PRELIMINARY EVALUATION OF LIMESTONE-BASED PASSIVE TREATMENT SYSTEMS FOR LOW-pH ACID MINE DRAINAGE IN ANDEAN BOLIVIA[1]

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Abstract. An Anoxic Limestone Drain (ALD) and Open Limestone Channel (OLC) are primary components of the Project for the Restoration of Rio Juckucha, in Potosí, Bolivia; the goal of which is to improve water quality for irrigation use in the high Andes. The OLC is treating low-pH (2.9) acid mine drainage from a man-made alpine lake receiving discharges from portals, tailings, and waste-rock from active and abandoned mining operations. The ALD is treating milder acid mine drainage (pH 5.4) from an abandoned mine portal. Both systems treat waters that run to Laguna Santa Catalina, which forms the headwaters of Rio Juckucha, a key irrigation water resource. The alkalinity generation and metals removal performance of the recently-constructed ALD and partially-constructed OLC was investigated to determine early-stage treatment characteristics. The results indicated that the OLC at 20% completion was having relatively little impact. The recently-constructed ALD is showing water quality improvements (higher pH and alkalinity). However, there is a concern with increased Zn and Mn concentrations in the ALD effluent. Studies will continue upon construction completion to determine long term performance.

Additional Key Words: watershed, acidity, mining, conductivity, acid rock drainage, agriculture.

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Introduction

The communities of La Lava, Kantuyo, and Okoruro in the Southern Bolivian Andes have been impacted by centuries of mining for Ag, Pb, Zn and Sn without environmental controls. Currently the primary metal mined in the area is Sn. The population of the region is Approximately 8,500 people live near Rio Juckucha in the aforementioned communities. These communities are affected by the elevated concentrations of metals present in the water, soils, and produce. These primarily indigenous communities are made up of miners, engineers, mine owners, farmers, llama and cattle herders, as well as the commuting workers from the nearby city of Potosí.

Rio Juckucha sits within a valley in which mining has occurred since the colonial period over five centuries ago and perhaps before that time (Fig. 1). Mining continues today and acid mine drainage (AMD) from abandoned and active underground mines join acid rock drainage (ARD) from mineral processing tailings, ore piles, and waste rock to severely degrade the surface waters of the valley. Two small man-made lakes, Khomer Khocha ("Green Lake" in Quechua, an indigenous language of the Andes) and Muyu Khocha ("Round Lake" in Quechua), drain to Laguna Santa Catalina via two ephemeral streams, Rio Khomer Khocha and Rio Muyu Khocha, respectively. Khomer Khocha receives AMD from upgradient ore piles and waste rock, as well as AMD from several active and abandoned mines. Muyu Khocha receives AMD from waste rock piles that ring its northern shore as well as the discharge of a large abandoned mine.

The Rio Juckucha watershed lies in an alpine setting approximately 3,000-5,000 m above mean sea level on the western slope of the Bolivian Cordillera Oriental. The watershed is considered desert, with a highly seasonal average yearly precipitation of 41 cm, the bulk of which (98%) falls from September to April (BSNMH, 2003). The soils of highland Bolivia are immature, thin, and of poor quality due to nitrogen, organic matter, and moisture deficits (LeBaron et al., 1979; Guillet, 1987; Baied and Wheeler, 1993; Brenner et al., 2001). Agriculture in the region would be difficult under the best of circumstances, but is rendered yet more daunting by the lack of appropriate water resources.

