

Low Molecular Weight Carboxylic Acids in Oxidizing Porphyry Copper Tailings

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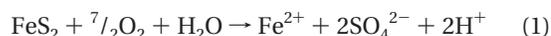
The distribution of low molecular weight carboxylic acids (LMWCA) was investigated in pore water profiles from two porphyry copper tailings impoundments in Chile (Piuquenes at La Andina and Cauquenes at El Teniente mine). The objectives of this study were (1) to determine the distribution of LMWCA, which are interpreted to be the metabolic byproducts of the autotroph microbial community in this low organic carbon system, and (2) to infer the potential role of these acids in cycling of Fe and other elements in the tailings impoundments. The speciation and mobility of iron, and potential for the release of H⁺ via hydrolysis of the ferric iron, are key factors in the formation of acid mine drainage in sulfidic mine wastes. In the low-pH oxidation zone of the Piuquenes tailings, Fe(III) is the dominant iron species and shows high mobility. LMWCA, which occur mainly between the oxidation front down to 300 cm below the tailings surface at both locations (e.g., max concentrations of 0.12 mmol/L formate, 0.17 mmol/L acetate, and 0.01 mmol/L pyruvate at Piuquenes and 0.14 mmol/L formate, 0.14 mmol/L acetate, and 0.006 mmol/L pyruvate at Cauquenes), are observed at the same location as high Fe concentrations (up to 71.2 mmol/L Fe(II) and 16.1 mmol/L Fe(III), respectively). In this zone, secondary Fe(III) hydroxides are depleted. Our data suggest that LMWCA may influence the mobility of iron in two ways. First, complexation of Fe(III), through formation of bidentate Fe(III)–LMWCA complexes (e.g., pyruvate, oxalate), may enhance the dissolution of Fe(III) (oxy)hydroxides or may prevent precipitation of Fe(III) (oxy)hydroxides. Soluble Fe(III) chelate complexes which may be mobilized downward and convert to Fe(II) by Fe(III) reducing bacteria. Second, monodentate LMWCA (e.g., acetate and formate) can be used by iron-reducing bacteria as electron donors (e.g., *Acidophilum* spp.), with ferric iron as the electron acceptor. These processes may, in part, explain the low abundances of secondary Fe(III) hydroxide precipitates below the oxidation front and the high concentrations of Fe(II) observed in the pore waters of some low-sulfide systems. The reduction of Fe(III) and the subsequent increase of

iron mobility and potential acidity transfer (Fe(II) oxidation can result in the release of H⁺ in an oxic environment) should be taken in account in mine waste management strategies.

Introduction

Low molecular weight carboxylic acids (LMWCA) can alter minerals by complexing ions at the surface, weakening metal–oxygen bonds, and catalyzing dissolution reactions. Thus, LMWCA can play an important role in many geological processes (1). Ligands also can affect reaction rates indirectly by complexing ions in solution, thereby lowering the saturation state. Monodentate ligands, such as acetate and formate, increase the extent of mineral dissolution much less than bidentate ligands, such as oxalate and pyruvate. The latter carboxylic acids are important in enhancing the dissolution of silicate minerals (2) and secondary Fe(III) and Mn(III) hydroxides (3). Laboratory mineral-weathering studies, conducted using oxalate, show a significant increase in the release of major ions from rocks and minerals (e.g., 4). Oxalate is also widely used for characterization of secondary Fe(III) hydroxide phases by differential X-ray diffraction (DXRD) and in studies of the dissolution kinetics of Fe(III)-bearing phases (5–9).

Mill tailings, derived from mining sulfide-bearing ore deposits, are essentially composed of crushed rock. These systems are typically devoid of organic carbon, which limits biological cycling of sulfur, iron, and other metals in these environments. Sulfide-oxidizing bacteria, such as *Acidithiobacillus ferrooxidans*, are autotrophic and can assimilate organic carbon from CO₂. These bacteria derive energy through the catalysis of inorganic reactions. Microorganisms can act directly in the oxidation of metal sulfides (e.g., pyrite; eq 1) as a catalyst for ferrous to ferric iron oxidation (eq 2), in element liberation, as well as in retention and neutralization processes in mine-waste environments.



Microorganisms produce and excrete a variety of LMWCA including acetate, formate, oxalate, and citrate among others (4, 10, 11). The *Acidithiobacillus ferrooxidans* strain TM is reported to produce small amounts of pyruvic acid (12). In the supernatants of *Acidithiobacillus* cultures from mine tailings, Fortin et al. (13) detected small amounts of formate and acetate.

The interactions between the mineralogy, microorganisms, and organic metabolites are some of the key parameters to understand the formation of contaminated mine wastes.

