Mineralogical and geochemical study of the sulfide-rich Excelsior waste rock dump at the polymetallic Pb-Zn-Ag-Bi-Cu mineralization Cerro de Pasco, Peru

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Abstract

The sulfide-rich Excelsior waste rock dump of the polymetallic Pb-Zn-Ag-Cu mineralization Cerro de Pasco (Central Andes, Peru; elevation 4,300m) is characterized by an excess of acid production potential (60 wt% pyrite, <5 wt% carbonates). The heavy metals Pb and Zn can be found in concentrations up to 12.7 wt% (Pb)/ 4.9 wt% (Zn), Cu, Cd and As as trace elements in concentrations up to 1.1 wt% (Cu), 6020 mg/kg (As) and 381 mg/kg (Cd). Acid mine drainage (AMD) is observed (pH 0.8-7.3). Secondary minerals in form of efflorescent salts were found mainly at the base of the waste dump. X-ray diffraction analyses identify as secondary minerals gypsum, hydronium jarosite, goethite, schwertmannite and metal sulfates (Fe, Zn, Mg, Mn). Cd is found as substituent in metal sulfates, As as co-precipitation with Fe(III) hydroxides. Leach tests confirm high solubility of secondary minerals (sulfates) and acid/element liberation (pH 2.8-4.9/heavy metal concentrations up to 447.1 mg/l for Zn, 16.7 mg/l for Cu, 14.8 mg/l for Cd, 2.3 mg/l for Pb). The climatic variation with an average precipitation of 1,030 mm/a and an average evaporation of 1,100 mm/a suggests that AMD is controlled by precipitation of sulfates in the dry winter season and re-dissolution in the rainy summer season. AMD infiltrates partly into an underlying tailings impoundment, causing further sulfide oxidation and metal leaching

Introduction

In this work the Excelsior waste rock dump of the Cerro de Pasco polymetalic Pb-Zn-Ag-Bi-Cu deposit was investigated (Figure 1a). This system is characterized as sulfide-rich (ca. 60 wt% pyrite), carbonate-poor (<5 wt%) and already AMD-generating.

Pore water and drainage solutions in AMD systems are characterized by acidic pH values and high mineralization (Nordstrom & Alpers, 1999). Heavy metal concentrations in the pore solutions are mainly controlled by their precipitation together with Fe(III) hydroxides and / or sulfates (Gieré et al. 2003). Precipitation and evaporation of water influences strongly formation and dissolution of secondary minerals, especially efforescent salts (Frau, 2000; Dold & Fontboté, 2001). Leach test can help to estimate solubility, acid-generation and element liberation of these secondary minerals (Zhixun, 1996).

With the knowledge of the geochemical processes, different types of waste rock – AMD - systems and their environmental impact can be characterized (Hammarstrom et al., 2003; Herbert, 1999). In this work, this characterization is made for a large, sulfide-rich waste rock dump. Although tailings systems and low-sulfide systems are widely discussed in the literature, less is still known about high-sulfide waste dumps. The hydrological connection between waste rock dumps and tailings impoundments, a in the literature disregarded, but often found situation, is also discussed.

Terminology

For the description of the mineralogy the classification proposed by Jambor (1994) is used. The term 'primary' mineral is used for all minerals originated in the deposit including alteration and weathering products formed prior to emplacing material on the waste rock dump.

