

THE PAILAVIRI TAILINGS DEPOSIT, POTOSÍ, BOLIVIA: EXTREME ACID ROCK DRAINAGE GENERATION¹

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Abstract: The historic mining center of Cerro Rico de Potosí, Bolivia is marked with many tailing piles, with the Pailaviri tailings deposit being of great concern. These polymetallic sulfide tailings release some of the highest concentrations of ecotoxic metals observed in natural waters. In order to obtain a deeper understanding of the deposit, water samples were taken in transects throughout the deposit. Total metal concentrations in the waters were extremes: Al (25-2.9 g/L), As (1700-330 mg/L), Cu (850-140 mg/L), Fe (100-24 g/L), Mn (110-70 mg/L), Pb (36-21 mg/L), and Zn (3.1-1.9 g/L). Dissolved concentrations were essentially equivalent indicating these metals were in aqueous phase. Sulfate ranged from 136 to 400 g/L. Due to the extremely acidic nature of the water, the pH probes quickly degraded and became inoperable, rendering accurate pH measurements impossible. These results provided evidence of highly toxic conditions and likely downstream impacts due to close proximity of Rio Huayna Mayu. The extremely elevated concentrations of metals indicate that the Pailaviri deposit may be reprocessed at a profit and safely disposed of, an option which should be investigated.

Additional Key words: mine waste, acid rock drainage, metals, acidity, tailings

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Introduction

Potosí, Bolivia has a rich history of mining that can be traced back to the 15th century. The processing of ores via flotation or gravimetric methods has created tens of millions of tonnes of tailings deposits in the immediate vicinity of the city. The Pailaviri tailings deposit is one of the most conspicuous piles in the region, as it lies only tens of meters from highly populated areas of the city (population approximately 150,000). Nearly four million tonnes of mine waste has been accumulated on the Pailaviri tailings according to Corporación Minera de Bolivia (COMIBOL).

The Pailaviri deposit occupies a large tract on the northern slope of Cerro Rico (Fig. 1). The tailings consist of materials that were left over from the gravimetric separation for Sn, of which the concentrate was smelted approximately 15 km to the northeast of Potosí at the La Palca smelter (Cunningham et al., 1996). The Pailaviri deposit accrued tailings from 1975 until 1985, when the international Sn market crashed. The pile was created using a belt driven conveyer and bulldozers. When the conveyer had too much tailings piled underneath it, a bulldozer would then push the pile to the edges, growing the deposit outward and downward over time. As a result, oldest layers are towards the bottom and center, with the newest at the top and sides of the pile.



Figure 1: Cerro Rico and the Pailaviri tailings pile in Potosí, Bolivia

Pailaviri is less than 40 m from a few dwellings at the edge of Potosí and less than 150 m from densely populated neighborhoods. The top of the deposit is frequently transited by ore trucks and other vehicles transporting mine workers. In addition, the pile is tracked by numerous pathways that local workers take to walk to work. The Pailaviri pile is within the Huayna Mayu watershed, which is located along the north slope of Cerro Rico. The water from this stream is highly contaminated from active and abandoned mining operations (Strosnider et al., 2011). The runoff from the Pailaviri deposit is a contribution of the highly elevated ecotoxic metal concentrations in this river. Metals and metalloids such as Al, As, Cd, Zn, Pb and others can be toxic to flora and fauna. The elevated concentrations of these metals are of primary concern due to the dense populations of humans nearby that are at risk from exposure to highly contaminated water and the possibility of inhalation/ingestion of windblown dust from the pile.

Cerro Rico de Potosi was created by volcanic eruptions of the Neogene period intruding through an Ordovician base of shales and slates (Cunningham et al., 1996; Aranibar and Mancilla, 2003). It lies within a Neogene-Quaternary volcanic-plutonic complex stretching for approximately 800 km along the Eastern Cordillera of the Andes (Zartman and Cunningham, 1995; Kamenov et al., 2002). The lithologic units that comprise the Cerro Rico formation include the Pailaviri conglomerate, Venus breccias, Caracoles tuff, and Cerro Rico dacite dome, from the bottom to the top, respectively (Cunningham et al., 1996). The Pailaviri unit contains a breccias conglomerate with shale, quartzite and igneous rocks (Evans, 1940; Cunningham et al., 1996). The ore veins throughout Cerro Rico are primarily encased in pyrite and polymetallic sulfides, which are the “fuel” for acid rock drainage.

Tailings piles in Potosí have been sparsely studied (Strosnider et al., 2011; Kossoff et al., 2008, 2011, 2012) and no research has yet been done to study the weathering of the Pailaviri tailings deposit on Cerro Rico. The purpose of this research was to characterize the acid rock drainage (ARD) flowing from the Pailaviri tailings deposit. From the water samples analyzed and results from comparable ARD sites it can be presumed that the Pailaviri deposit contains some of the most extreme ARD characteristics encountered in the world today.