Studies of the complexation potential of LMWCA in soils have been conducted (14, 15). However, fewer studies of the importance of LMWCA have been conducted on mine wastes (13, 16, 17). Burckhard et al. (17) demonstrated that the presence of carboxylic acids can increase the solubility of Zn in mine tailings samples. Fortin et al. (13) detected low concentrations of formate and acetate in the oxidation zone from tailings of the Kam Kotia Cu–Zn mine, Canada, and inferred that the local sulfate-reducing bacteria (SRB) community uses acetate and formate as electron source. Fe(III) reducing bacteria can also use LMWCA as electron donor (18, 19).

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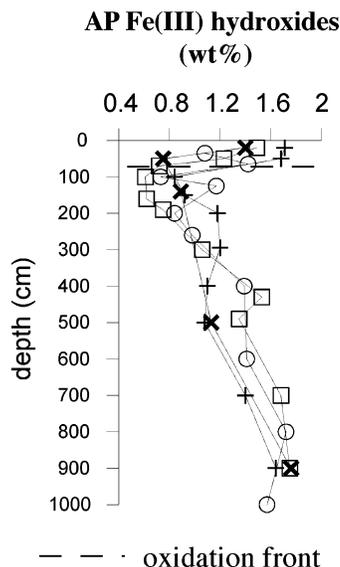


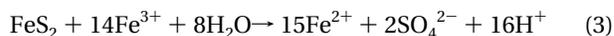
FIGURE 1. Distribution of secondary Fe(III) hydroxides in four drill cores at the low-sulfide Piuquenes impoundment (La Andina/Chile). Data show the Fe concentrations in the 0.2 M oxalic acid leach (1 h in darkness) from sequential extractions (5) after the procedure described by Dold (7).

Dold and Fontboté (5) observed a decrease of secondary ferric oxyhydroxides or hydroxysulfates at and below the oxidation front in two tailings impoundments with low sulfide content and low neutralization potential (Figure 1).

The potential role of LMWCA in the depletion of secondary ferric oxyhydroxides and oxyhydroxysulfates in the low-sulfide tailings is the subject of this study. It is hypothesized that the highest level of activity of sulfide-oxidizing bacteria takes place at the oxidation front, and as a consequence the metabolic LMWCA show increased concentrations in this zone. These LMWCA can influence the solubility of iron because of complexation or can be used as electron donors by iron- and sulfur-reducing bacteria at and below the oxidation front, resulting in the reduction of iron and sulfate.

Highest *Acidithiobacillus ferrooxidans* populations are usually reported at the oxidation front (20), whereas the heterotrophic species *Acidiphilium* spp. show higher populations in the upper part of the oxidation zone of the mine tailings. The microbial distribution at the Piuquenes tailings impoundment (Figure 3A) shows similar trends (21). At the oxidation front, 100 times more bacteria ($1.37E + 09$ cells/g dry weight) were measured than in other depths in the tailings stratigraphy (Figure 3A). Below the groundwater level (135 cm at sampling time for the microbiological study; October 2002), no bacteria could be detected using the techniques that were applied (cultivation and molecular techniques). Cultivation has shown that iron and sulfur oxidizers were present in the oxidation zone and at the oxidation front. Isolation confirmed the presence of *Acidithiobacillus ferrooxidans* and *Sulfobacillus* spp., and the latter is able to oxidize or reduce Fe(III) and oxidize sulfur. The cells detected directly by 16S rRNA in the tailings samples from the vicinity of the oxidation front showed a strong predominance of a *Leptospirillum*-like iron-oxidizing bacteria. Heterotrophic bacteria were detected by cultivation in the upper oxidation zone and below the oxidation front down to the groundwater level. Heterotrophic isolates suggested by 16S rRNA analysis indicate that *Acidiphilium* spp., an iron reducer, is present around the oxidation front, and *Acidobacterium*-like cells are present throughout the oxidation zone. Sulfate-reducing bacteria were detected by the cultivation method around and below the oxidation front down to the groundwater level at 135-cm depth. Understanding the biogeochemical factors

controlling the solubility and mobility of iron species (Fe(II)/Fe(III)) is essential in understanding the kinetics of sulfide oxidation, as Fe(III) is a dominant oxidant at low pH (eq 3),



and the production of acidity via hydrolysis of Fe^{3+} (eq 4).



Experimental Section

Pore Water Sampling. (1) *Vadose Zone Sampling.* Pore water from the vadose zone was extracted from sealed core samples, collected in 7.63-cm-diameter thin-walled aluminum casings in April 2000. The cores were cut into portions of 50-cm lengths and the ends of the casings were fitted with O-ring sealed end-plates, isolating the samples from atmospheric oxygen. The cores were frozen (-20°C) at the field site and were maintained frozen until pore water extraction. The cores were thawed at room temperature ($25\text{--}30^\circ\text{C}$) and the pore water was displaced from 25-cm-long cores using epoxidized soybean oil, which is immiscible with water, modified after the method described by Patterson et al. (22). Determination of pore water pH and Eh was made immediately after pore water extraction. The performance of the pH electrode was controlled by pH 4.0 and 7.0 standard buffer solutions. The performance of the Eh electrode was confirmed by comparison to Zobell's solution and Light's solution (23, 24). All Eh values were corrected to the standard hydrogen electrode (SHE). All samples were filtered through 0.2- μm nylon syringe filters and split into two aliquots. One was acidified to pH < 2 with HNO_3 for cation analysis. The second untreated sample was frozen until analysis for anions and carboxylic acids.

