GEOCHEMISTRY AND SECONDARY MINERALOGY AT THE SULFIDE-RICH EXCELSIOR WASTE ROCK DUMP FROM THE POLYMETALLIC Zn-Pb-(Ag-Bi-Cu) MINERALIZATION CERRO DE PASCO, PERU[1]

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Abstract. The Excelsior waste rock dump of the polymetallic Zn-Pb-(Ag-Bi-Cu) Cerro de Pasco deposit, Peru is characterized by high acid-production potential due to its waste rock composition with 60 wt% pyrite and <5 wt% carbonates. The waste dump is locally rich in minerals that contain up to 12.7 wt% Pb, 4.9 wt% Zn, 1.1 wt% Cu, 6020 mg/kg As, and 381 mg/kg Cd. Acid mine drainage (AMD) at the base of the waste rock dump is rich in Fe, Zn, Pb, Cd and As. The object of this study is to determine the source of metals in AMD and if metal contamination was related to seasonal fluctuations of precipitation. Main secondary minerals are gypsum, hydronian / plumbo- / K-jarosites, goethite, schwertmannite, and efflorescent salts (Fe-, Zn-, Mg-, Mn-sulfates). Leach tests of mine waste material simulated rain events and demonstrated the high solubility of efflorescent salts and acid/metal liberation. Leachates have pH between 2.8 and 4.9 and contain a maximum of 447.1 mg/L Zn, 16.7 mg/L Cu, and 14.8 mg/L Cd. AMD appears to be controlled by precipitation of secondary efflorescent salts in dry seasons and re-dissolution in rainy seasons.

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Introduction

Worldwide, sulfidic waste rock dumps are an important source of acid mine drainage (AMD). Metals and acids from AMD can be stored as efflorescent salts, which precipitate from oversaturated pore solutions due to evaporation and consist for a big part of heavy metal sulfates (Gierè et al., 2003). After rain events, the salts dissolve easily in water, producing acidic, metal-rich solutions (Hammarstrom et al., 2005). This study focuses on the formation and dissolution of secondary minerals at the sulfide-rich Excelsior waste rock dump from the Cerro de Pasco Mine, Central Andes, Peru (Fig. 1). The climate at the high altitude of this side (altitude: 4.300m) is characterized by an average precipitation of 1,025 mm/a and an average evaporation of 988 mm/a.

The main ore minerals of the polymetallic Pb-Zn-(Ag-Bi-Cu) deposit are pyrite (FeS_2), sphalerite (ZnS) and galena (PbS) with minor enargite (Cu_3AsS_4), tennantite ($(Cu,Ag,Fe,Zn)_{12}As_4S_{13}$), and luzonite ($Cu_3AsS_4$). Gangue minerals are dominantly quartz ± hematite ± siderite ± muscovite (Einaudi, 1977). The waste rock dump contains 26,400,000 m^3 of broken rocks with an average size of 10 cm. Ca. 60 ha of the 94 ha large waste rock dump cover a tailings impoundment located downstream (Figure 1A). The primary mineral assemblage of the Excelsior waste rock dump were dominated by pyrite (ca. 60 wt%), less than 5 wt% of the waste rocks were carbonates with a capacity of neutralizing AMD.

Objectives and Methods

The objectives of this study were: (1) characterization of primary elemental constituents of waste rocks; (2) characterization of the secondary mineral assemblage; (3) characterization of AMD from the waste rock dump; and (4) an estimatation of the influence of the highly variable mountain climate on element transport and the formation/dissolution of secondary minerals within the waste rock dump.

At the surface of the Excelsior waste rock dump, 68 solid samples were collected at 52 sampling points (Fig. 1B), using two different sampling strategies: (1) sampling of altered primary rocks ("AR" samples) with low content of secondary minerals, and (2) sampling of efflorescent salts ("ES" samples). These samples were divided into samples from the upper levels ("top" samples) and samples from the base of the waste rock dump ("base" samples).

Water was sampled at four seeps at the base of the waste rock dump. Water samples were geochemically analyzed by inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC). Solid samples were analyzed mineralogically and geochemically by X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), and thin sections. Low crystalline Fe^{+3}- hydroxides were analyzed by differential X-ray diffraction (DXRD as described by Dold (2003).

