result of bacterial leaching. The release of Fe and As continued throughout the time course (Fig. 2A). The leaching reaction was acid producing, with a final pH of 1.12 after 11 days of leaching.

The second experiment, experiment B, was carried out at 10% (wt/vol) pulp density. Because of the larger amount of FeS_2(s), the pH decreased to <1 (Fig. 1). Ferrous iron (35 mM) appeared in solution at pH 0.83, suggesting that the low pH was inhibiting bacterial iron oxidation. Inhibition of bacterial activity was also apparent from the decline of the redox potential from 772 to 718 mV toward the end of the time course (Fig. 1) and by the lack of release of arsenic from the sulfide concentrate (Fig. 2B).

Bacterial leaching led to the concurrent precipitation of two minerals, jarosite [$KFe_3(SO_4)_2(OH)_6$] and scorodite ($FeAsO_4 \cdot 2H_2O$), upon pyrite solubilization (Fig. 3). The ratios of these two minerals showed a different trend in the two leaching experiments. After 3 days, the scorodite/jarosite (S/J) ratio was similar in both series, but thereafter the proportion of scorodite decreased in experiment A and increased in experiment B (Table 1). The ratios given in Table 1 are calculated from the respective intensities of two selected peaks and should not be construed as a direct measure of proportions of scorodite and jarosite. However, the values show the directions of change in the relative proportions of the two minerals in the precipitate. Of all the precipitates examined, the sample from the pure culture, KU, displayed the largest relative amount of scorodite. At the time of sampling, culture KU contained 1.35 mM ferrous iron and 30.7 mM ferric iron. The lower S/J ratio for strain BC13 may be a result of the lower concentration of ferric iron in solution (3.25 mM ferrous iron and 12.7 mM ferric iron).

These data indicate that an increasing proportion of As is bound in the precipitate in the course of experiment B, whereas in experiment A the proportion of As bound decreases with time. This could be due to different rates of pyrite dissolution or different rates of formation of these minerals under the experimental conditions used. The pulp

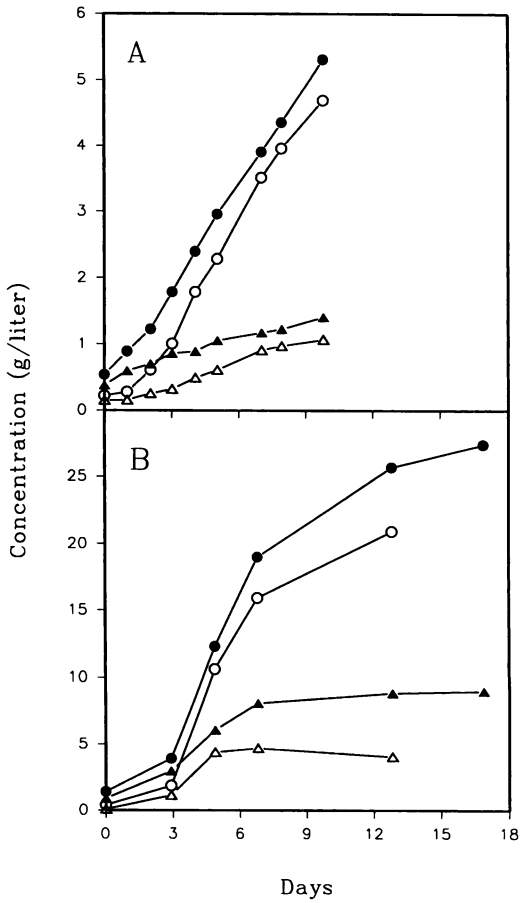

FIG. 2. Release of iron and arsenic during the bacterial leaching of arsenical pyrite at (A) 1.5% (wt/vol) and (B) 10% (wt/vol) pulp density. Symbols: ●, Fe_{total}; ○, Fe_d; ▲, As_{total}; △, As_d.

density in experiment A (1.5%, wt/vol) and B (10%, wt/vol) may also account for the relative differences in the ratio of the two minerals. Semiquantitative energy-dispersive elemental X-ray spectroscopic data showed Fe, As, K, and S as the main elements in precipitate samples (Fe > As > S ≈ K). Minor amounts of Mn, Cu, Zn, Cr, Ca, P, and La were also detected, representing minor and trace elements in the concentrate as well as those initially present in the mineral salts solution.