(2) *Saturated Zone Sampling.* A piezometer nest was installed in each tailings impoundment (AP1 and TC1) with six individual drive-point piezometers during the field campaign 2000 to obtain water samples from the saturated zone. All piezometers were developed by repeated pumping. The water samples from the saturation zone were obtained using a peristaltic pump and pH, Eh, temperature, and specific conductivity were measured using sealed flow-through cells. Alkalinity determinations were made in the field using a digital titrator, and Fe(II) was analyzed by titration with potassium dichromate. Fe(III) concentrations were calculated as the difference between the Fe_{tot} obtained by inductively coupled plasma atomic emission spectrometer (ICP-AES; Jerrrol-Ash Iris) and the Fe(II) concentrations.

Pore Gas Sampling. Pore gas samples were collected using stainless steel tubes of narrow diameter (0.63 cm), which were driven vertically into the tailings. The pore gas samples were collected at 10-cm intervals by displacing deionized water in inverted glass bottles. The gas was analyzed by gas chromatography (GC) at the Water Quality Laboratory at the University of Waterloo.

Chemical Analysis of the Pore Water Samples. The samples from the vadose zone were analyzed at the Water Quality Laboratory and the Chemical Engineering Analytical Services Laboratory, both at the University of Waterloo, Ontario, Canada. Anions were analyzed by ion chromatography (IC, Dionex, DX-500).

LMWCA Determination. Sample Preparation. A 0.5-mL aliquot of each sample was diluted to 2.5 mL with high-purity water. For all dilutions and standard solution preparation, high-purity 18 M-cm water (Milli-Q Plus, Millipore, Ann Arbor, MI) was used. It was observed that the concentrations of Fe and SO_4 were high in samples from the oxidation zone (up to 2470 mg/L and 25400 mg/L, respectively). Toward the saturated zone, the concentrations decreased to values

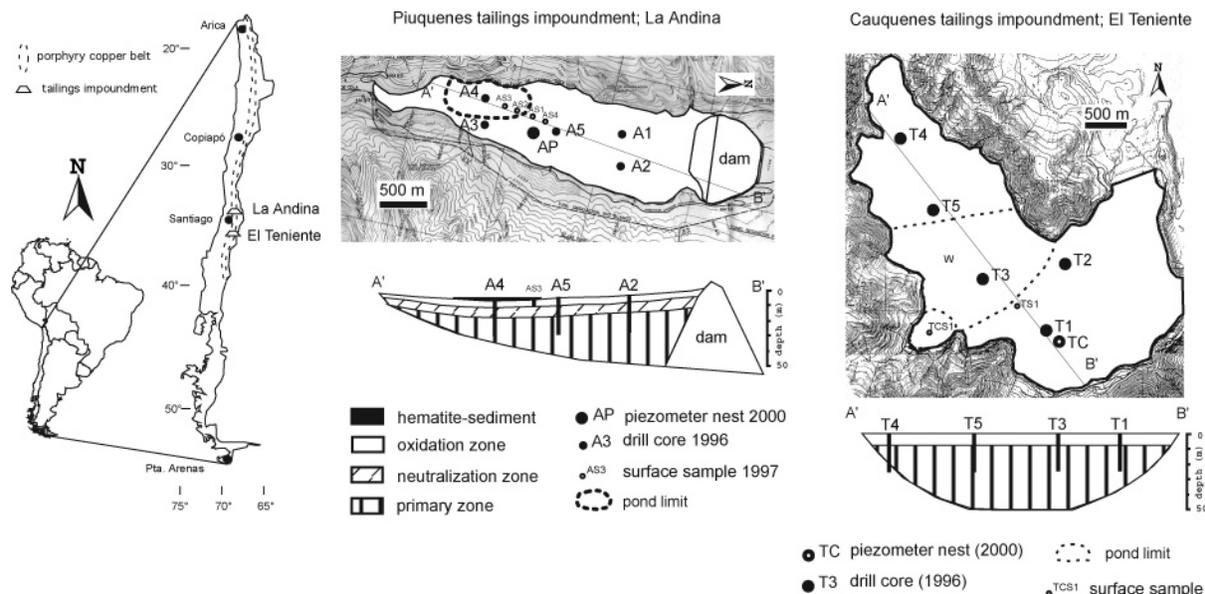


FIGURE 2. Overview of the tailings impoundment Piouenes and Cauquenes from the La Andina and El Teniente porphyry copper mines, Chile. The stratigraphic zonation in the cross section is vertically exaggerated.

