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DETECTION AND DISTRIBUTION OF FERRIC OXYHYDROXIDES AND OXYHYDROXIDE SULFATES IN SULFIDE MINE TAILINGS; THEIR IMPORTANCE TO SELECTIVE METAL RETENTION AND ACID PRODUCTION

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The stratigraphy of an oxidizing sulfidic mine tailing is usually divided into an oxidation zone at the top (pH 1.5 - 3.5, high sulfate contents), followed by a neutralization zone below (pH 3.5 - 5) and an underlying primary zone with near neutral pH (Figure 1).

Schwertmannite (ideally $Fe_8O_8(OH)_6SO_4$ or $Fe_{16}O_{16}(OH)_{10}(SO_4)_3$) has been reported from several locations around the world, as precipitate in heavy metal and sulfate loaded drainage systems (Bigham et al., 1990, 1994, 1996; Childs et al., 1997; Schwertmann et al., 1995; Yu et al., 1998). During the present investigation, the application of differential X-ray diffraction (DXRD) has allowed, to detect schwertmannite (sh) in the oxidation zone of two sulfidic mine tailings as a minor phase in bulk samples (Piuquenes tailing of the La Andina porphyry copper deposit, humid climate; and the Cauquenes tailing of the El Teniente porphyry copper deposit, semi-arid climate, both located in central Chile). Schwertmannite occurs as a significant secondary phase together with the main secondary minerals jarosite ($KFe_3(SO_4)_2(OH)_6$; jt) and a vermiculite-type mixed layer (ver).

The presence of schwertmannite in the oxidation zone of the two tailings mentioned above is also supported by SEM-EDS element mapping, fast dissolution kinetics in NH_4-oxalate, and Fe/S mol ratio of 4.9.

A dissolution kinetic test with eight natural and synthetic schwertmannite and ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$; fh) samples was performed using 0.2 M ammonium oxalate at pH 3 under exclusion of light (NH_4-OxD) to study the possibility of discrimination of one of these minerals by its dissolution kinetics. Results of this test indicate that it is not possible to discriminate schwertmannite and ferrihydrite (2-line) by their dissolution kinetics, but by their Fe/S mol ratios. This allows selective leaching of these minerals which minimizes the dissolution of other reducible phases (e.g., hematite (hm), magnetite (mt), goethite (gt), and jt).

Nevertheless, higher potassium values in NH_4-OxD leach of samples from the oxidation zone and DXRD control show that an easily reducible part of jarosite is dissolved in this step. The results of the dissolution kinetic test were taken into account for the design of the sequential extraction, applied in this study. This sequence was adapted to the secondary mineralogy of the studied mine tailings.

The variations of Fe/S mol ratios in the NH_4-OxD leach (Figure 1) suggest that schwertmannite together with jarosite is limited to the oxidation zone and that the predominant ferric oxyhydroxide in the zones below is possibly ferrihydrite. This pH controlled distribution of these minerals is consistent with observations made by Schwertmann et al. (1995) in a natural stream environment showing that fh is stable at less acidic conditions (pH > 4) than sh (pH 3 - 4) and jt (pH < 3).

In the Piuquenes tailing, the higher values of Mo, As and SO_4 in the NH_4-OxD leach in samples from the oxidation zone and in situ microprobe analysis indicate that schwertmannite and jarosite play an important role to oxyanion adsorption by ligand exchange under acidic condition. In contrast, bivalent cations (e.g., Cu^{2+}, Mn^{2+}, Zn^{2+}) are not adsorbed by these minerals, because of competitive proton adsorption at outstanding OH^- groups. Below the oxidation zone, ferrihydrite together with other adsorbents (clay minerals, Mn-oxides) plays a major role in the pH controlled adsorption of bivalent cations mobilized downwards from the oxidation zone (Figure 1).

