

GEOCHEMISTRY AND MINERALOGY OF THE QUIULACOCHA TAILINGS IMPOUNDMENT FROM THE POLYMETALLIC Zn-Pb-(Ag-Bi-Cu) DEPOSIT CERRO DE PASCO, PERU.

Cheikh Wade², Bernhard Dold^{3*}, and Lluís Fontboté²

Abstract: 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. 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 excesses 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 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 tailings. Additionally, the AMD seepage from the base of the Excelsior waste-rock dump is channeled 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, a hydrological separation of the different mine-waste systems might be a first step to prevent further extension of the AMD problem.

Additional Keywords: Flotation, tailings, waste-rock dump, cemented zone, hydrology, acid mine drainage

¹ Paper presented at the 7th International Conference on Acid Rock Drainage (ICARD), March 26-30, 2006, St. Louis MO. R.I. Barnhisel (ed.) Published by the American Society of Mining and Reclamation (ASMR), 3134 Montavesta Road, Lexington, KY 40502

² Department of Mineralogy, University of Geneva, Rue des Maraîchers 13, CH-1205 Geneva Switzerland. ^{3*} Corresponding Author.: Bernhard.Dold@unil.ch, Centre d'Analyse Minérale, Bâtiment Humense, Institute of Mineralogy and Geochemistry, University of Lausanne, CH-1015 Lausanne, Switzerland.

Introduction

A mineralogical and geochemical study of the inactive Quiulacocha and the active Ocroycoc tailings impoundments, Cerro de Pasco, Peru, is presented. The goal of this study is to understand 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. 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). The ore is rich in pyrite and sulfides are the main base-metal carrier. Two different types of ore have been exploited in the history of the mine. During the first decades of the 20th century, copper mineralization associated with enargite (Cu_3AsS_4) has been mined. The flotation plant for the Cu-ore was located in the south-western (SW) part of the Quiulacocha tailings impoundment, where the tailings were directly deposited in the depression of the natural Quiulacocha lake (today located below the AMD pond on the surface of the impoundment). From around 1947, due to improvement of flotation process, the exploitation of Pb-Zn was