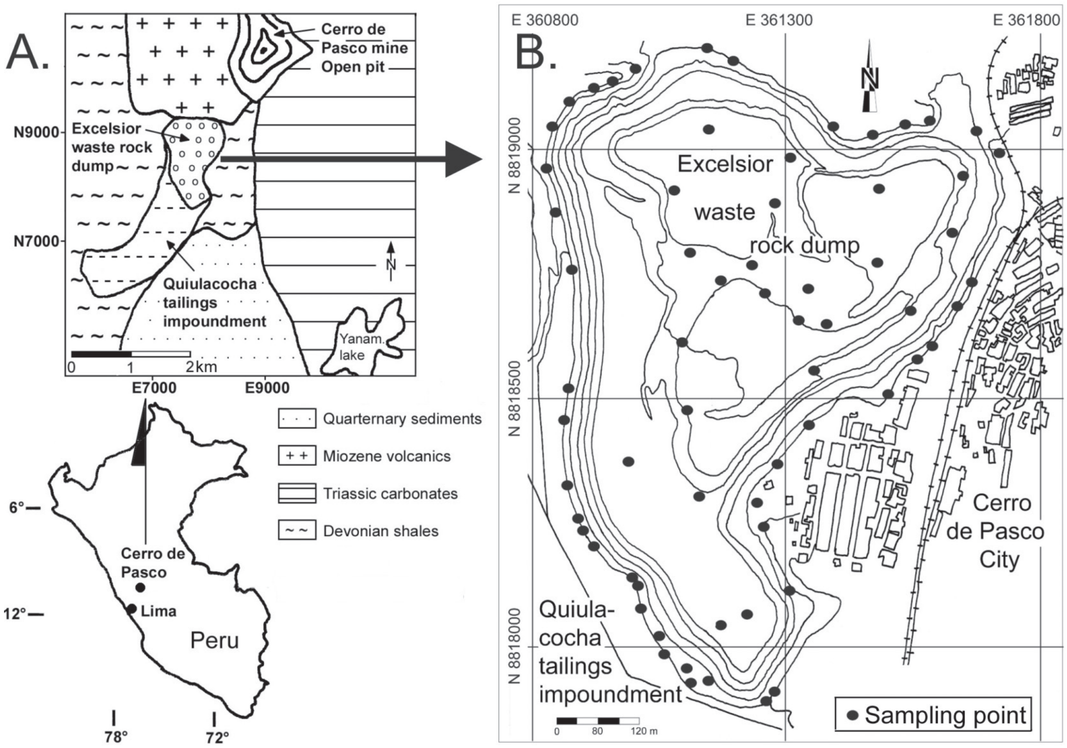

Figure 1, A: Location and geological surrounding of the Cerro de Pasco mine/Peru; B: Overview of the samplesd Excelsior waste rock dump

Description of the Excelsior waste rock dump

The studied site is located in the central Ands at an altitude of 4300 m above sea-level. Local climatic conditions are characterized by dry winter and wet summer seasons with high precipitation (1,030 mm/a) and high evaporation (1,100 mm/a), the average annual temperature is 4.2°C (Cerro de Pasco meteorological station).

The Cerro de Pasco deposit has its origin in a Miocene volcanic and intrusion complex. It consists of a pyrite-quartz replacement body in carbonatic host rock and different sulfidic ore deposition stages (Einaudi, 1977). Main ore minerals are pyrite, massive sphalerite-galena-pyrite and enargite (Baumgartner et al., 2002). Gangue is dominantly quartz and sericite. The host carbonate assemblage is largely controlled by hydrothermal alteration and consists of variable amounts of dolomite ± siderite ± calcite ± sericite ± hematite ± quartz. Devonian red-beds and Miocene volcanic rocks overlay the ore body and his host rock sequence.

The waste rock dump occupies an area of 94 ha with estimated 26,400,000 m^3 broken rocks, partly overlaying (estimated 60 ha) the downstream located Quiulacocha tailings impoundment (Figure 2a). The dump consists of three levels with a maximum height of 55 m, rock sizes are from less than 1 mm up to 2,5 m, the fraction of grains lesser than 2 mm is estimated 10 vol%. Surfaces of the different levels are floored with up to 30 cm pyrite-quartz rocks to prevent heavy mine equipment from getting stuck.

Precipitation follows two main water pathsway, infiltration into the waste dump and surface run-off (Figure 2b). At the southern base of the Excelsior waste rock dump a broad spring zone can be observed.

The main waste rock fraction belongs to the pyrite-quartz body, minor fractions are volcanic quartz monzonite, Permian red-bed sediments and Jurassic carbonates, respectively. The mineral assemblage contains estimated a minimum of 60 wt% sulfides (pyrite) and lesser than 5 wt% carbonates.

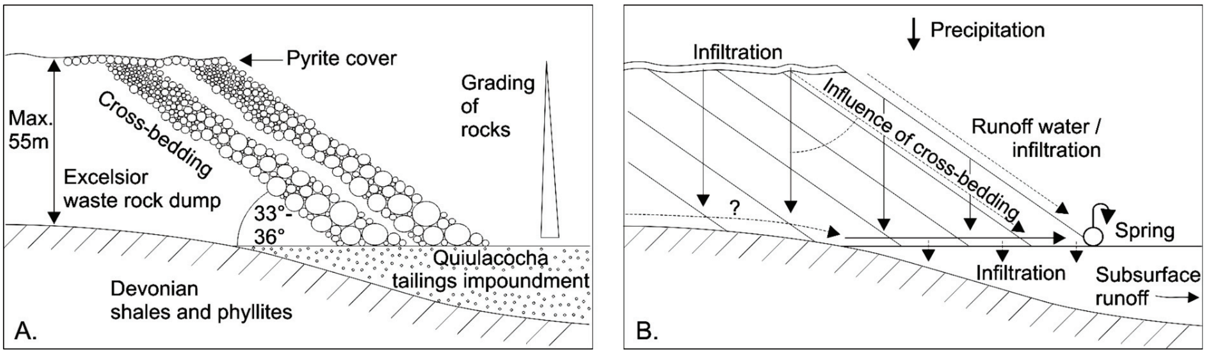

Figure 2, A: Schematic cross-section of the Excelsior waste rock dump B: Main water pathways

Methods

Sampling: 78 solid samples at 66 sampling points were taken during the dry season in 2003 (May to July) and classified as altered rock samples (AR), efflorescent salts (ES) and tailings samples (T). Samples were taken mainly at the base of the waste rock dump, efflorescent salts also at the plateau zones. Of all samples, pH was measured (paste pH according to MEND, 1991; WTW ph-meter). Each sampling point was described (type of rocks around the sampling point, type of sedimentation, colour of sample in the field, description and, when possible, identification of mayor/minor mineral fractions).