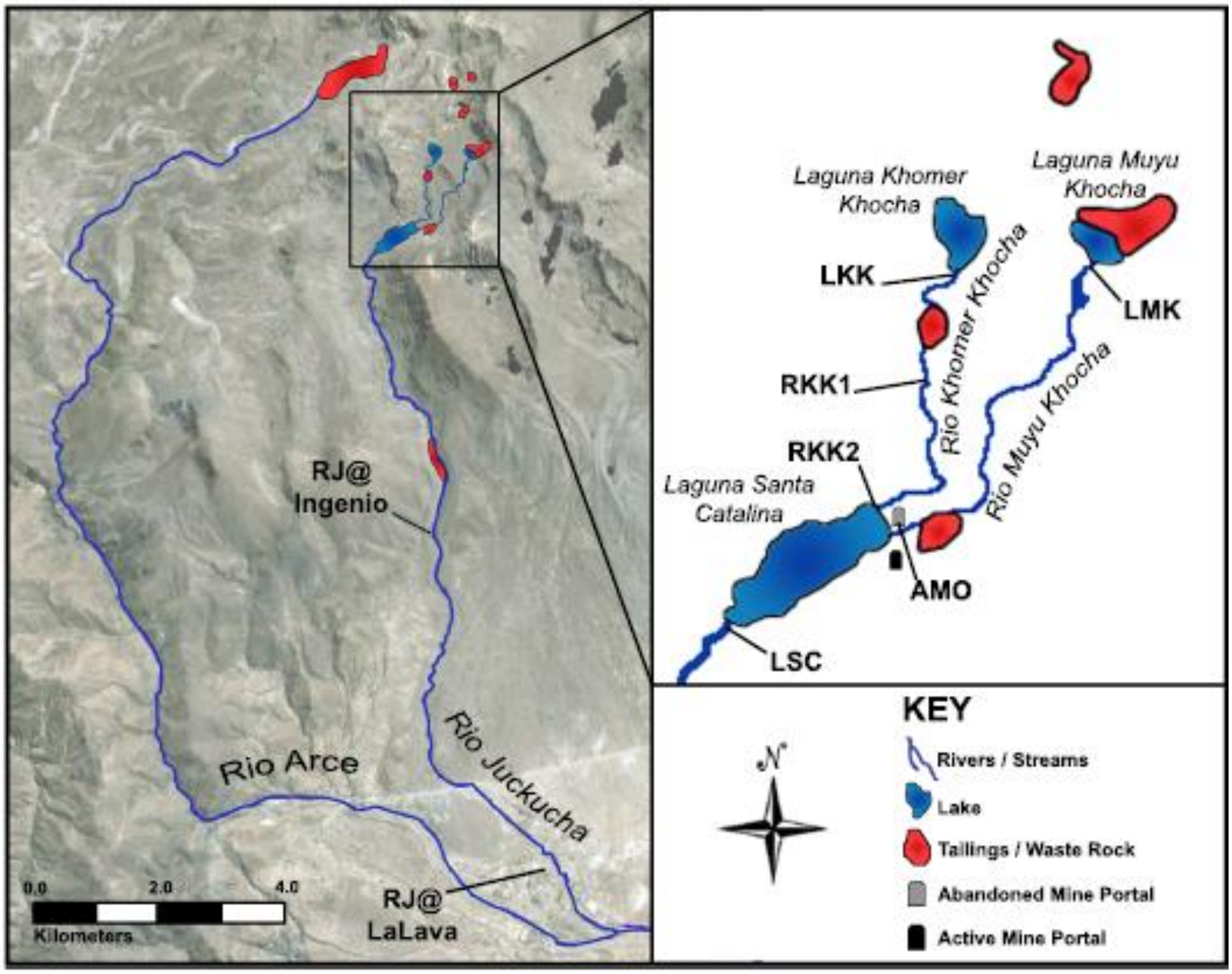

Figure 1: The Rio Juckucha watershed with sampling sites shown.

The contamination of Rio Juckucha by historic and ongoing mining operations has polluted downstream soils and agricultural produce. Garrido et al. (2009) found that Al, As, Cd, Co, Cu, Fe, Mn, Ni, and Zn concentrations in Rio Juckucha exceeded United Nations Food and Agriculture Organization standards for agricultural use. As a likely consequence, agricultural soils irrigated with waters from Rio Juckucha had Cd and Zn concentrations that exceeded agricultural soil guidelines (Garrido et al., 2009). Garrido et al. (2009) also found that potatoes grown with irrigation water from Rio Juckucha exceeded numerous food health guidelines for Cd, Pb, and Zn concentrations. Despite these concerns, Rio Juckucha is still regularly used for irrigation and local crops are consumed by growers or sold elsewhere. Local residents understand to some degree that their irrigation water sources are contaminated, but continue to use them due to the severity of water shortages in the region.

Project Plan

The Project for the Restoration of Rio Juckucha was initiated in 2008 with the goal to improve the water quality of Laguna Santa Catalina and Rio Juckucha to make them safe for irrigation use. The Project is a multinational, public-private collaboration between Rotary International, Empresa Minera Agricola Kumurana, the University of Oklahoma, Universidad Autónoma de "Tomás Frías", Engineers In Action, Pennsylvania State University College of Medicine, the local communities, the Prefecture of Potosí, Cardinal Engineering, and Saint Francis University. There are four primary objectives of the project: 1) the design and construction of an active treatment system for AMD emanating from an operating mine and mine tailings, 2) the removal and ex-situ reprocessing of polymetallic sulfide tailings, 3) the design and construction of two open limestone channels (OLCs) to improve streams flowing from low pH lakes into Laguna Santa Catalina, 4) the design and construction of an ALD to treat AMD from an abandoned mine. The following study describes the preliminary performance of initiatives 3 and 4.