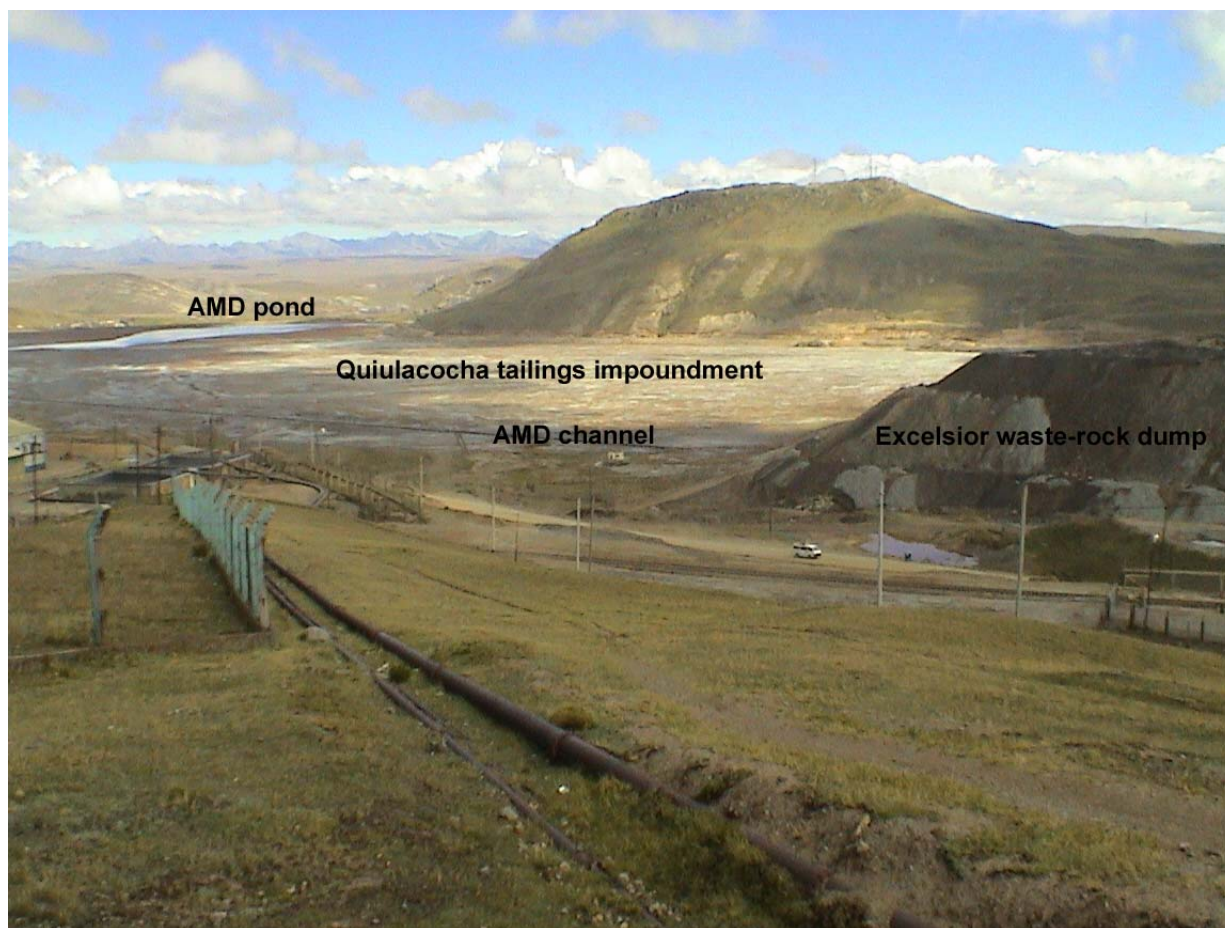


Figure 1: Overview of the Quiulacocha tailings impoundment with the overlying Excelsior waste-rock dump on the right and the AMD pond in the southwestern part of the tailings impoundment.