Methods

Study Area

The Pailaviri tailings pile is on the north slope of Cerro Rico near several abandoned and active mines, including the Pailaviri mine. The runoff and leachate discharges from the deposit drain into the Rio Huayna Mayu, which transports stormwater, wastewater, acid mine drainage (AMD), ARD, and ore processing effluent to the Rio de La Ribera de Vera Cruz. The Rio de La Ribera forms the Rio Tarapaya, a key branch of the upper Rio Pilcomayo, a crucial South American water resource for agricultural irrigation.

Water samples were collected from the tailings deposit (Fig. 2). The water samples were labeled PTWB, PTW1, and PTW2. PTWB was a small terminal pool near the former location of the conveyor belt that dumped the tailings onto the pile. PTW1 was another small terminal pool near a frequently used path where miners walk to and from the mines. PTW2 was a flowing discharge (flow rate approximated at 0.01 L/s) about 1 m wide at the toe of the pile, just a few meters from several work areas.

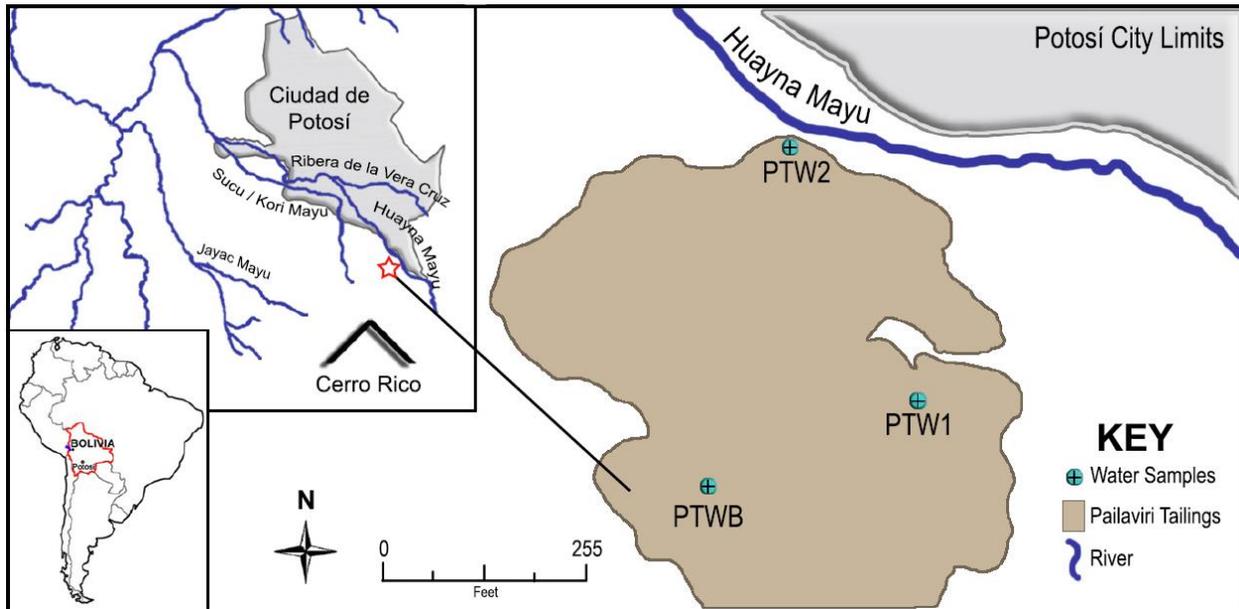


Figure 2: Pailaviri tailings deposit sample location map

Data Collection

The water samples were collected in the beginning of the dry season in May 2011. No sign of precipitation was observed during sample collection. Each sampling location was recorded using a Garmin GPS unit (Fig. 3).



Figure 3: Photos of water sampling locations along the Pailaviri tailings deposit, from left to right: PTWB (roughly 4 m in average diameter), PTW1 (roughly 3 m in average diameter), and PTW2 (taken at an elevated angle from atop Pailaviri) sample sites.

A Hach® Sension 156 meter was used to obtain specific conductivity, pH, and temperature readings. The instrument was calibrated by performing a pH 4, 7, and 10, 1413 $\mu\text{S}/\text{cm}$ specific conductivity, and 100% dissolved oxygen calibration. A pH standard of 1.68 was used as a lower-end pH check. Sulfate, dissolved metals and total metals samples were collected using 60-mL HDPE bottles. All grab samples were analyzed in the University of Oklahoma Center for Restoration of Ecosystems and Watersheds (CREW) laboratories. The anion samples were stored at 4°C until filtered through 0.2 μm nylon filters and Dionex OnGuard II H cartridges. Total metal samples were stored at 4°C until microwave acid digestion. Dissolved metal samples were collected using 0.45 μm nylon filters and then preserved with concentrated nitric acid and stored at 4°C until microwave acid digestion. All microwave acid digestions followed USEPA method 3015. Processed metal samples were analyzed via a Varian Vista-Pro® simultaneous inductively coupled plasma-optical emission spectrometer following USEPA method 6010. A MetrOhm® 761 ion chromatograph unit was used to quantify sulfate concentrations following USEPA method 300. Duplicate or triplicate measurements of metal concentrations and field readings were randomly obtained for quality assurance and control following USEPA methods.