The dissolution of minerals and the liberation of metals from weathered waste rocks during rain events were simulated using the German standard procedure for leach tests DIN38414 S4 (1984): 10 g of dry, milled sample were mixed with 100 ml deionied water, shaked for 24 hours, filtered and analyzed for dissolved ions.

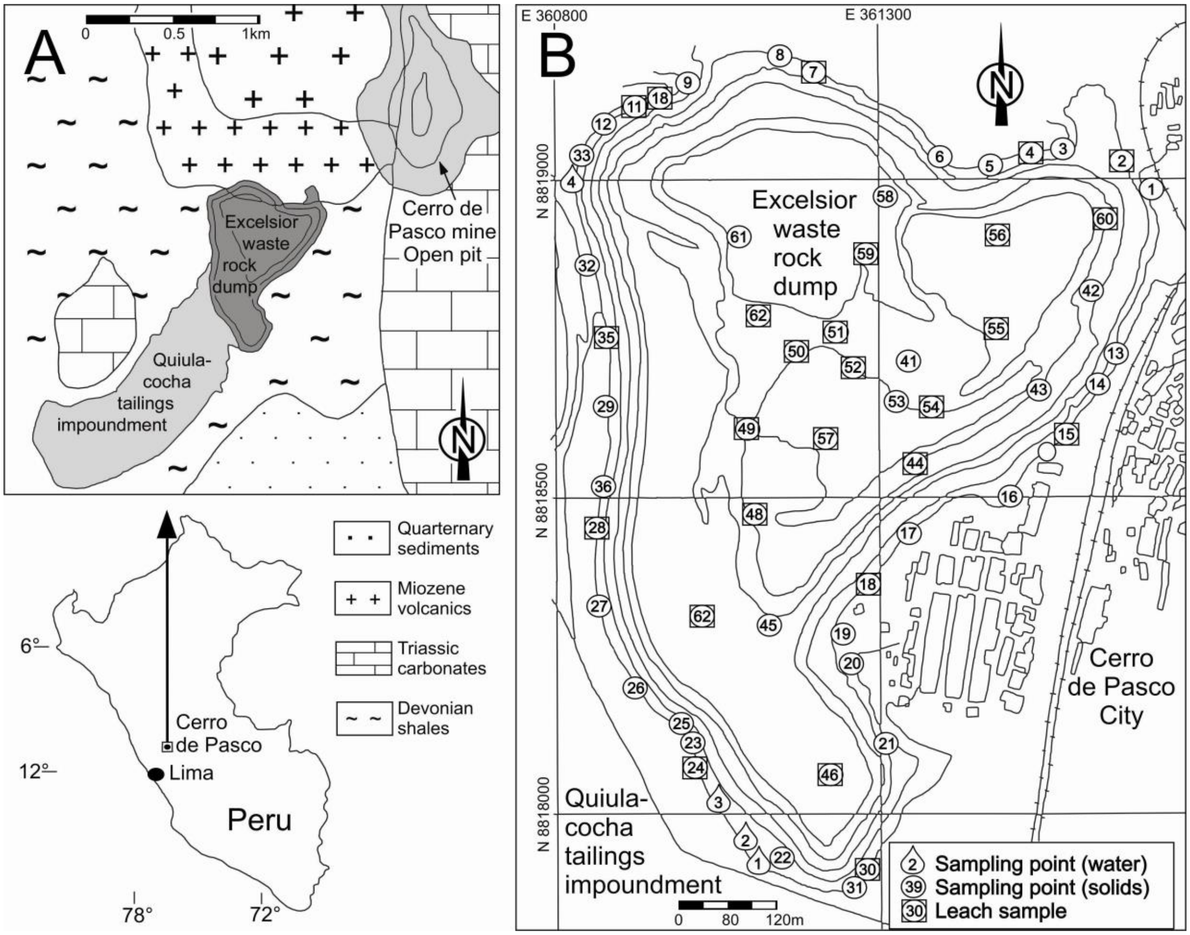

Figure 1: A: Location and geology of the Cerro de Pasco Mine, Peru; B: Overview of the sampled Excelsior waste rock dump

