ABSTRACT

The geochemical and mineralogical study of the Quiulacocha tailings impoundment has shown that the hydrological connection of the three mine-waste systems at Cerro de Pasco (Excelsior, Quiulacocha, Ocroyoc) is the most critical concern for the waste management. The Quiulacocha tailings cover 114 ha, comprising 79 Mt of tailings, which contain ~50 wt% pyrite. The tailings are located at 4340 m altitude in a tropical puna climate with about 1025 mm/a rainfall. The tailings are partly overlain by the Excelsior waste-rock dump, which contains about 26,400,000 m$^3$ of waste rocks that cover 94 ha and contain ~60 wt% of pyrite. In the Quiulacocha impoundment there are two different types of tailings recognized: 1) Zn-Pb-rich tailings and 2) Cu-rich tailings. During the sampling campaign, the Zn-Pb-rich part of Quiulacocha was not producing important excess of acid mine drainage (AMD) from the oxidation zone, where pH is increased to near neutral values at 1 m depth. The underlying tailings were still able to neutralize the acidity, produced in the oxidation zone through sulfide oxidation, by the underlying carbonates (dolomite and siderite). The main source of AMD in this mine-waste system is from the Excelsior waste-rock dump. Its acid seepage infiltrates into Quiulacocha forming a Fe-Zn-Pb plume with a pH 5.5 – 6.1 and containing up to 7440 mg/L Fe, 627 mg/L Zn, and 1.22 mg/L Pb. The plume was detected between 10 m to 13 m depth in the stratigraphy of Quiulacocha. Additionally, the AMD seepage from the base of the Excelsior waste-rock dump is channelled on the tailings surface to the pond of Quiulacocha (pH 2.3), which covers Cu-rich tailings. Infiltration of this Fe(III)-rich AMD increases oxidation of tailings in the southwestern part of the impoundment and subsequently liberates As by enargite oxidation. Additionally, the AMD collected in the Quiulacocha pond was pumped into the active Ocroyoc tailings impoundment, where sulfide oxidation was strongly enhanced by the input of dissolved Fe(III). Therefore, the AMD management and a hydrological separation of the different mine-waste systems might be a first step to prevent further extension of the AMD problem.
Introduction
The goal of this study is to investigate the geochemical processes taking place in each mine-waste deposit (tailings, waste-rock dump) and the effects resulting from the hydrological connection between these different mine-waste systems (Figs. 1 and 2). The material for both tailings impoundments originate from the polymetallic Zn-Pb-(Ag-Bi-Cu) deposit at Cerro de Pasco, Peru (Baumgartner et al., 2002; Einaudi, 1977).

Methods
Solids (88 samples) were obtained by flush drilling at 4 locations (CPQ/A, CPQ/B, CPQ/C, CPQ/D) down to a maximum depth of 26 m (Fig. 2). The mineralogical study included thin and polished section microscopy, SEM-EDS analyses, X-ray diffraction and differential X-ray diffraction (DXRD). Selected solid samples (39) were analyzed for 38 elements by X-ray fluorescence. 11 water samples (pore water and surface waters) were analyzed for 37 elements by ICP-MS, and major cations and anions by ion chromatography.

Results and Discussion
The hydrological situation was characterized by a strong water input from the Excelsior waste-rock dump towards the Quiulacocha tailings impoundment (Fig. 2). This resulted in a nearly complete water saturation of the Quiulacocha tailings. Two different tailings types could be distinguished in the Quiulacocha tailings impoundment: 1) Cu-rich tailings and 2) Zn-Pb-rich tailings.

The Cu-sulfide tailings were characterized by the association of pyrite-enargite-chalcopyrite-sphalerite-galena. Quartz is the dominant gangue mineral and is associated with aluminosilicates such as dickite/kaolinite as well as with alunite. The Cu-sulfide tailings were deposited in the SW part of Quiulacocha, in the former natural lagoon of Quiulacocha, underlying the Zn-Pb tailings in the central part of Quiulacocha, which were separated by a floating dike (Fig. 2).