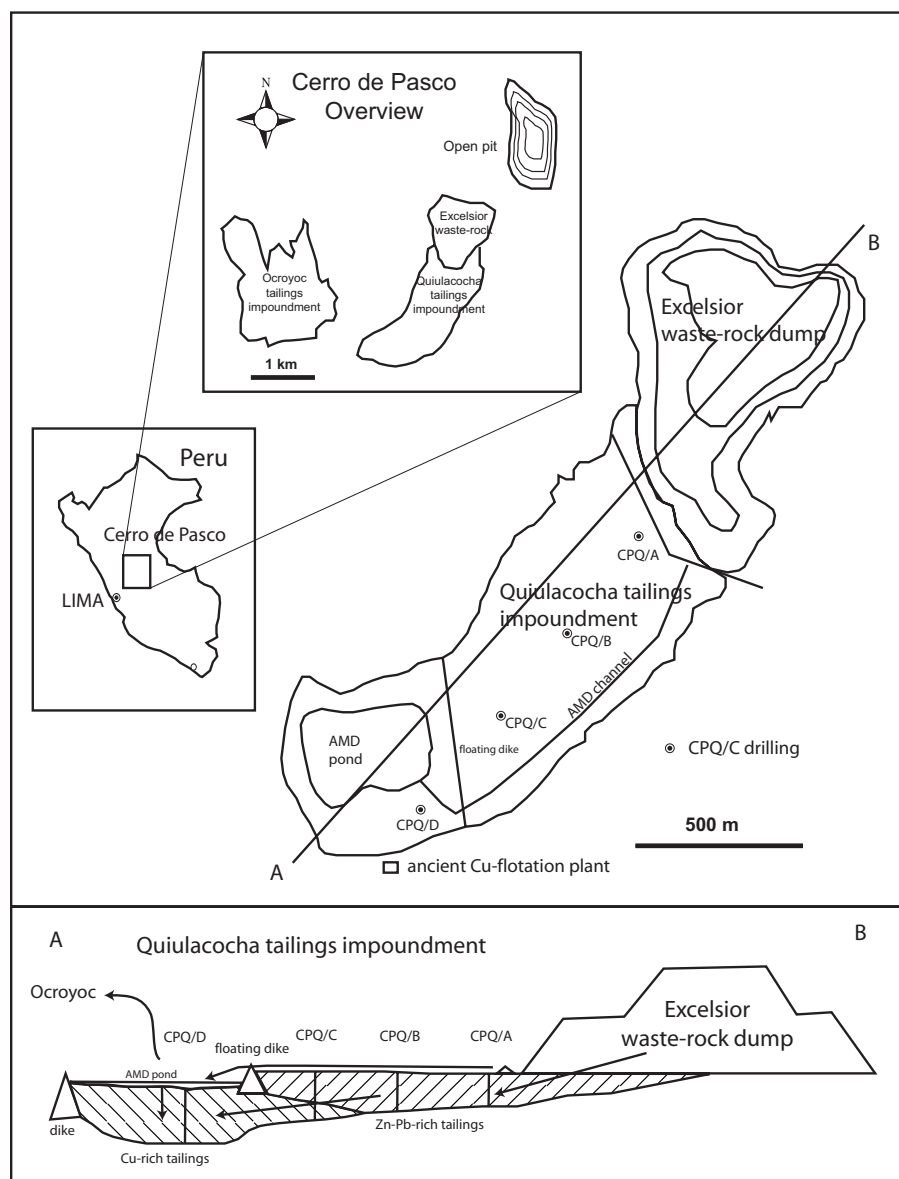


Figure 2: Location map of the open pit, waste-rock dump and tailings impoundments at Cerro de Pasco, Peru. The Quiulacocha tailings impoundment and the overlaying Excelsior waste-rock dump at Cerro de Pasco are shown in detail. The profile shows the hydrological connection between the two systems, location of drillings, and the distribution of the Cu-rich and Zn-Pb-rich tailings in the impoundment. The vertical scale of the profile is exaggerated for better visibility.

avored and a new flotation plant was built close to the open pit. Therefore, the discharge and deposition point was moved to the north-eastern (NE) part of the tailings, which is closer to the flotation plant. Due to this deposition history the Cu-tailings are today found in the SW part of Quiulacocha, in the former natural lake of Quiulacocha, underlying the Zn-Pb tailings in the central part of Quiulacocha, which were separated by a floating dike (Fig. 1 and 2). Quiulacocha is located at 1.5 km S-SW of the mine, 170 km N-NE of Lima at an altitude of 4340 m. The tailings are exposed to a humid climate ("tropical puna"; ~1025 mm/y rainfall/ ~988 mm/y

evaporation). The deposition of tailings at Quiulacocha stopped in 1992 after 50 years of operation. The Quiulacocha tailings (114 ha, 79 Mt tailings @ ~ 50 wt% pyrite) are partially overlain by the Excelsior waste-rock dump, which contains about 26,400,000 m³ of waste rocks (94 ha, ~60 wt% of pyrite; Smuda et al., in review). The active Ocroyoc tailings impoundment is located 7km SW of the Cerro de Pasco mine (Fig. 2). During the sampling period in June 2003, the three mine-waste systems were hydrologically connected. Acid mine drainage (AMD) seeping from the base of the Excelsior waste-rock dump was collected and conducted into a channel on the surface of the Quiulacocha tailings towards the AMD pond on the SW part of the tailings impoundment (Fig. 1 and 2). Field observations suggest that a significant amount of the AMD from the Excelsior waste-rock dump infiltrates into Quiulacocha tailings. The excess AMD, which is collected in the pond had a pH of 2.3, conductivity of 18.7 mS/cm, Eh of 434 mV, 44,424 mg/L SO₄²⁻, 1691 mg/L Fe, 56.7 mg/L Al, 578.1 mg/L Zn, 26.8 mg/L Cu, 6.54 mg/L As, and was pumped into the active Ocroyoc tailings.