Results and Discussion

The Excelsior waste rock dump had at most parts of the surface an acidic environment with an average paste-pH of 2.8. Gypsum, solid solutions of different jarosite-types, and a variety of Fe-sulfates including melanterite $Fe(SO_4)•7(H_2O)$ and rozenite $Fe(SO_4)•4(H_2O)$ were the dominant secondary minerals. Less frequent secondary minerals were Fe(III)-hydroxides, like schwertmannite $Fe_{16}O_{16}(OH)_{12}(SO_4)_2$ and fibroferrite ($Fe(SO_4)(OH)•5H_2O$), and Mg-, Mn- and Zn-sulfates including starkeyite $Mg(SO_4)•4(H_2O)$, mallardite $Mn(SO_4)•7(H_2O)$, and goslarite $Zn(SO_4)•7(H_2O)$, respectively.

For the elemental constituents of the primary mineral assemblage, XRF data are shown in Table 1. The heavy metals Mn, Cu, Zn, Pb and Cd and the semi-metal As had high average concentrations in the waste rock samples. An enrichment of the heavy metals Mn, Cu, Zn and Cd was observed in efflorescent salt samples. Mn, Zn, and Cd were enriched at the base of the waste rock dump in primary mineral samples as well as in efflorescent salt samples. Arsenic showed enrichment in efflorescent salt samples only at the base of the waste rock dump.

Table 1: Average values ± s.d. of XRF data from solid samples/ ICP-MS data from leachates and water samples from the Excelsior waste rock dump

	Solid samples			
Element (conc.)	**AR (top) samples** (n=17)	**AR (base) samples** (n=32)	**ES (top) samples** (n=5)	**ES (base) samples** (n=12)
Na (wt%)	0.11±0.11	0.22±0.24	0.36±0.21	0.46±0.34
K (wt%)	1.00±0.55	0.99±1.36	0.13±0.28	0.19±0.27
Ca (wt%)	1.37±3.02	3.47±3.30	0.25±0.29	2.64±4.27
Al (wt%)	3.30±1.38	3.14±2.35	0.58±0.81	0.49±0.53
Si (wt%)	13.17±4.89	15.20±7.01	1,31±2.12	1,76±1.98
Mg (wt%)	0.40±0.21	0.92±1.18	1.22±0.80	1.55±1.19
Mn (wt%)	0.23±0.23	0.65±0.74	1.14±0.59	2.73±3.05
Fe (wt%)	18.81±6.61	15.63±8.44	15.25±4.13	13.12±8.67
S (wt%)	7.44±2.81	6.83±4.48	11.99±1.25	11.38±2.45
Cu (wt%)	0.11±0.21	0.08±0.20	1.27±2.36	0.81±2.79
Zn (wt%)	0.87±0.57	1.19±1.13	2.94±1.31	3.40±2.90
Pb (wt%)	1.10±0.82	1.14±2.28	0.10±0.22	0.13±0.18
Cd (mg/kg)	23±15	48±83	77±62	80±88
As (mg/kg)	2030±1433	1205±1052	896±561	2043±3694

	Leachates		Water
Element (conc)	**AR (top) leachates** (n=10)	**AR (base) leachates** (n=9)	**AMD water (CPE-W1)** (Main seep)
Na (mg/L)	7.73±1.67	0.8±1.0	73.8
K (mg/L)	5.94±1.76	2.1±4.3	19.2
Ca (mg/L)	236±178	541±73	411
Al (mg/L)	n.m	n.m.	n.m
Si (mg/L)	n.m	n.m.	n.m.
Mg (mg/L)	77±44	276±330	3158
Mn (mg/L)	107±60	n.m.	2250
Fe (mg/L)	1506±2164	286±454	3685
S (mg/L)	2283±3000	1261±616	8100
Cu (mg/L)	8.83±12.19	6.05±6.77	1.08
Zn (mg/L)	271±397	366±250	1845
Pb (mg/L)	0.27±0.56	0.35±0.73	1.17
Cd (mg/L)	0.86±1.29	2.40±4.69	0.92
As (mg/L)	7.68±10.35	0.08±0.09	2.81