Results and Discussion

Physiochemical measurements were obtained for each location (Table 1). Due to the extremely acidic nature of the water, the pH probes quickly degraded and became inoperable, rendering accurate measurements impossible. Previous research by Strosnider et al. (2011) with

different equipment estimated a pH of 0.9 during the rainy season of March 2007. Due to the similarities in metal and SO_4^{2-} concentrations to other extreme mine waters with negative pH (e.g., Iron Mountain studied by Nordstrom et al. (2000)), it is likely that some of the waters of Pailaviri may have much lower pH values, the measurement of which would require more durable probes and specially prepared sulfuric acid standards for calibration. Strosnider et al. (2011) recorded a specific conductivity of 54.6 mS/cm, which is much higher than this study's range of 33.4-23.0 mS/cm. The sampling time and location could cause this strong difference between the specific conductivity values. The Strosnider et al. (2011) sampling location, 4T, was directly west of PTW2 at a flowing discharge near the edge of the pile.

Table 1: Pailaviri water physiochemical parameter measurements with comparison to previous measurements (4T) by Strosnider et al. (2011).

	Avg. Temperature °C	pH s.u.	Specific Conductivity mS/cm
PTWB	17.5	1*	25.6
PTW1	19.9	0*	23.0
PTW2	13.9	No Result*	33.4
4T	8.9	0.90 ⁺	54.6

*No accurate pH measurements obtained because extreme conditions rapidly degraded probe.

⁺ Value is suspect due to the extreme pH.

As seen in Tables 2 and 3, metal concentrations were extremely elevated at each location. Sulfate concentrations were 140, 400, and 370 g/L for PTWB, PTW1, and PTW2, respectively. Total and dissolved metal concentrations were within the expected variability inherent in the 1:10,000 dilutions necessary for quantifying metals concentrations, indicating that metals in the samples were essentially all dissolved. From the metal and sulfate concentrations in waters leaching from the tailings deposit, it was clear that Pailaviri produces an extreme case of ARD (Younger et al., 2002; Watzlaf et al., 2004). Other sites that present similar elevated metal concentrations are Iron Mountain in California, Iron Duke mine in Zimbabwe, and Peña de Hierro in Spain (Nordstrom et al., 2000; Williams and Smith, 2000; Romero et al., 2011). These three sites exhibit some of the most ideal geological settings for ARD production in the world. The similarity of the waters produced indicates that the Pailaviri tailings deposit may provide similar conditions.

Table 2. Total metal concentrations in mg/L for water samples in comparison to previous measurements (4T) by Strosnider et al. (2011) data (n=1).

	Al	As	Cd	Cu	Fe	Mn	Pb	Zn
PTWB	2900	580	12	140	43000	100	21	1900
PTW1	25000	1700	31	850	100000	70	36	3000
PTW2	14000	330	18	470	24000	110	25	3100
4T	7500	890	17	310	73000	96	25	1700

Table 3. Dissolved metal concentrations in mg/L for water samples in comparison to previous measurements (4T) by Strosnider et al. (2011) data (n=1)

	Al	As	Cd	Cu	Fe	Mn	Pb	Zn
PTWB	3300	570	12	140	44000	100	20	2100
PTW1	23000	1800	28	930	90000	65	36	3200
PTW2	14000	310	20	450	26000	120	24	2800
4T	7400	820	15	300	71000	92	26	1600

The metal concentrations measured for PTWB and PTW1 were possibly the result of evapoconcentration (e.g., Nordstrom, 2008) because they were terminal ponds. If this is the case, more extreme concentrations may be noted at the end of the dry season (August-September). Due to the seasonal climate of Potosí, it is likely that a perched water table within the pile fluctuates markedly during the year. The oscillation of the water table could encourage the oxidation of metal sulfides as the water table rises in the rainy season to wet substrate with low-pH waters and subsequently exposes them to oxygen as the water table falls in the dry season (e.g., Strosnider et al., 2011). Soluble metal sulfate salts such as melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) could be deposited as the water table falls during the drier periods and then dissolve as the water table rises, concentrating aqueous metals and sulfate within the pile over time (e.g., Koffi et al., 2003).

Although relatively little research has been performed on the Pailaviri tailings deposit, it can be concluded that the site produces some of the most extreme ARD in the world. The elevated metal concentrations prove the tailings deposit to be a contributor of ecotoxic metals, as well as a potential risk to the people of Potosí. However, it is possible that these tailings could be reprocessed economically and then safely disposed, as have other metal sulfide tailings deposits

which generate much less extreme waters (e.g., Benn and Cornell, 1993; Boulet and Larocque, 1998; Blight, 2011) and therefore should have had lower concentrations of reclaimable metals than Pailaviri. With metal prices currently increasing it is more feasible to first reprocess the tailings before safe disposal (InfoMine Inc., 2012). As an example, a tailings deposit in the geologically-similar mining district of Oruro, Bolivia is being reprocessed as low grade silver ore using chloride leaching (Kappes, 2002). More intensive study is needed to determine the anthropogenic circumstances that create these extreme waters and the feasibility of mineral reprocessing.

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