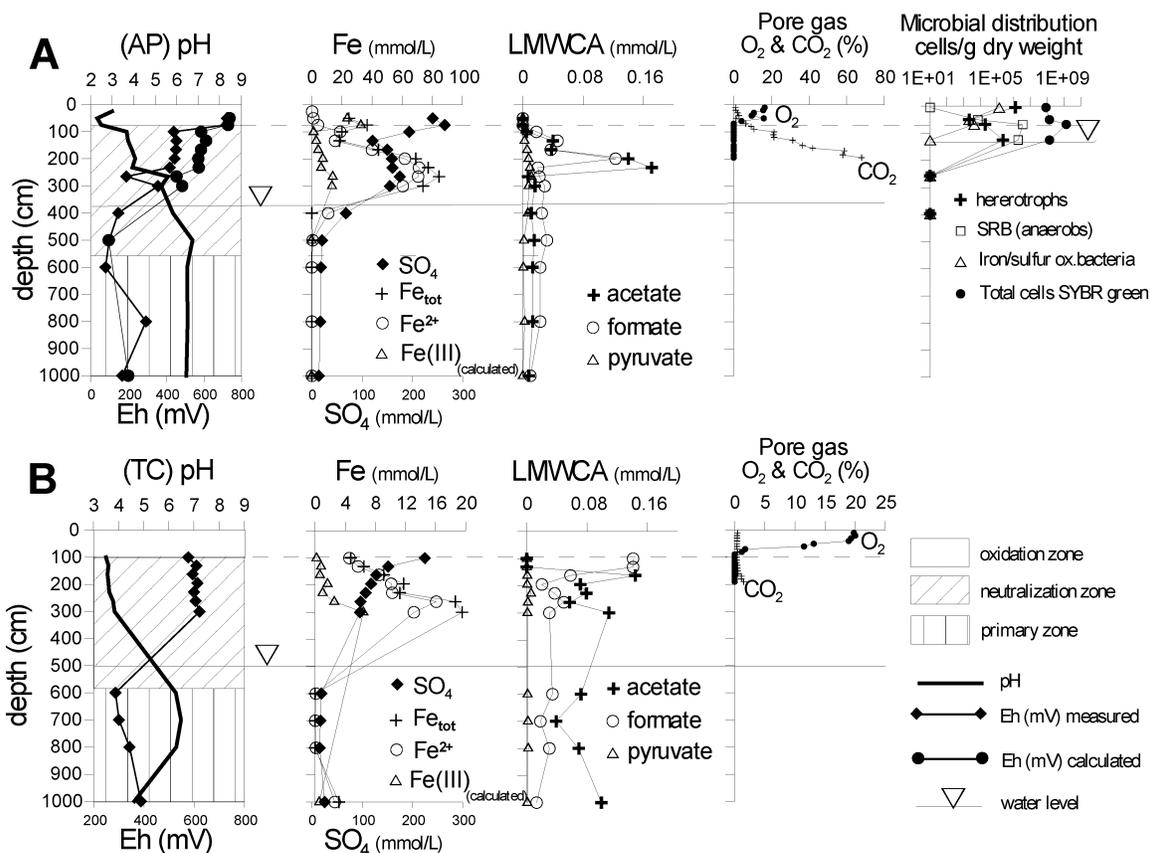


FIGURE 3. Results of the pore water chemistry (Eh, pH, SO₄, Fe speciation) and LMWCA at the piezometer nests from the two studied tailings impoundments: (A) AP from the Piouenes tailings impoundment (La Andina/Chile). (B) TC from the Cauquenes tailings impoundment (El Teniente/Chile). The right diagrams show the pore gas concentrations of O₂ and CO₂ of the upper 2 m of the unsaturated zone. The scale for pore gas and Fe data are different in A and B. The distribution of the microbial population is shown in the right diagram for Piouenes. Total cell counts were obtained by SYBR green staining and counting under the microscope (cells/g dry weight). Data for distribution of heterotrophs, SRB (anaerobs), and iron/sulfur oxidizing bacteria were obtained by cultivation (colonies/g dry weight).

as low as below the detection limit for Fe and for sulfate to concentrations between 1000 and 2000 mg/L. The matrix changes, through the tailings stratigraphy, produced severe changes in elution times and reproducibility of the LMWCA analyses. To improve their chromatography, the diluted samples were passed through Dionex OnGuard-Barium

cartridges to remove sulfate and decrease cation concentrations. The treated samples were stored frozen until analysis. Organic anions were quantified using Dionex DX500 chromatographic system with a Dionex IonPac 4-mm AS11 analytical column and detection by conductivity. The eluent was 0–60 mM NaOH delivered in a curve 8 (concave) gradient