All soil samples were air-dried (<35 °C), homogenised by crushing/milling and sealed in polyethylene (PET) bags. ES samples were sealed, when humid, directly in field in PET-sampling bottles to prevent alteration of secondary minerals, e.g. by loosing crystal water.

Geochemical methods: 78 samples were analysed by X-ray fluorescence spectroscopy (XRF). Mayor elements were analysed as melted pellets with wavelength dispersive spectrometer (S4 Pioneer from Bruker axs Company, rhodium tube with 4 kW). Trace elements were measured by energy dispersive XRF (Spectro XLab 2000 from Spectro Company, a palladium tube (3kW), Bragg-polarized Pd-L-X-ray spectrum).

For the leach test procedure the German standard method DIN 38414 (1984) was chosen. 10 samples were analysed taking 10 g of milled sample and 100 ml of deionised water (pH 7). After 24 h of shaking at 100 rpm, the leachates were filtered through 0.45 μm-cellulose-nitrate filters and analysed by ICP-AES (Spectroflame P/M from Spectro A.I. with calibration by ICP multi-element standard solution Merck IV). Conductivity and pH of the leachates were immediately measured. The leached samples were dried at 30°C and weighed to calculate the percentage of soluble phases.

Mineralogical methods: Polished sections and polished thin sections of selected bulk samples were analysed by optical microscopy using crossed light and reflected light.

All samples were analysed as bulk samples by wavelength x-ray diffraction (XRD), using a Siemens D5000 diffractometer with a Cuα anode X-ray tube and a quartz monochromator. ES samples were crushed directly by hand, without drying procedure before, to prevent alteration of minerals. Step scan settings were 3-70° 2θ, 2-s count time at 0.05 degree steps. Peak interpretation was made by using the program Eva as part of DIFFRAC AT suite.

The poorly crystalline Fe(III) hydroxide schwertmannite was detected by differential X-ray diffraction (DXRD) as described by Dold (2003). The diffractometer settings were 0.05° 2θ step size and 20s counting time per step. The samples were treated in darkness with 0.2 M ammonium oxalate at pH 3, for 15 min (after Dold, 2003). Scans were measured before and after treatment. The treated scans were intensity corrected and then subtracted from the untreated scan.

Results and discussion

Mineralogical results

Alteration of primary rocks and minerals. Four types of primary rocks can be found at the Excelsior waste rock dump, an overview over these rock types and their alteration characteristics give Table 1.

Table 1: AMD-relevant characteristics of rock types at the Excelsior waste rock dump

Rock type	Miocene Quartz-pyrite / ore body	Miocene Quartz monzonite / tuff	Permian Red-bed sediments	Triassic-Jurassic Carbonates
Acid producing minerals	Pyrite, Zn sulfides	Pyrite		
Acid consuming minerals		Albite		Dolomite
Fraction of acid producing/consuming minerals	ca. 60 wt%	ca. 10 wt% (pyrite) < 5 wt% (albite)		<5 wt%
Alteration degree (estimated in field)	Low (<20 vol%)	Very high (>95 vol%)		High (>50 vol%)
Liberated elements (mayor fraction)	Fe, Zn, Cu, Cd, S	Fe, S	Fe	Ca, Mg
Liberated elements (minor fraction)	Pb, As	K, Na, Ca		
Secondary minerals	Gypsum, hydronium jarosite, metal sulfates, Fe(III) hydroxides	Gypsum, hyronian jarosite, kaolinite, Fe sulfates, Fe(III) hydroxides		Gypsum, Mg sulfates

Rocks from the main waste rock source pyrite-quartz body are characterized by slow oxidation of sulfides. Different alteration of small pyrite grains (up to 2 mm) is observed in thin sections. Nearly intact, idiomorphic pyrite crystals can be found beside pyrite relicts with high alteration (>95 vol%). Coarser pyrite grains (up to 0.7 cm) show alteration rims of different thickness (up to 1.5 mm), consisting of microcrystalline Fe(III) hydroxides. Beside the above-mentioned minerals, quartz was identified as major phase of this waste rock type, ore minerals (sphalerite, tennantite, anglesite, cerussite, galena, coronadite) as minor and trace phases.