Methodology

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, which crosses the whole stratigraphy of the Quiulacocha tailings (Fig. 2). A detailed study of the oxidation zone was conducted by surface sampling at 7 locations. To sample the pore water, 3" diameter aluminum tubes were used for coring at several depths of the drillings and were quickly frozen (-20°C) until pore water extraction. The pore water was obtained by replacement with epoxidized soybean oil (PARAPLEX®) in the laboratory. Water and pore-water pH, Eh, and alkalinity were measured immediately during water sampling or pore-water extraction. Alkalinity was measured with a Hach digital titrator, and pH electrodes were calibrated with pH 4 and 7 standard solutions. The Eh values were corrected to the standard hydrogen electrode (SHE). All water samples were filtered through 0.2 µm regenerated cellulose and stored at +4°C in the dark prior to analysis. Samples for cation analyses were acidified to pH < 2 with suprapure HNO₃. During solid sampling, pH was measured with a WTW pH-meter (WTW pH 323) with a special pH-electrode (WTW-Sentix RP) inserted directly into the tailings. The mineralogical study included thin and polished section microscopy, SEM-EDS studies, X-ray diffraction (Philips 3020) and differential X-ray diffraction (DXRD). Selected solid samples (39) were analyzed for 38 elements and mineralogical analysis by X-ray fluorescent (Philips PW 2400). The 11 water samples were analyzed for 37 elements by ICP-MS (Perkin Elmer HP 4500 Series 100) and major cations and anions by ion chromatography (Dionex DX 120). O₂, CO₂, and H₂S concentrations in the pore gas of the unsaturated zone were measured by a Dräger® Multiwarn II.

Results and Discussion

The hydrological situation was characterized by a strong water input from the Excelsior waste-rock dump towards the Quiulacocha tailings impoundment. This resulted in a nearly complete water saturation of the Quiulacocha tailings. The groundwater level was close to the surface near the Excelsior waste-dump and down to 1 m depth in the area of the floating dike. The southwestern part with the AMD pond was nearly completely water saturated.

Two different tailings types could be distinguished in the four drillings (max. 26.7 m depth) performed in the Quiulacocha tailings impoundment: 1.) Cu-rich tailings, and 2.) Zn-Pb-rich tailings.

1.) Cu-sulfide tailings

The Cu-sulfide tailings were characterized by the association of pyrite-enargite-chalcopryrite-sphalerite-galena. Quartz is the dominant gangue mineral and is associated with aluminosilicates such as dickite/kaolinite as well as alunite. Primary carbonates (dolomite ($\text{CaMg}(\text{CO}_3)_2$) and siderite (FeCO_3)) were almost absent. 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). In the particular acid conditions of the SW part of the tailings (near the AMD pond pH around 2.3), the oxidation of sulfide minerals such as enargite (Cu_3AsS_4) and chalcopryrite (CuFeS_2) caused the liberation of Cu, which is mobile in acidic conditions. Cu 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 (3.5m depth) to 5890 mg/kg (9.5 m depth).

2.) Zn-Pb-rich sulfidic tailings:

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 and siderite, though silicates mainly quartz, were also present. The Zn-Pb-rich tailings represent two thirds of the tailings surface and were deposited in the NE part, partially overlaying the older Cu-tailings (Fig. 2). Due to the tailings deposition process, a grain size fractionation from coarser close to the Excelsior waste-rock dump (former deposition point) to finer with increasing distance from the deposition point could be observed. 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 11 years, the Quiulacocha tailings have developed an oxidation zone with a thickness from several mm to a maximum 25 cm, with pH ranging between 1.9 and 4.8. Areas with a very thin oxidation zone were characterized by cementation of the pore space by secondary minerals, giving the oxidation zone a hard and compact appearance, called the “cemented zone”. The mineralogy of the oxidation zone was characterized by an assemblage of residues of pyrite, quartz and secondary phases such as jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), siderite, and Fe(III) hydroxides, mainly goethite (confirmed by DXRD). The oxidation of sulfide minerals generated acid solutions and mobilizing the associated metals (Fe, Cu, Zn, Pb). The interaction of these acid waters with the gangue minerals caused their dissolution and subsequent liberation of cations such as K^+ , Na^+ and Ca^{+2} . These cations played a key role in the formation of secondary phases such as jarosite, gypsum, and siderite.