TABLE 1. Analytical Control and Spike Recovery of the Applied IC Method for LMWCA Analysis in Tailings Pore Water Samples

	Analytical Control					
	acetate	formate	pyruvate	tartrate	oxalate	citrate
target (mg/L)	3.759	4.011	3.741	4.042	3.717	3.781
mean (mg/L)	3.902	4.181	3.725	4.08	3.746	3.741
bias (%)	3.8	4.2	-0.4	0.9	0.8	-1
CV (%)	2.9	2.2	2	1.5	1.2	2.2
n	14	14	14	14	14	14
Lower limit of detection (mg/L)	0.100		0.009	0.092	0.051	0.072

sample	spike recoveries (%)					
	acetate	formate	pyruvate	tartrate	oxalate	citrate
tcp 7	87.7	85.7	93.5	76.7	69.3	31.1
tcp 8	88.7	99.1	98.3	84.2	47.8	11.2
tcs 9	85.3	61.2	96.3	85.6	41.1	68.6

over 25 min, and the injection volume was 25 μ L. For data acquisition and processing, the Waters Millennium-32 Chromatography Manager software package was used. Two stock solutions were prepared containing 1000 mg/L of each organic anion (acetate, formate, tartrate, oxalate, citrate). One was used for preparation of the calibration solutions and the other for control of analytical bias, precision, and recovery. Quality control (QC) samples of various types constituted approximately 20% of the overall chromatographic work. The QC samples consisted of procedure blanks, method blanks, analytical controls, and spiked duplicates. Sample spikes were around the 8 mg/L level for all parameters. Quality control data are summarized in Table 1. All procedure blanks were below detection. Method blanks were similar except for traces of formate and oxalate at around 10 μ g/L. Sample matrix has a significant effect on analyte recoveries, particularly the polydentate ligands oxalate and citrate showed lower recoveries and were variable. It is assumed that they form insoluble salts (e.g., Ba-salts).

Solid-Phase Microextraction and Gas Chromatography-Mass Detection (SPME-GC-MS). As fluoride and acetate elute closely, the identity of acetate was controlled by SPME and GC-MS detection (25). A 100- μ m poly(dimethylsiloxane) (PDMS) fiber was immersed into 4 mL aqueous sample. A 15-min adsorption time and a 5-min desorption time were used. For GC-MS analyses, an HP GC 5890 equipped with a DB-624 column (30 m \times 0.25 mm, 1.4- μ m film thickness) and a Mass Selective Detector HP 5971 was used. The injection was made at 250 $^{\circ}$ C. The detector was maintained at 300 $^{\circ}$ C. After an initial period of 1 min at 40 $^{\circ}$ C, the column was heated to 220 $^{\circ}$ C at 20 $^{\circ}$ C/min followed by an isothermal period of 5 min.

Data Treatment. The geochemical computer program PHREEQC, Version 2, (26) with the thermodynamic database WATEQ4F (27) was used for Eh calculations.

Results and Discussion

The geochemical and mineralogical data of the Piuquenes and the Cauquenes tailings impoundment at La Andina and El Teniente porphyry copper deposits, respectively, (Figure 2) are published in Dold and Fontboté (5). These previous observations are summarized briefly in conjunction with the results of current measurements.

Piuquenes/La Andina Tailings Impoundment. The Piuquenes tailings impoundment from the La Andina porphyry copper deposits (Rio Blanco-Los Bronces ore body; alpine climate) can be characterized as low sulfide (1.7 wt % pyrite equivalent) and low carbonate (1.4 wt % calcite equivalent). The hydrology of the Piuquenes tailings is controlled by an intercalation of fine sandy ($K = \sim 3 \times 10^{-7}$ m/s) and silty-clayey horizons ($K = \sim 2 \times 10^{-8}$ m/s) (5). The water flow takes

place in the coarser horizons, as connected aquifers. The climate is Alpine with 700 mm/a rainfall. The groundwater table in the tailings fluctuated from 3.7 m in late summer and 1.35 m in spring below surface. During the 16 years since tailings deposition ceased, a 50–70-cm-thick low-pH oxidation zone (pH 2.3–3) has developed. The low pH zone is underlain by a neutralization zone in which the pH rises to 6.7. High concentrations of dissolved constituents are observed in the low-pH oxidation zone and in the neutralization zone, as a result of sulfide (mainly pyrite) oxidation (up to 265 mmol/L SO_4 , 84.5 mmol/L Fe, 75.4 mmol/L Al, 18.6 mmol/L Cu, 3.04 mmol/L Zn).

Results from sequential extractions (5, 7) show that at and below the oxidation front, the Fe concentrations in the fraction of the secondary Fe(III) oxyhydroxides are lowest (0.6–0.9 wt %), whereas in the oxidation zone and in the primary zone these concentrations are around 1.6 wt % (Figure 1).