Figure 4 shows that the amount of Fe and As precipitated from solution was relatively constant at 1.5% (wt/vol) pulp density, whereas it continually increased in experiment B (10% [wt/vol] pulp density). Experiments A and B each had relatively constant Fe/As molar ratios of 1.93 and 1.37, respectively, in precipitates throughout the time course, calculated from the changes in solution chemistry. The solubility of scorodite is lowest at pH 4 and increases with decreasing pH (2). Therefore, the higher proportion of scorodite in the course of experiment B (10% pulp density) is due to the much higher concentration of As in solution compared with that in experiment A. This difference is a pulp density effect. Moreover, in view of the lower pH in experiment B (which had a higher proportion of scorodite), it can be concluded that pH is a major controlling factor in influencing the distribution of Fe(III) between jarosite and scorodite.

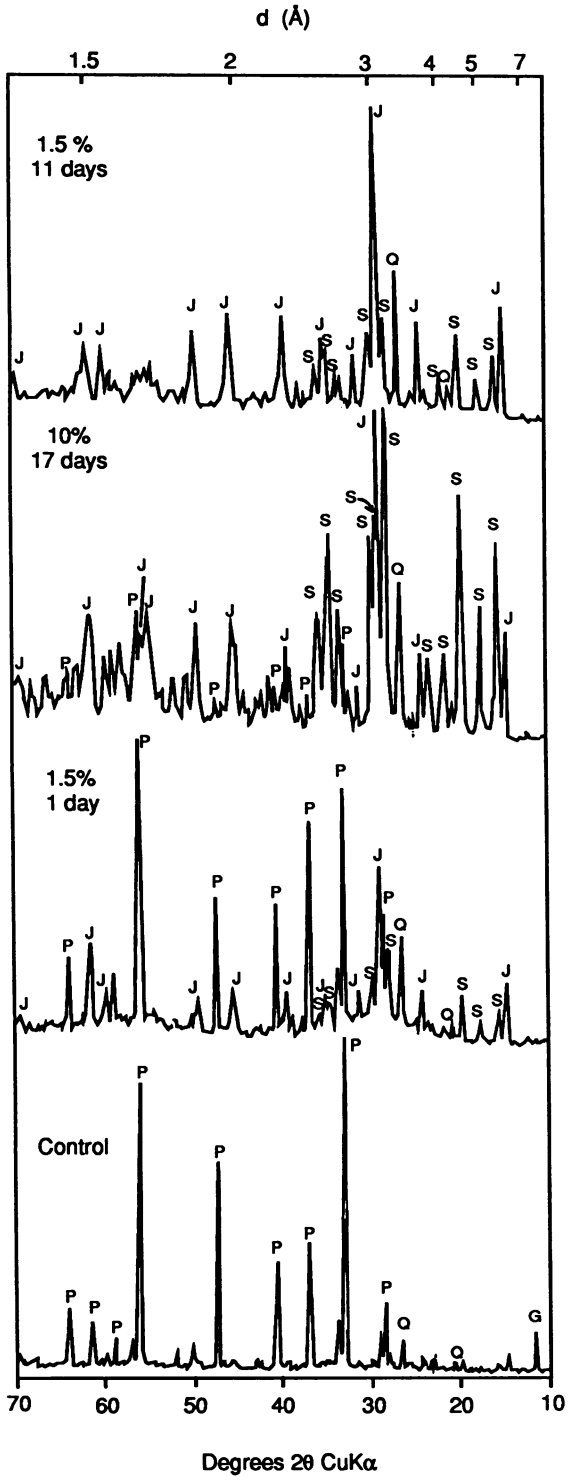

FIG. 3. X-ray diffractograms of arsenical pyrite before and after leaching. Symbols: P, pyrite; J, jarosite; S, scorodite; Q, quartz; G, gypsum.