Effects of rain events on the waste rocks were simulated by leach tests of (1) solid samples from the top, representing waste rocks leached by infiltrating rainwater and (2) solid samples from the base, representing rocks affected by AMD generated within the waste rock dump (Table 1). All leachates had acidic pH ranging from 1.2 to 5.6 and high concentrations of Fe, Cu, Zn, Cd, As, and Pb. Most of the secondary efflorescent salts were dissolved producing an average electrical conductivity of 9.7 mS/cm, generating acid, and liberating heavy metals. Leachates from samples from the base of the waste rock dump had lower Fe and As concentrations than leachates from samples from the top. Mineralogical analyses identified in these samples, as secondary minerals, higher amounts of jarosites and Fe(III)-oxyhydroxides including schwertmannite. This suggested that the secondary schwertmannite and jarosites at the base fix high amounts of Fe, coprecipitate As, and partially store these elements within the waste rock dump.

Analyses of the AMD seeps at the base of the waste rock dump generally correlated with the results from the leach tests. The seep waters were chemically similar to the leachates with acidic pH between 2.78 and 5.10, and oxidizing Eh between 319 and 684mV, but had higher concentrations of Fe, Zn, Pb and higher electrical conductivity between 19 and 26 mS/cm.

Conclusions

Pyrite at the Excelsior waste rock dump, estimated to be 60 wt% of the total mineral assemblage, was oxidizing to produce AMD. Carbonates with a capacity of neutralizing AMD were a trace fraction at <5 wt%. The waste rock dump produced AMD rich in Fe, Mn, Cu, Zn, Cd, S, and As. A comparison of data from leach tests with elemental/mineralogical data from waste rock samples suggested that AMD formation was strongly controlled by the local climate.

High evaporation during the dry winter season (Figure 2A) led to the precipitation of secondary efflorescent salts from pore solutions. These secondary minerals were mainly metal sulfates and hydroxides rich in Fe, Mn, Cu, Zn, Cd, and As.

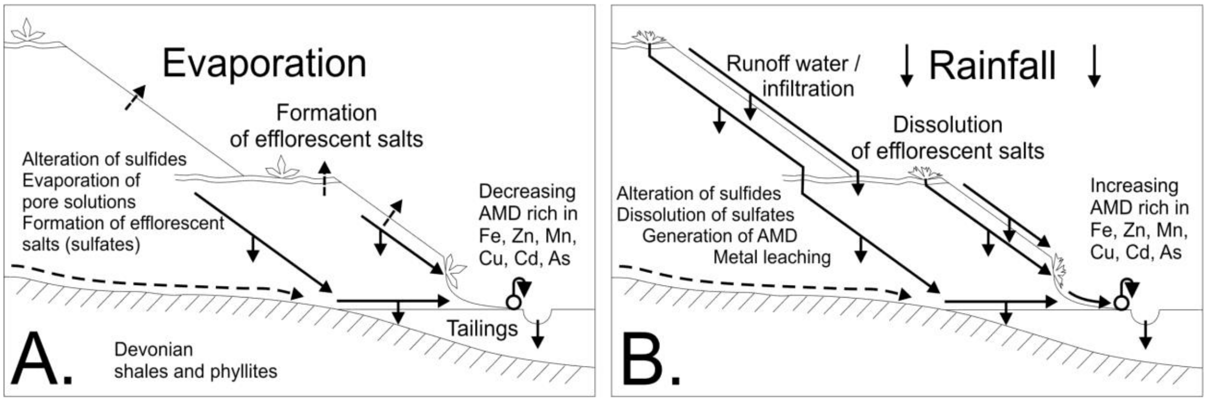

Figure 2: Element transport at the Excelsior waste rock dump. A: during the dry season; B: during the wet season

During the dry season, transport of metal-rich pore solutions from the upper zones of the Excelior waste rock dump to the base resulted in local enrichments of secondary efflorescent salts rich in Fe, Mn, Zn, Cd, S, and As at the base. The absence of a distinct enrichment layer suggested that rain events during the wet summer season (Figure 2B) cause the dissolution of a high portion of the secondary efflorescent salts. These rain events result in a washout of acid solutions rich in the heavy metals Fe, Mn, Zn, Cu, Cd, and the non-metals S and As. Fe and As were partly retained in the waste rock dump due to the precipitation of water-insoluble jarosite and Fe(III)-hydroxides (schwertmannite) and/or coprecipitation/sorption of arsenic with these minerals.

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