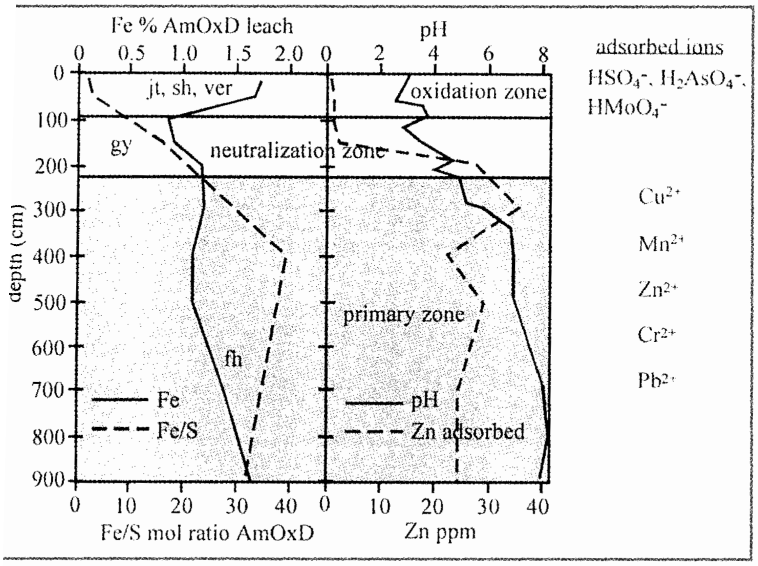

Figure 1. Typical tailings stratigraphy (e.g. Piuquenes A2) with secondary mineralogy (jarosite = jt, schwertmannite = sh, vermiculite-type mixed layer clay mineral = ver, gypsum = gy, ferrihydrite = fh), pH, and Fe, and Fe/S mol ratio variation in the ferric oxyhydroxide leach (NH_4-OxD). Adsorbed Zn is from a 1M NH4-Acetate leach). The general trend of adsorbed ion species is shown at the right.

In the Cauquenes tailing (semi-arid climate), the adsorption behavior is similar, but in places, the very mobile elements Cu and Zn are enriched in the oxidation zone as water soluble secondary minerals (e.g., chalcanthite $CuSO_4 \cdot 5H_2O$). This overprint is induced by capillary upwards migration of these metals which is controlled by high evaporation, finer grain size, and higher humidity. In extreme arid conditions (El Salvador; Atacama desert, Northern Chile) copper is enriched up to 5 % in the upper part of the tailings stratigraphy as water soluble fraction (mainly chalcanthite).

Results have shown that the main secondary ferric phases in the oxidation zone are jarosite and schwertmannite. In acid-base accountings (ABA) in general it is assumed that $Fe(OH)_{3(s)}$ or ferrihydrite hydrolyses from solution with the production of 3 mole H^+/mole Fe^{3+} hydrolyzed. The hydrolysis of jarosite produce only 2 mole H^+ and schwertmannite between 2.625 and 2.75, respectively (Table. 1). This difference must be taken into account by calculation of the quantity of acid produced, as hydrolysis of the secondary ferric phases is the main acid producing process in sulfide oxidation. Nevertheless, it is important to be aware that for calculation of the acid potential (AP) in case of carbonate treatment, due to increased pH values, ferrihydrite or goethite will be produced, leading to the production of 3 mole H^+/mole Fe^{3+}.

Our results illustrate the importance of secondary mineralogy to the adsorption properties in mine tailings and the production of acidity. The distribution of schwertmannite, jarosite, and ferrihydrite is mainly controlled by pH and the activity of Fe, K, and SO_4. Their selective adsorption behavior is essentially pH controlled.

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Phase		Equation	mole H^+/mole Fe^{3+}hydrolysed
amp. $Fe(OH)_{3(s)}$	$Fe^{3+} + 3H_2O$ =	$Fe(OH)_{3(s)} + 3H^+$	3
ferrihydrite	$10Fe^{3+} + 60H_2O$ =	$5Fe_2O_3 \cdot 9H_2O + 30H^+$	3
goethite	$Fe^{3+} + 2H_2O$ =	$FeO(OH) + 3H^+$	3
hematite	$2Fe^{3+} + 3H_2O$ =	$Fe_2O_3 + 6H^+$	3
schwertmannite	$8Fe^{3+} + SO_4^{2-} + 14H_2O$ =	$Fe_8O_8(OH)_6SO_4 + 22H^+$	2.75
	$16Fe^{3+} + 3SO_4^{2-} + 26H_2O$ =	$Fe_{16}O_{16}(OH)_{10}(SO_4)_3 + 42H^+$	2.625
jarosite	$3Fe^{3+} + K + 2SO_4^{2-} + 6H_2O$ =	$KFe_3(SO_4)_2(OH)_6 + 6H^+$	2

Table 1: Amount of protons produced by the hydrolysis of the different secondary Fe(III)phases.