Volcanic rocks, the second source of waste rocks, are already completely decomposed into acidic (paste pH 1.3-2.6), white, loose material with grain sizes of some mm. Primary mineral fractions of these rocks are quartz (ca. 15 vol%) and altered relicts of albite $NaAlSi_3O_8$ (ca. 5 vol%). The unaltered volcanic rocks can contain up to 15 wt% disseminated pyrite. This pyrite content is in volcanic rocks at Excelsior strongly altered and represents <1 vol% of total mineral assemblage; Agglomerates of microcrystalline Fe(III) hydroxides, sericite and gypsum are the mayor fraction (>50 vol%) in form of loose matrix. The pyrite content oxidize rapidly due to the small size of the pyrite crystals (<1mm) and the high porosity of this rock type producing a strongly acidic/Fe(III)-rich environment. This suggests that the volcanic rocks act as initial producers of acids after deposition at the waste rock dump, with the capability to liberate ferrous iron, which causes further alteration of metal sulfides.

The third rock type carbonatic sediments from the host rock formation appear as minor fraction (<5 wt%); carbonates with neutralising capacity still exist in small amounts at the surface, often close to oxidizing pyrite. Due to rapid infiltration of precipitation and high evaporation rates acidic solutions cannot react with these carbonates. Inside the Excelsior waste dump, due to the water flow/pore water carbonates are assumed as mostly dissolved.

Continental Devonian red-bed sediments as fourth rock type (10-15 wt%) show no alteration, their mayor compounds quartz and hematite are relatively stable also under the acidic environment of AMD.

Low soluble secondary minerals: The secondary minerals hydronium jarosite $(H_3O)Fe_3(SO_4)_2(OH)_6$ and less abundant K-jarosite $KFe_3(SO_4)_2(OH)_6$ are observed in most AR samples. Identification of hydronium jarosite can result from similar X-ray pattern of solid solution of K and Na-jarosite as pointed by Dutrizac and Jambor (2000). However, the small amount of feldspars and other K/Na-bearing minerals in the Excelsior waste rock dump resulting in low availability of K and Na may trigger the formation of hydronium jarosite instead of the thermodynamically more favoured K and Na jarosite.

Some AR samples were collected at superficial water paths. They are characterised by the already described primary mineral content of the AR samples, small gain sizes (<1mm) and a high content of secondary goethite/Fe(III) hydroxides (up to 60 vol%). Fe(III) hydroxides appear as light yellow up to nearly opaque agglomerates. In crossed polarized light they show light dark brown colours. For some samples a clear identification by XRD was not possible. 4 samples with high content of these ’poorly crystalline Fe(III) hydroxides' were selected for analyses by DXRD. In three samples a clear identification of schwertmannite $Fe_{16}O_{16}(OH)_{12}(SO_4)_2$ was possible.

Soluble secondary minerals: Gypsum and hydrated heavy metal sulfates are the most important phases in pure secondary mineralization samples, many samples consists only of these minerals. The most abundant heavy metal sulfates are Fe-sulfates with different water content (melanterite $FeSO_4{\bullet}7H_2O$, romerite $Fe_3(SO_4)_4{\bullet}14H_2O$, less frequent siderolite $FeSO_4{\bullet}5H_2O$, fibroferrit $Fe(SO_4)(OH){\bullet}5H_2O$, szomolnokite $FeSO_4{\bullet}H_2O$, copiapite $FeFe_4(SO_4)_6(OH)_2{\bullet}20H_2O$), followed by Mg-sulfates (epsomite $MgSO_4{\bullet}7H_2O$, starkeyite $MgSO_4{\bullet}4H_2O$, kieserite $MgSO_4{\bullet}H_2O$). Beside these minerals, Zn-sulfates (goslarite $ZnSO_4{\bullet}7H_2O$, gunningite $ZnSO_4{\bullet}2H_2O$, changoite $Na_2Zn(SO_4)_2{\bullet}4H_2O$) and Mn-sulfates (mallardite $MnSO_4{\bullet}7H_2O$) can be found in few samples.

Gypsum can be found in two different types; the first type is characterized by crystals with sizes between 0.05 and 0.4mm with irregular shapes and marginal intergrowth with microcrystalline Fe(III) hydroxides. To the second type belong very small idiomorphic crystals at the boundary to submicroscopical size, possibly resulting from fresh precipitation from pore water in field and tertiary mineralization during the drying process.