The concentrations of Fe(III) in the pore water were calculated by the difference of Fe_{total} and Fe(II)-iron and are therefore an indirectly measured value (Figure 3). The Eh was measured directly compared to the calculated with PHREEQC on the basis of the iron speciation. Measured and calculated Eh values are in good agreement in the samples from the oxidation zone (50–75 cm depth) and in the primary zone (500- and 1000-cm depth). However, in the neutralization zone (100–300 cm depth), the measured values are between 126 and 266 mV lower than the calculated Eh values. The iron speciation in the pore water in the unsaturated zone (Figure 3A) shows that in the oxidation zone iron is present mainly as Fe(III) (32.6 mmol/L), whereas below the oxidation front at 80-cm depth the Fe(III) concentration decreases to 1.18 mmol/L. This change is paralleled by a decrease of Eh from around 720 mV in the oxidation zone to 450 mV in the upper neutralization zone. The Fe(II) concentration increases from 0.23 mmol/L to 4.12 mmol/L in the oxidation zone to concentrations around 19 mmol/L below the oxidation front and then further to around 72 mmol/L at 232-cm depth in the neutralization zone. The indirectly measured Fe(III) concentrations increase from 1.18 mmol/L below the oxidation front at 100-cm depth to values up to 13.9 mmol/L at 232-cm depth. The total iron concentration decreases to below the detection limit in the saturated zone.

LMWCA concentrations were below the detection limit in the oxidation zone (Figure 3). At a depth of 199 cm, a maximum concentrations of formate (0.12 mmol/L) was detected and at 232-cm depth the maximum concentration of acetate (0.17 mmol/L) was observed. The maximum concentration of acetate, which elutes close to fluoride, was confirmed by SMPE GC-MS. Pyruvate was present at its

TABLE 2. O₂ and CO₂ Concentrations in the Pore Gas of the Unsaturated Zone from Piuquenes/Andina (APG) and Cauquenes/Teniente (TCG)

APG			TCG		
sample depth (cm)	O ₂ (%)	CO ₂ (%)	sample depth (cm)	O ₂ (%)	CO ₂ (%)
10	16.46	0.98	10	19.79	0.49
20	15.68	1.14	20	20.01	0.43
30	10.73	2.10	30	19.33	0.43
40	9.57	2.80	40	18.94	0.42
50	15.99	1.25	50	13.13	0.42
60	4.19	4.18	60	11.52	0.41
70	0	6.44	70	1.75	0.42
80	0	9.26	80	1.2	0.48
90	0	10.78	90	0	0.39
100	0	21.43	100	0	0.38
110	0	21.06	110	0	0.38
120	0	21.39	120	0	0.30
131	0	31.33	130	0	0.50
150	0	36.55	140	0	0.46
160	0	42.00	150	0	0.55
170	0	58.76	160	0	0.55
185	0	57.96	170	0	1.15
195	0	67.95	180	0	1.11
			190	0	1.53

highest concentration of 0.01 mmol/L at 265-cm depth. Below 265 cm, the LMWCA concentrations decreased sharply to values around 0.01 mmol/L for acetate, 0.02 mmol/L for formate, and 0.006 mmol/L for pyruvate or lower.

Iron Speciation. The increase of Fe(III) toward the base of the unsaturated part of the neutralization zone (Figure 3; 232-cm depth) must be interpreted with caution. The oxygen concentrations in the pore gas decrease to below detection at 70-cm depth (Table 2) and the redox potential indicates reduced conditions. The apparently increasing concentration values of Fe(III) in the zone where the LMWCA concentrations are also increasing (100–300 cm depth) contrast with the Eh and oxygen measurements. This suggests that the calculated values do not accurately represent the Fe(III) concentrations. It is more likely that the calculated Fe(III) concentrations represent Fe–LMWCA complexes, which were not detected by the dichromate titration.

Cauquenes/El Teniente Tailings Impoundment. The Cauquenes tailings impoundment from the El Teniente porphyry copper deposits (Mediterranean climate) can be characterized as low-sulfide (1 wt % pyrite equivalent) and carbonate-poor (0 wt % calcite equivalent). The low-carbonate content is the result of an acidic flotation circuit (pH 4.5) used in the mineral processing. This process consumes carbonate minerals and partitions pyrite into the concentrate, resulting in a low-pyrite content in the tailings. The hydrological situation at Cauquenes is also controlled by an intercalation of fine sandy ($K = \sim 2.3 \times 10^{-7}$ m/s) and silty-clayey horizons ($K = \sim 2.8 \times 10^{-8}$ m/s) (5) similarly as at Piuquenes. The climate is Mediterranean with 540 mm/a rainfall. The groundwater table in the tailings fluctuated from 5.0 m in late summer and 1.5 m in spring below surface. During the 20 years after operation ceased, these tailings developed a 100–150 cm thick low-pH oxidation zone (pH 1.7–3). Because of the dryer climate at the Cauquenes site, pore water could not be obtained from the oxidation zone, and less pore water was extracted from the deeper unsaturated zone. Because of the small sample volume, priority was on measuring concentrations for iron speciation. No platinum electrode Eh measurement could be obtained. Nevertheless, it can be assumed that the Eh in the oxidation zone of the Cauquenes is high. The pore gas oxygen concentration is high down to 80-cm depth (Figure 3B). The CO₂ concentration in the pore gas shows a slight increase to 1.53% in 190-cm