In the oxidation zone, in the absence of cementation, O_2 and CO_2 concentrations at 15 cm depth were 13.4% - 2.54% respectively. If a cemented zone was present, O_2 and CO_2 concentrations decreased to 9.80% and 0.94% respectively. The formation of a cemented zone constituted a diffusion barrier for gases, limiting the infiltration of oxygen to depth. This caused a decrease of oxidation kinetics, resulting in a thin oxidation zone. The data suggest that the parameters promoting the formation of a cemented zone are a combination of the high sulfide content, fine grain size, and the presence of carbonates.

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; Table 1). 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 (see equations in Fig. 3), may accelerate the oxidation processes in the tailings by equation 1, explaining the formation of the acid Fe-Zn-Pb plume (Fig. 3). 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). 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_3AsS_4), and to a lesser extent arsenopyrite (FeAsS) and tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$). 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.

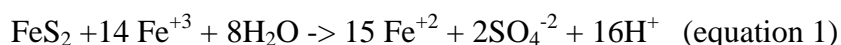


Table 1: Hydrochemical results from the water samples obtained by replacement with epoxylized soybean oil from the drillings at different depths and from the pond waters.

E	E	Ion Chromatography										ICP/MS					
		Anions				Cations											
Samples	pH	F ⁻ (mg/L)	CL ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Li ⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	NH ₄ ⁺ (mg/L)	Mg ²⁺ (mg/L)	Ca ²⁺ (mg/L)	²⁷ Al (mg/L)	⁵⁷ Fe (mg/L)	⁶³ Cu (mg/L)	⁶⁶ Zn (mg/L)	⁷⁵ As (mg/L)	²⁰⁶⁻⁷⁻⁸ Pb (mg/L)
Lagoon Quiulacocha	2.3	Trace	85.5	Trace	44424	Trace	111	63	Trace	4032	900	56.7	1691	26.9	578.1	6.54	0.63
Lagoon Ocroyoc	10	Trace	26.3	6.4	1642	Trace	50.8	15.5	2	Trace	974	0.16	3.63	0.03	1.09	0.1	0.52
CPQ/A 50cm	3.4	2	13.9	Trace	1791	Trace	27.8	17.8	2.2	Trace	Trace	0.07	3.51	0.03	0.65	0.12	0.18
CPQ/A 4.7m	5.4	1.9	19.2	Trace	3779	Trace	31	Trace	Trace	243	825	0.39	96.1	0.03	4.18	0.55	0.74
CPQ/B 50cm	3.3	Trace	Trace	Trace	3204	Trace	50.2	18.7	2.4	215	634	0.27	65.0	0.06	6.56	0.12	0.76
CPQ/B 10m	6.1	Trace	Trace	Trace	5582	Trace	23	27	22	1742	507	0.23	1262	0.03	153.2	0.25	1.12
CPQ/B 16.7m	6.4	Trace	Trace	Trace	813	Trace	35.3	16.9	12.9	115	853	0.163	144.5	0.05	2.54	0.57	0.85
CPQ/C 50cm	3.7	Trace	17.6	Trace	21336	Trace	31.3	30.6	8.2	1424	408	0.18	58.9	0.04	3.87	0.16	0.23
CPQ/C 13m	5.5	Trace	Trace	Trace	> 20000	Trace	5.6	5	Trace	247	857	2.19	7440	0.03	627	0.45	1.22
CPQ/D 50cm	---E	---	---	---	---	Trace	8.5	2.5	3.6	10.4	234	8.74	10890	2.04	632.9	2.08	1.69

---E not measured

TraceE= below detection limit

Conclusion

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. As the Zn-Pb-rich part of Quiulacocha was not liberating significant amounts of AMD to the system because the underlying carbonate-rich material of the oxidation zone was partly able to neutralize the acidity produced through sulfide oxidation, the main source of AMD was the waste-rock dump Excelsior. Its acid seepage infiltrated into Quiulacocha forming a Fe-Zn-Pb

plume (Fig. 3). The infiltration of Fe(III)-rich solutions resulted in enhanced acid production through equation 1 and also increased the kinetics of sulfide oxidation and dissolution in the Quiulacocha tailings. The collection of AMD emanating from the Excelsior waste-rock dump and transfer to the AMD pond of Quiulacocha increased the oxidation of the Cu-rich tailings (equation 1) in the SW part of the tailings impoundment and promoted liberation of arsenic from sulfide minerals such as enargite, arsenopyrite, and tennantite to the environment. The pumping of the Fe(III)-rich acid surface water of the Quiulacocha pond to the active Ocroyoc tailings also increased sulfide oxidation and acid production through equation 1 in the fresh tailings. The results suggest that a hydrological separation of the different mine-waste systems might be a first step to prevent further extension of the AMD problem.