Geochemical results

Main element concentrations: Si, Fe and S from the pyrite-quartz body dominate the element composition of the AR samples (Figure 3a). The other primary mineral sources, Permian red-bed sediments and Tertiary volcanic rocks, consists also mainly of these elements. Fe and S are strongly enriched in the ES samples (Figure 3b), forming Fe(III) hydroxides and water-bearing Fe-sulfates. Silicon in ES samples results mainly from impureness of these samples (primary silicate fraction in efflorescent salt crust). Aluminium in AR samples has its origin in sericite from the ore host rock and altered volcanic rocks. Significant Al concentration in ES samples is only found in samples with high Si concentrations, therefore high Al concentrations are mainly related with primary silicates. The high percentage of ignition loss in all samples, also in samples without carbonates, indicates already high secondary mineral content (water rich sulfates and Fe(III) hydroxides). Ca and Mg both as primary minerals (carbonates) as well as resultant secondary minerals (gypsum, Mg sulfates) reach locally concentrations over 10 wt%.

The high variance of all element concentrations in AR samples represents the heterogeneity of the Excelsior waste rock dump with tits random storage of the different types of waste rocks.

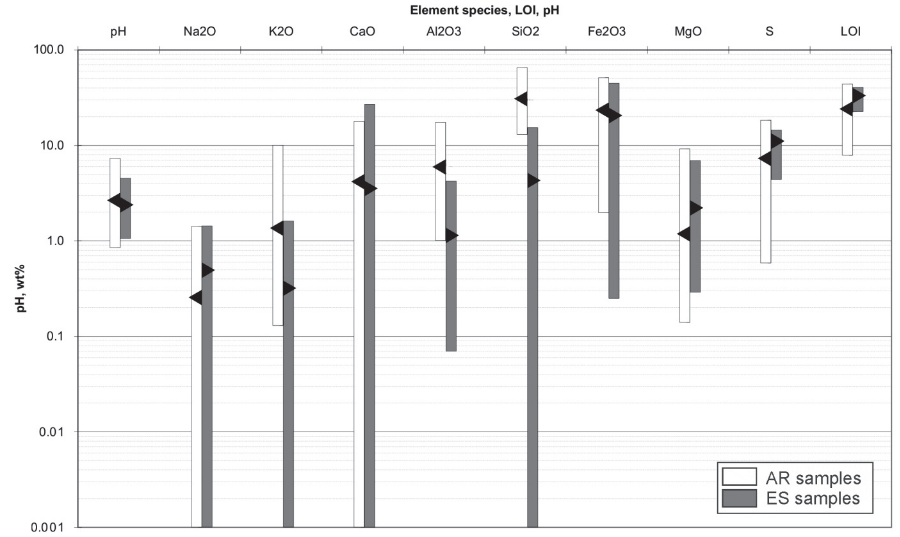

Figure 3: XRF analyses of AR and ES samples: Maximum, minimum and average concentration of selected element species, LOI and pH

Element concentrations vary in ES samples also extremely. Water flow over long distances in the waste rock dump, for example in the case of horizontal water pathways, can homogenize element concentrations and should result in similar precipitation of efflorescent salts at the water outcrop. This is not the case, but quite vice versa, precipitation of secondary minerals at the base of the waste dump is highly heterogeneous in its element concentration and depends strongly on local primary mineral assemblage. This suggests that water in the upper dump body does not cover long horizontal distances. Main direction is vertical infiltration with uncertain influence by the cross-bedding. At the base of the waste dump the grain size change. Springs at the SW limits of Excelsior suggest that the subjacent tailings impoundment retards infiltration by its fine material causing a water-saturated layer at the base of the Excelsior waste rock dump. However, infiltration into the underlying tailings impoundment seems to take place on a significant scale, data from Wade (2005) suggest that an acid plume (pH 4.7 in deeper zones) from Excelsior is entering into the downstream-located Quiulacocha tailings impoundment. Thus, this tailings system and the Excelsior waste rock dump are by this infiltration pathway hydrologically connected (Figure 2b).

Heavy metal and As enrichment: To show more specific results of transport and enrichment of the environmentally critical elements Cu, Zn, Pb, As and Cd from the ore, metal concentrations are compared with focus on the relationship between AR and ES category (Table 2). The tailings impoundment is discussed as possible zone of enrichment for metals coming from Excelsior, more detailed investigations are can be found in Wade (2005).

Table 2: Maximum, minimum and average element concentrations of AR, ES and T samples

Element	**AR samples**			**ES sample**			**T samples**		
	Max.	*Min.*	*Av.*	*Max.*	*Min.*	*Av.*	*Max.*	*Min.*	*Av.*
Cu (wt%)	1.12	0.00	0.10	10.10	0.00	0.83	0.11	0.01	0.05
Zn (wt%)	4.93	0.03	1.11	8.50	0.09	2.87	4.67	0.27	1.58
Pb (wt%)	12.66	0.01	1.16	0.65	0.00	0.14	1.29	0.12	0.60
Cd (mg/kg)	381	3	40	300	0	71	153	8	47
As (mg/kg)	6020	74	1503	19330	6	2652	15777	653	6095