depth, contrasting with the 67.95% reached in Piuquenes at 195-cm depth (Table 2). This difference is probably due to the absence of carbonates. High concentrations of dissolved constituents are observed in the pore water below the low-pH oxidation zone and primary (pH 3.5–6.5) zone as a result of the oxidation of sulfide minerals (mainly pyrite). Concentrations of up to 225 mmol/L SO₄, 19.5 mmol/L Fe, 95.8 mmol/L Al, 35.9 mmol/L Cu, and 0.38 mmol/L Zn are observed. The iron speciation showed trends below the oxidation zone that are similar to those observed at Piuquenes (no pore water data are available from the oxidation zone; Figure 3B). High concentrations of Fe(II) are observed at 261-cm depth with a maximum concentration of 16.1 mmol/L. The acetate was below the detection limit from the tailings surface to 131-cm depth (Figure 3) before increasing to 0.14 mmol/L. Acetate then showed a slight decrease in concentration with increasing depth but was present at concentrations between 0.04 and 0.11 mmol/L. Formate was present at concentrations of 0.14 mmol/L below the oxidation zone and sharply decreased to concentrations below 0.05 mmol/L at greater depth. Pyruvate was present at its highest concentration of 0.0056 mmol/L at a depth of 228 cm.

LMWCA and Iron Mobility. The speciation of the dissolved Fe showed that Fe(III) was the dominant Fe species in the oxidation zone (>90%). As the dissolved ferric ion is only stable at very low pH, hydrolysis, that is, deprotonation of the hexa-aquo ion, takes place in the environment of the oxidation zone. This process occurs stepwise and results in the precipitation of Fe(III) oxides or hydroxides with increasing deprotonation of the hexa-aquo ion (8), resulting in an immobilization of Fe(III) and production of H⁺ (eq 4). The pH increases sharply from 2.5 in the oxidation zone to around 4 below the oxidation front. This sharp pH gradient should initiate the precipitation of Fe(III) hydroxides and represents a geochemical barrier limiting the downward movement of Fe(III). Therefore, Fe(III) should be only mobile in the low pH oxidation zone, where it is able to react with sulfide minerals (e.g., eq 3). The Fe(II) released through reaction 3 will be oxidized nearly completely to Fe(III) by the high microbial activity observed at the oxidation zone. Below the oxidation front (between 75 and 300 cm depth), Fe(II) predominates (Figure 3) and the abundance of secondary Fe(III) hydroxides shows a minimum (Figure 1; on the basis of data from sequential extractions (5)). This suggests that iron reduction or complexation processes increase the mobility of iron and may limit secondary Fe(III) hydroxide precipitation. Microbiological activity is highest in the zone of active sulfide oxidation (i.e., oxidation front) (5, 21). Consequently, it is likely that the activity of byproducts of microbial respiration, including carboxylic acids, would be highest in the vicinity of the oxidation front. This hypothesis was confirmed in this study, where an increase of acetate, formate, and pyruvate below the oxidation front was detected (Figure 3).

At Piuquenes, the LMWCA show a sharp decrease below 232-cm depth. This decrease parallels a decrease in the Eh from values around 450 mV to 188 mV, which is similar to the reduced conditions observed in the saturated zone (~200 mV), and an increase in pH from around 4 to 5.6. Acid neutralization via reaction with siderite, the dominant carbonate mineral in Piuquenes, could explain the pH increase and the increase of CO₂ and the decrease of Eh. These trends are probably enhanced by the use of LMWCA by Fe(III) reducing bacteria (e.g., the detected *Acidophilum* spp., *Sulfobacillus* spp., *Acidithiobacillus ferrooxidans*), as observed in other settings (19, 28). The relatively low concentrations of LMWCA are interpreted as the result of recent microbial activity in this low organic carbon system, whereas the higher concentrations of Fe(II) represent an accumulation that has occurred over a longer time period.