Figure 2. Location map of the open pit, waste-rock dump and tailings impoundments at Cerro de Pasco, Peru. The Quiulacocha tailings cover 114 ha, comprising 79 Mt of tailings, which contain ~50 wt% pyrite. The tailings are located at 4340 m altitude in a tropical puna climate with about 1025 mm/a rainfall. The tailings are partially overlain by the Excelsior waste-rock dump, which contains about 26,400,000 m³ of waste rocks that cover 94 ha and contain ~60 wt% of pyrite. The profile shows the hydrological connection between the two systems, location of drillings, and the distribution of the Cu-rich and Zn-Pb-rich tailings in the impoundment. The arrows indicate the water flows. The vertical scale of the profile is exaggerated for better visibility.
In the particular acid conditions of the SW part of the tailings (near the AMD pond with pH around 2.3), the oxidation of sulfide minerals such as enargite (Cu$_3$AsS$_4$) and chalcopyrite (CuFeS$_2$) caused the liberation of Cu and As. Copper was then leached out towards the primary zone (low pH and reducing condition) where it precipitated in the form of secondary sulfides such as covellite (CuS). This process generated secondary enrichments with copper concentrations rising from 1560 mg/kg (3.5 m depth) to 5890 mg/kg (9.5 m depth).

The mineralogy of the Zn-Pb-rich sulfidic tailings was characterized by an assemblage of pyrite-sphalerite-galena-pyrrhotite. Gangue minerals were mainly the carbonates dolomite (CaMg(CO$_3$)$_2$) and siderite (FeCO$_3$), though silicates, mainly quartz, were also present. Sulfide oxidation and the subsequent AMD formation induced the dissolution of primary carbonates and silicates, resulting in the formation of secondary minerals such as gypsum and, possibly, siderite. Siderite was mainly encountered close to the contact with the Excelsior waste-rock dump and below the oxidation zone.

In the three drill holes, CPQ/A, B, and C, immediately below the tailings surface (1 m depth, primary zone), the pH values varied between 5.5 and 8. At greater depth, 10 – 13 m respectively, a zone with lower pH (5.6 – 6.1) and high metal contents were observed (Fe = 1262 - 7440 mg/L; Zn = 153 - 627 mg/L; Pb = 1.12 - 1.22 mg/L). Additionally, the pH of the primary zone increased from 5.5 close to Excelsior (CPQ/A) to 7.5 with increasing distance from the waste-rock dump Excelsior at CPQ/C. These observations suggest an infiltration of acid Fe(III)-rich waters from the waste-rock dump Excelsior towards the underlying Quiulacocha tailings impoundment. This infiltration of AMD, which was produced by sulfide oxidation in the Excelsior waste-rock dump, accelerates the oxidation processes in the tailings by equation 1:

$$\text{FeS}_2 + 14 \text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$$  \hspace{1cm} (equation 1)

explaining the formation of the acid Fe-Zn-Pb plume.

The Cu-rich tailings in the SW part of Quiulacocha (drilling CPQ/D), with a pH around 4.5, was influenced by infiltration of AMD from the pond (pH = 2.3, conductivity of 18.7 mS/cm, Eh of 434 mV, 44424 mg/L SO$_4^{2-}$, 1691 mg/L Fe, 56.7 mg/L Al, 578.1 mg/L Zn, 26.8 mg/L Cu, 6.54 mg/L As). The arsenic content in this pond remained high (6.54 mg/L) and constituted a major pollutant. The main source of arsenic was enargite (Cu$_3$AsS$_4$), and to a lesser extent arsenopyrite (FeAsS) and tennantite (Cu$_{12}$As$_4$S$_{13}$). Thus, the Cu-rich tailings were also influenced by the AMD from the Excelsior waste-rock dump. The pumping of the Fe(III)-rich acid waters from the pond of Quiulacocha in the active tailings impoundment Ocroyoc represents also an export of acid potential by equation 1.

**Conclusions**

The geochemical and mineralogical study of the Quiulacocha tailings impoundment has shown that the hydrological connection of the three mine-waste systems at Cerro de Pasco (Excelsior, Quiulacocha, Ocroyoc) is the most critical concern for the waste management. The main source of AMD in this mine-waste system is from the Excelsior waste-rock dump. Its acid seepage infiltrates into Quiulacocha forming a Fe-Zn-Pb plume with a pH 5.5 – 6.1 and containing up to 7440 mg/L Fe, 627 mg/L Zn, and 1.22 mg/L Pb. The plume was detected between 10 m to 13 m depth in the stratigraphy of Quiulacocha tailings. The AMD seepage from the base of the Excelsior waste-rock dump is channelled on the tailings surface to the pond of Quiulacocha (pH 2.3), which covers Cu-rich tailings. Infiltration of this Fe(III)-rich AMD increases oxidation of tailings in the southwestern part of the impoundment and subsequently liberates As by enargite oxidation. The AMD collected in the Quiulacocha pond was pumped into the active Ocroyoc tailings impoundment, where sulfide oxidation was strongly enhanced by the input of dissolved Fe(III). Therefore, a hydrological separation of the different mine-waste systems might be a first step to prevent further extension of the AMD problem.

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