Copper: The Cu average concentration (0.10 wt%) in AS samples is relatively low, due to the low copper concentration in the main ore body. Enrichment (factor 8.3) in efflorescent salts is observed, resulting from high mobility of Cu. With 0.05 mean wt% T samples have the half of the waste dump Cu concentration; dissolved Copper is transported without enrichment in the oxidised surface layer as it can be seen in other tailings impoundments with high evaporation rates (e.g. Dold and Fontboté, 2001). The climatic conditions with high precipitation and resultant transport into deeper zones inhibit a stable enrichment of secondary Cu-bearing minerals (efflorescent salts). In contrast, at positions protected against rainfall by overhangs of the slope, conditions for formation of highly water-soluble secondary minerals are given and the concentration of Cu can reach maximum values of 10 wt%. Cu minerals are not identified by XRD; Cu is substituting metals in other sulfates, mainly melanterite, as also described from other sites, e.g. by Jambor et al. (2000).

Zinc: The primary mineral assemblage of the waste dump has high average concentrations of Zn minerals (sphalerite and marmatite (Zn, Fe)S from the ore body). Enrichment processes for Zn can be observed in the secondary mineralization. The high Zn concentration in the oxidised layer of the tailings in comparison with the AR samples results from the concentration of Zn-minerals in the processed ore rocks. In the secondary mineralization (located at the base of the Excelsior waste dump, mainly) Zn is enriched (factor 2.6) in form of efflorescent salts especially at overhangs at the base of Excelsior (protection against dissolution by rain).

Lead: The lead concentration in the Excelsior waste rock dump is mainly due to the appearance of the ore sulfide mineral galena PbS and its alteration product anglesite $PbSO_4$. Comparing the concentrations, the T samples have half the Pb concentration of the average AR samples; this concentration has its origin in the not extractable Pb mineral fraction after flotation. In the secondary mineralization zones (mainly the base of the waste rock dump), the Pb average concentration is almost ten times lower than the value of Pb in the AR samples. The low concentrations in the ES samples in comparison to the concentrations of Cu and Zn, which has similar average values like Pb in AR samples, show the low solubility of anglesite (Glynn, 2000) in the Excelsior waste rock dump.

Cadmium: Cd occurs as substituent in sulfide minerals of the ore body, e.g. in sphalerite. Tailings samples have nearly the same average Cd concentration as the waste rock dump. The Cd average concentration in the ES samples shows enrichment (factor 1.8); Cd concentration in secondary minerals can vary strongly. The concentrations and variation rates indicate high solubility of secondary Cd-bearing minerals/ weak adsorption and high mobility of Cd. Hence, enrichment appears at places which are protected against rain (overhangs).

Arsenic: Sources for As at the Excelsior waste rock dump are mainly the sulfide minerals arsenopyrite FeAsS from the Pb-Zn ore body and enargite Cu_3AsS_4 / luzonite Cu_3AsS_4 from the Cu-Ag ore body and veins, but also realgar As_4S_4 and orpiment As_2S_3, which are part of the supergene mineral assemblage of the Cerro de Pasco mine. Samples of the T category have a four times higher As average concentration than AR samples. The processed Pb-Zn-ore rocks with their arsenopyrite content (Einaudi, 1977) as source of the tailings waste material cause partly these higher values. Further enrichment processes in the oxidized zone of the tailings impoundment are assumed, especially in secondary Fe(III) hydroxides. Various investigations confirm As adsorption in this mineral group in oxidized zones of tailings impoundments (e.g. Dold and Fontboté, 2001). The values of the ES samples show also an enrichment of As, indicating the mobility of As. The enrichment is not as high as it can be observed in the tailings impoundment. A reason for this fact can be, that Fe(III) hydroxides, e.g. schwertmannite, which act as strong scavenger for As, are not found in efflorescent salts (ES samples).

Leach tests

Leach analyses are focused on As and metals, derived from the dissolution of primary and secondary phases of the Excelsior waste dump.

9 AR samples were chosen for leaching test. Only one sample of pure efflorescent salts was analysed to investigate the solubility difference between AR and ES samples. The element concentrations of the leachates are compared with the spring water results.

All leachates had acidic pH values after 24 hours stirring in a range between 5.6 and 2.7 for the AR samples, and 2.5 for the ES sample. Leachates are highly mineralized (conductivity between 2408 and 9701 µS/cm for AR samples, 21120 µS/cm for the ES sample. Both sample types shows that secondary mineralization can be easily solved. The soluble fraction of the leached AR samples represents between 3.3 wt% and 27.4 wt%, of the ES sample 37.4 wt%. Main fractions of the solved minerals are metal sulfates, producing a high conductivity in the leachates.

Element concentrations of leachates: The analyses of solved elements in leachates of AR samples show high average concentrations for the heavy metals as well as for Ca, Mg and Al (Figure 4). Element concentrations vary strongly, so the here presented data show the range of solubility and demonstrate the possible mobilization of different elements during rain events.