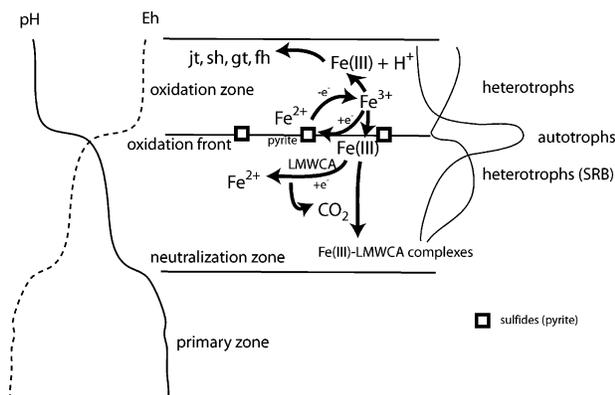


FIGURE 4. Schematic model of LMWCA–CO₂ and Fe(II)–Fe(III) iron cycling in porphyry copper tailings. Pyrite is oxidized at the oxidation front by autotroph bacteria. The liberated ferrous ion is oxidized by iron oxidizers (e.g., *Leptospirillum* spp.). The ferric ion either increases the rate of pyrite oxidation or hydrolyzes to Fe(III) species and secondary Fe(III) hydroxides under the liberation of protons. Its mobility is limited downward by the pH–Eh barrier at the oxidation front. At and below the oxidation front, where the bacterial population is highest, the metabolic LMWCA have their highest concentrations. Bidentate or tridentate LMWCA can form Fe(III)–LMWCA complexes and increase the solubility of Fe(III) and subsequently its mobility, or the LMWCA are used by iron- or sulfate-reducing bacteria as electron donor and Fe(III) as electron sink, resulting in the reduction to Fe(II) and liberation of CO₂. Abbreviations: jt = jarosite; sh = schwertmannite; gt = goethite; and fh = ferrihydrite.

In Cauquenes, the distribution of the LMWCA is similar to Piuquenes. From the oxidation zone at Cauquenes, no pore water samples could be obtained because of dryness. However, the distribution of acetate shows similar trends, with concentrations below detection limit in the oxidation zone. In the saturated zone, the values for the LMWCA acids do not decrease as sharply as in Piuquenes, possibly because of the lower pH conditions (pH 4.5–5) prevalent in the Cauquenes tailings. This low pH may suppress the activity of sulfate- and iron-reducing bacteria in Cauquenes, as in general LMWCA are much more toxic at lower pH (29). For example, Küsel et al. (30) observed that at low pH no growth of *Acidiphilium cryptum* or reduction of Fe(III) occurred in the presence of acetate. The Cauquenes tailings have virtually no carbonates because of the low pH of the flotation circuit (pH 4.5). In the zone where the LMWCA are present, however, a slight increase of CO_{2(g)} is observed. This increase in CO_{2(g)} may indicate the activity of iron- or sulfate-reducing bacteria. Far below the oxidation zone (Figure 1, below 4-m depth), the presence of secondary Fe(III) hydroxides in the primary zone is suggested by the data from sequential extractions. An Eh–pH stability diagram field (e.g., 31) constructed using low activities of Fe and S (10^{–4}) suggests that the redox conditions of 200 mV Eh and near neutral pH plot in the stability field of Fe(III) hydroxides (possibly Fe(OH)_{3(a)} or ferrihydrite). This could indicate that because of the increase of pH the oxidation and slow hydrolysis to Fe(OH)₃ may be initiated. The very low iron concentrations in the zone (generally below detection limit) support this interpretation.

The role of LMWCA on iron mobility in mine waste systems can be summarized in the following schematic model of LMWCA–CO₂ and Fe(II)–Fe(III) cycling (Figure 4) in the studied low-sulfide porphyry copper tailings. The principal sulfide oxidation activity takes place at the oxidation front shown by high autotroph activity because the sulfide content of the upper oxidation zone is nearly obliterated (5). Fe(II) is oxidized to Fe(III) at the oxidation front, limiting strongly the mobility of iron through hydrolysis. LMWCA are the metabolic byproducts of the high microbial activity at the

oxidation front. Complexation with bidentate LMWCA as, for example, pyruvate or oxalate, will increase the solubility of ferric iron by the formation of Fe(III)–LMWCA complexes lessening the precipitation of Fe(III) (oxy)hydroxides and increasing the mobility of Fe(III) enabling it to pass the geochemical barrier of the oxidation front. Iron- and sulfate-reducing bacteria may use the monodentate LMWCA (e.g., acetate and formate) as electron donor. The Fe(III) reducers use ferric iron as electron acceptor, resulting in the reduction of Fe(III) and the liberation of CO₂. The Fe(II) released through this reaction can migrate through the underlying tailings downstream. When it encounters geochemical changes in the flow path (e.g., discharge at the base of the tailings dam or pH–Eh changes), ferrous iron can reoxidize to ferric iron and hydrolyze resulting in the precipitation of ferric oxyhydroxides and liberation of protons. Thus, these iron reduction processes can transfer the acid potential downstream. Although limited by the low concentrations of LMWCA at the sites investigated, this process should be considered in predictions of acid mine drainage production from sulfidic mine waste.

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