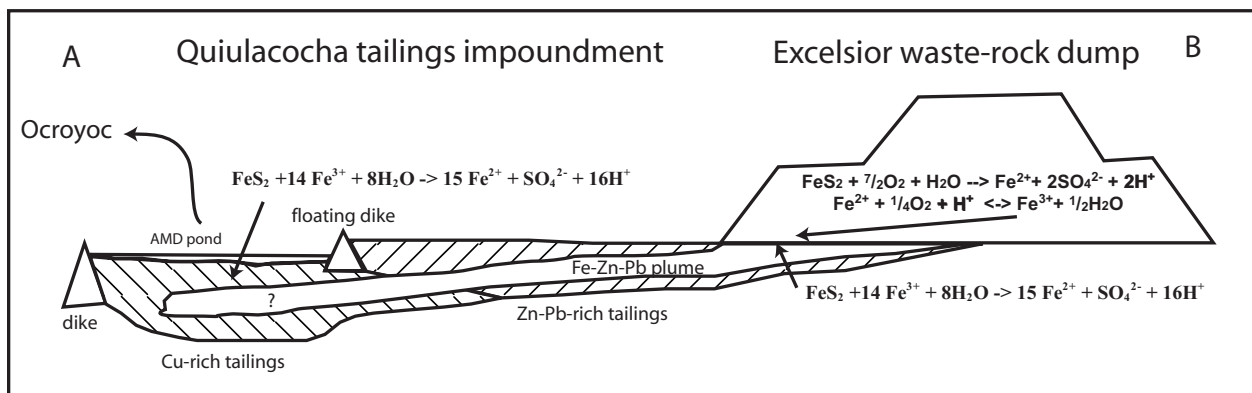


Figure 3: Profile and relationships between AMD production in the Excelsior waste-rock dump and the export of Fe(III)-rich solution to the Quiulacocha tailings impoundment. The infiltration of Fe(III)-rich AMD enhanced the sulfide oxidation in Quiulacocha and the formation of a Fe-Zn-Pb plume detected in the Zn-Pb-rich tailings. In the Cu-rich tailings, the overlying AMD pond enhanced the oxidation of this material and the liberation of the associated arsenic. The exportation of Fe(III)-rich AMD to Ocroyoc from the AMD pond at Quiulacocha, increased importantly sulfide oxidation in the active tailings impoundment.

Acknowledgement

We would like to thank the management of CENTROMIN, Peru for their interest, support and access to their properties, especially Antonio Cornejo and Juana Rosa del Castillo. Special thanks are due to Volcan S.A.A for their logistic support and hospitality during the sampling campaign in 2003, especially Victor Gobitz, F. Grimaldo, Luis Osorio, and Walter Hevedia. The project was organized with the support of Silvia Rosas (Pontificia Universidad Católica del Perú, Lima) and was financed by the Swiss Commission for Research Partnerships with Developing Countries (KFPE).

Literature Cited

- Baumgartner R., Fontboté L., and Jobin Y. (2002) Carbonate hosted zinc-lead high-sulfidation mineralization at the Cerro de Pasco deposit, Peru. *XI Congres Peruano de Geologia*, 75.
- Einaudi M. T. (1977) Environment of Ore Deposition at Cerro de Pasco, Peru. *Economic Geology* **72**, 893-924.
- Smuda J., Dold B., Friese K., Morgenstern W., and Gläser W. (in review) The mineralogy and geochemistry of the Excelsior waste-rock dump from the polymetallic Zn-Pb-(Ag-Bi-Cu) deposit Cerro de Pasco, Peru. *Journal of Geochemical Exploration*.