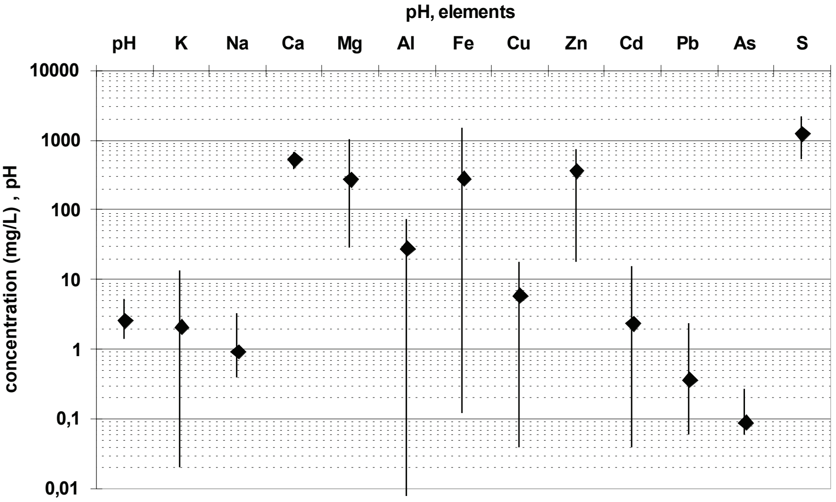

Figure 4: ICP-AES results of leachates (AR samples): Maximum, minimum and average concentrations of selected elements

Ca and Mg show high concentrations in the leachates, representing strong solubility of secondary gypsum and Mg-sulfates (e.g. starkeyite, $MgSO_4 \cdot 4H_2O$). Dissolution of the primary mineral dolomite can be considered as a second main source for Ca and Mg due to the low pH values of the leachates. However, the narrow range of the Ca concentration for samples both with dolomite as without dolomite content suggests that the secondary minerals are the main Ca/Mg source.

The high iron concentration (average concentration 286 mg/L) can, especially when infiltrating into the underlying tailings impoundment, react with sulfides and acidify the underground water flow. Cu and Zn show concentrations in the leachates demonstrate, that in comparison with the Cu and Zn concentration of the samples lesser than one third of Cu and Zn is soluble (average soluble fraction for Cu: 13.8 wt%; for Zn: 32.1 wt%). The not oxidized sulfide fraction is an explication of this observation.

Different solubility and mobilization of Cd, Pb and As is observed in the Excelsior waste rock. Pb and As are less soluble (average soluble fraction Pb: 0.3 wt%; As: 6.3 wt%), Pb due to the low solubility of anglesite, As due to the strong fixation on Fe(III) hydroxides. Cd shows a higher solubility with average percentage of the soluble fraction of 31.1 wt%. Not leachable Cd is assumed as still fixed in sulfides.

Conclusion

At the Excelsior waste rock dump Fe sulfides (pyrite) from two different sources (pyrite-quartz body/vulcanites) are present as acid producer in high concentration (estimated 60 wt% of the total mineral assemblage). Heavy metal-bearing (Zn, Pb) sulfides from the ore body also can be found in concentrations up to more than 1 wt%. Minerals with capacity of AMD-neutralization (carbonates, albite) are only minor or trace fractions (<5 wt%). The other main mineral fractions quartz and stable Fe oxides have no influence on the acid production/consumption balance. Table 3 gives an overview over the AMD-relevant characteristics of the different rock types.

Alteration already takes place to an increasing degree. Pore water is acidified in contact with the altered waste rocks (average paste pH 2.8), dissolving primary minerals and leaching heavy metals (Fe, Zn, Cu, Cd). Especially the already strong altered volcanic rocks with originally high pyrite concentrations (up to 15 wt%), which is in field observed as already strong oxidized (> 95 vol%), produce on a large scale AMD and liberates Fe(III), which causes further sulfide alteration even under anoxic conditions. The heavy metals Zn, Cu, Cd (as cations), the metals Ca, Mg, Fe (as cations) and the anion SO_4 are in the waste dump system mobile. Arsenic is retarded in the system by Fe(III) hydroxides. The mobility of Pb is limited by the low solubility of anglesite.

High evaporation (1,100mm/a) concentrates pore solutions at the Excelsior waste rock dump up to oversaturation and successive precipitation of efflorescent metal salts. At the base of the Excelsior waste dump, formation of secondary gypsum, goethite, schwertmannite and Fe sulpfates as well as minor amounts of Mg, Zn and Mn sulfates can be observed.