All accessible lengths of Rio Khomer Khocha and Rio Muyu Khocha with significant bed slope were chosen for OLC installation. To ascertain the feasibility of this approach, samples of the limestone to be used were exposed to the waters from each respective lake in 1-L cubitainers and agitated on a shaker table at 5-minute intervals, with pH taken at each interval. The pH was brought to above 6 with both waters at the 5-minute mark, which was about a third of the residence time calculated for an average rain event in this climate. A previous study also indicated that local limestone could be employed to generate relatively high alkalinities when exposed to local AMD (Strosnider and Nairn, 2010). Residence time was calculated dividing the distance by the flow found by manipulating Manning's equation. The variables were found by evaluating the slope of the channels from survey data, hydraulic radius from the high-water mark noted in the topographic survey, and a coefficient of roughness from Sturm (2001). The OLCs were designed for rainy season conditions because that is when the vast majority of water will pass through them. Also, the high-intensity flows of the rainy season are necessary to take advantage of all faces of the limestone and provide scouring and stone movement necessary to provide optimal unarmored limestone for dissolution. The OLC design necessitated 1,895 tons of limestone. The size of the limestone varied from about 10 to 80 cm in diameter. Limestone of 80-95% $CaCO_3$ (supplier claims were verified with analysis at the Laboratorio Químico del

Instituto de Investigaciones Geológicas at the Universidad Mayor de San Andrés) was trucked from quarries approximately 40 km away and then placed into the channels with heavy equipment and by volunteer laborers from the local community as well as undergraduate students from the University of Oklahoma and Saint Francis University. At the time of this study, only approximately 20% of the OLC in Rio Khomer Khocha had been installed and no portion of the OLC in Rio Muyu Khocha had been installed.

Due to the paucity of data available, the ALD was sized conservatively. Dry season flows in 2008 were measured at 0.15 L/s. Since a neighboring active mine was reported to only have a small (~20%) increase in wet-season flows, it was determined that a very liberal safety factor of 5 was utilized to provide sufficient contact time in the ALD. To determine the amount of limestone necessary, the amount needed for 20 h of contact time at dry season flow was determined and then multiplied by the safety factor. The 20 h contact time guidance was taken from Watzlaf et al. (2004). The design necessitated 165 tonnes of limestone. The size of the limestone varied from approximately 10 to 80 cm in diameter and 80-95% $CaCO_3$. That limestone was hand-placed by contractors within the mine portal and then a reinforced concrete seal was installed with piping extending through it below grade to guard from freezing. At the time of this study, the ALD had been in sealed for approximately three weeks.

Methods

A properly calibrated Hach SensIon 156 meter and probers were used to measure pH, dissolved oxygen, and specific conductivity. Alkalinity titrations were conducted in accordance with standard methods (APHA, 1998) and Hach Method 8203 (Hach, 2002). These field readings as well as samples for anion, dissolved metal, and total metal analyses were taken from the watershed at multiple sampling points noted on Fig. 1 and described in Table 1.

Table 1. Water sampling locations as identified on Figure 1.

LMK - Lake Muyu Khocha Outlet
LKK - Lake Khomer Kocha Outlet
RKK1 - Rio Khomer Kocha (In the approximate middle of the river's length)
RKK2- Rio Khomer Kocha (at the river's end)
LSC - Laguna Santa Catalina
RJ – Rio Juckucha
RJ@Ingenio - Rio Juckucha just downstream of the ore processing plant
RJ@LaLava - Rio Juckucha in the town of La Lava

Anions and total and dissolved metals samples from each location were collected in 60-mL HDPE bottles, prepared for shipment to the University of Oklahoma Center for Restoration of Ecosystems and Watersheds (CREW) laboratories, and stored at 4°C upon arrival until processing. According to United States EPA method 3015 the samples were microwave acid digested. Total metal samples were analyzed via a Varian Vista-Pro® simultaneous inductively coupled plasma optical emission spectrometer following EPA method 6010. Anion samples were stored at 4°C were filtered with Dionex OnGuard® II H cartridges and 0.22 µm nylon filters as were the dissolved metals samples. Anion concentrations were determined with a MetrOhm® 761 compact ion chromatograph unit following EPA method 300.