TABLE 1. Intensity of selected peaks of scorodite, jarosite, and pyrite and scorodite/jarosite intensity ratio

Expt	Time (days)	Intensity[a] of:		S/J ratio	Intensity of pyrite[a]
		Scorodite	Jarosite		
A (1.5% pulp)	1	164	448	0.37	748
	3	196	536	0.37	486
	5	279	852	0.33	243
	8	347	1,169	0.30	—[b]
	10	333	1,131	0.29	—
B (10% pulp)	3	159	436	0.37	1,124
	6	377	839	0.45	652
	13	491	723	0.68	251
	17	515	687	0.75	266
Culture KU[c]		776	584	1.33	297
Culture BC13[c]		570	1,203	0.47	252

[a] Intensity was measured as the number of counts at the top of the peak.
[b] —, not detected.
[c] Stationary-phase cultures.

Biological factors that have a direct impact on the pH in bioleaching systems are involved in determination of the relative distribution of As(V) and Fe(III) in solid-phase products. Bacterial oxidation of pyrite is an acid-yielding process which, in the presence of dissolved arsenate at pH ≈ 1, favors the incorporation of Fe(III) into the scorodite phase, while jarosite formation is virtually negligible as a result of the low pH. Factors controlling the biological oxidation of iron are also important in influencing the distribution of arsenate in solution and solid-phase products because scorodite formation is effectively prevented in the absence of Fe(III). The chemical oxidation of ferrous iron in solution and of the iron entity in pyrite is insignificant at the pH values used in bacterial leaching processes.

The formation of scorodite controls the level of dissolved arsenate in solution and therefore has a direct impact on the bacteria used in bioleaching systems. The need for increased resistance of bacteria to arsenate in mineral biotechnology is partially alleviated by scorodite formation, which was shown to occur even at pH < 1. The bacterial oxidation of arsenical pyrite and arsenopyrite proceeds via the intermediate arsen-

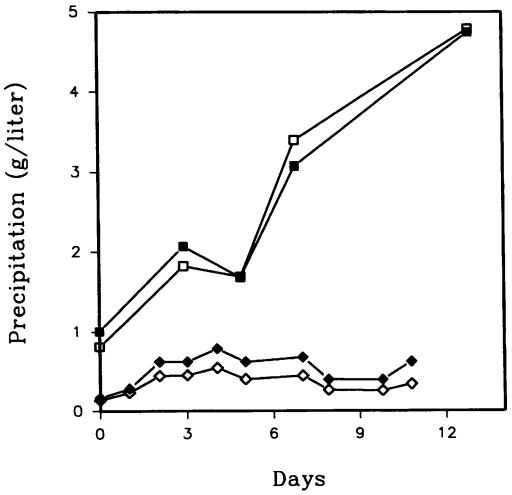

FIG. 4. Precipitation of Fe and As in leach solutions. Symbols for experiment A: ◆, Fe_{ppt}; ◇, As_{ppt}. Symbols for experiment B: ■, Fe_{ppt}; □, As_{ppt}.

ite, which is fully soluble under these conditions. Arsenite is more toxic than arsenate to acidophilic bacteria involved in leaching processes (1, 5). It is important to elucidate the mechanism of arsenite oxidation in bioleaching systems because the transformation to the pentavalent form is associated with a decrease in both solubility and toxicity. Additionally, our data signify the geochemical role of microorganisms in the mobilization and immobilization of arsenic in oxic environments. A good understanding of the conditions controlling the oxidation and precipitation of Fe- and As-containing compounds also has utility for management of environmental problems at mine sites as well as controlled biohydrometallurgical processes.

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