The metal sulfates are highly water-soluble and liberate acid and metals in high concentration during rain events. The local climatic conditions with dry and wet season result in a precipitation-solution rhythm with “shock events” with high metal and acid output during the wet season. These high mineralized, acid solutions are conducted to superficial outcrops at the base of the waste rock dump where they enter superficially the Quiulacocha tailings system. A second water pathway exists via direct infiltration from the waste rock dump into the underlying parts of the Quiulacocha tailings impoundment. Effects of infiltration from the Excelsior waste dump to the Quiulacocha tailings impoundment are already clearly notable (acid plume, pH 4.7).

Due to the high acid potential by oxidizing pyrite and the low neutralization potential a long-term AMD potential for the Excelsior waste rock dump must be assumed.

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References

JAMBOR, J. L., NORDSTROM, D. K., ALPERS, C. N., 2000. Metal-sulfates Salts from Sulfate Mineral Oxidation. In: ALPERS, C. N., JAMBOR, J. L., NORDSTROM, D. K.. Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance. Washington, D.C., Mineralogical Society of America, pp. 277-301.

BAUMGARTNER, R., FONTBOTÉ, L., JOBIN, Y., 2002. Carbonate hosted zinc-lead high-sulfidation mineralization at the Cerro de Pasco deposit, Peru. Abstract volume, XI Congres Peruano de Geologia, Resúmenes: pp. 75.

DIN38414, 1984. DIN 38414 Teil 4, Deutsche Einheitsverfahren zur Wasser-, Abwasser und Schlammuntersuchung, Schlamm und Sedimente (Gruppe S), Bestimmung der Eluierbarkeit mit Wasser (S 4). Berlin, Beuth Verlag.

DOLD, B., FONTBOTÉ, L., 2001. Element cycling and secondary mineralogy in porphyry copper tailings as a function of climate, primary mineralogy, and mineral processing. Journal of Geochemical Exploration 74 (Special Issue:geochemical studies of mining and the environment), pp. 3-55.

DOLD, B., 2003. Dissolution kinetics of schwertmannite and ferrihydrite in oxidized mine samples and their detection by differential X-ray diffraction (DXRD). Applied Geochemistry, v. 18, pp. 1531-1540

DUTRIZAC, J.E., JAMBOR, J.L., 2000. Jarosites and their application in hydrometallurgy. In: Alpers, C.N., Jambor, J.L.,Nordstrom, D.K.. Sulfate Minerals: Crystallography, Geochemistry & Environmental Significance. Reviews in Mineralogy & Geochemistry, 40, pp. 405-452.

EINAUDI, M., 1977. Environment of Ore Deposition at Cerro de Pasco, Peru. Economic Geology 72, pp. 893-924.

FRAU, F., 2000. The formation-dissolution-precipitation cycle of melanterite at the abandoned pyrite mine of Genna Luas in Sardinia, Italy: environmental implications. Min. Magazine, vol. 64, no. 6, pp. 995-1006.

GLYNN, P., 2000. Solid-Solution Solubilities and Thermodynamics: Sulfates, Carbonates and Halides. In: ALPERS, C. N., JAMBOR, J. L., NORDSTROM, D. K., 2000. Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance. Washington, D.C., Mineralogical Society of America, pp. 481-511.

HAMMARSTROM, J.M., PIATAK, N.M., SEAL, II; R.R., BRIGGS, P.H., MEIER, A.L., MUZIK, T.L., 2003. Geochemical Characteristics of TP3 Mine Wastes at the Elizabeth Copper Mine Superfund Site, Orange County, Vermont. Open-File Report 03-431, v. 1.0, U.S. Geological Survey

HERBERT, R.B., 1999. Sulfide oxidation in mine waste deposits: A review with emphasis on dysoxic weathering, MiMi report 1999, pp. 1., ISSN 1403-9478, ISBN 91-89350-06-5.

JAMBOR, J. L., 1994. Mineralogy of Sulfide-rich Tailings and Their Oxidation products. In: Environmental Geochemistry of Sulfide Mine-wastes, Mineralogical Association of Canada Short Course Vol. 22., pp. 59-102.

MEND, MINE ENVIRONMENT NEUTRAL DRAINAGE PROGRAM, 1991. Acid rock drainage prediction manual, report 1.16.1b. Ottawa, CANMET, Department of Natural Recources, Canada.

NORDSTROM, D.K. AND ALPERS, C.N., 1999. Geochemistry of acid mine waste. In: Plumlee, G. S. and Logsdon, M.J. (Eds.), Reviews in Economic Geology, The environmental geochemistry of ore deposits. Part A: Processes, techniques, and health issues, v. 6A, pp. 133-160.

WADE, C., 2005. Mineralogical and geochemical study of tailings from Cerro de Pasco (Peru). Diploma Thesis, University of Geneva, Geneva.

ZHIXUN, L., 1996. Leachate chemistry and precipitates mineralogy of rudolfsgruvan mine waste rock dump in central Sweden. Water Science and Technology, Vol. 33, No 6, pp. 163–171.