Results and Discussion

Preliminary results of the treatment systems were mixed (Tables 2-4). The limited amount of OLC installed did not appear to be making a difference on water quality as metal concentrations did not decrease. The similarity between total and dissolved metal concentrations across all sampling locations indicated that the metals were primarily in the more bioavailable aqueous phase. The pH changed from 3.00 to 3.28 to 3.25 as waters traveled downstream from LKK to RKK1 to RKK2, respectively. The ongoing hydrolysis of iron, and resultant proton liberation, was overwhelming the proton neutralization from the carbonate alkalinity generated by limestone dissolution. However, the ALD was generating alkalinity just weeks after its completion.

Table 2. Total metal concentrations upstream to downstream.

All concentrations in mg/L

Location	**Al**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
LMK	6.2	<0.022	0.14	0.015	0.003	0.58	1.46	4.2	0.022	1.6	43.0
LKK	11.0	0.25	0.22	0.065	0.013	2.6	24	4.9	0.042	0.24	71.0
RKK1	22.0	0.056	0.23	0.12	0.003	2.3	27	12.0	0.074	0.17	104.0
RKK2	14.0	0.026	0.11	0.03	0.03	1.1	8.5	7.9	0.059	0.11	60.0
LSC	9.9	<0.022	0.086	0.05	0.006	1.1	3.8	4.5	0.042	0.14	33.0
RJ@Ingenio	27.0	0.12	0.12	0.34	0.057	5.6	420	13.0	0.24	0.20	64.0
RJ@LaLava	18.0	<0.022	0.098	0.21	0.006	5.0	38	7.4	0.12	0.067	33.0

Table 3. Dissolved metal concentrations upstream to downstream.

All concentrations in mg/L

Location	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
LMK	6.68	<0.022	0.13	0.018	<0.001	0.64	1.04	4.1	0.019	1.5	45.0
LKK	12.0	0.19	0.23	0.065	0.006	2.8	24.0	4.8	0.042	0.22	73.0
RKK1	24.0	0.054	0.22	0.12	0.003	2.4	26.0	11.0	0.07	0.18	104.0
RKK2	14.0	<0.022	0.10	0.073	0.011	1.2	8.3	7.6	0.05	0.11	59.0
LSC	11.0	<0.022	0.082	0.061	0.004	1.18	3.9	4.4	0.041	0.15	33.0
RJ@Ingenio	30.0	0.082	0.14	0.33	0.009	6.05	401	13.0	0.22	0.19	64.0
RJ@LaLava	18.0	<0.022	0.092	0.19	0.008	5.30	32.0	7.1	0.11	0.06	33.0

Table 4. ALD water quality impacts in the sealed abandoned mine. All metal/metalloid total and dissolved metal concentrations are in mg/L.

Sample Date	Al	As	Cd	Fe	Mn	Pb	Zn	pH	Alkalinity (mg/L as $CaCO_3$)
May-09* Total	0.021	0.025	0.002	3.10	0.838	0.039	1.41	5.4	0
Dissolved	0.012	<0.022	0.002	1.99	0.815	0.017	1.32		
May-11** Total	0.07	<0.022	0.007	0.99	6.4	0.036	9.3	7.3	47
Dissolved	0.17	<0.022	0.006	0.975	6.11	<0.012	8.92		

*Open Mine, pre-ALD
**Sealed Mine, post-ALD

The elevated concentrations of dissolved and total metals at RJ@Ingenio, especially Fe and Zn, is likely due to the impact of mineral processing effluent, tailings, and inadequately treated AMD from ongoing mining operations. It may be assumed that metal concentrations are decreased at RJ@LaLava due to natural attenuation. The pH decreased along this reach from 2.98 to 2.70, likely due to the hydrolysis of Fe, which stains the channel deep red.

The preliminary performance of the ALD was promising. Table 4 shows the change in the total metal concentrations, pH and alkalinity of the abandoned mine outflow before (2009) and after (2011) it was sealed an ALD. The pH and alkalinity increased (Table 4). Of primary importance, dissolved oxygen (DO) was 0.34 mg/L flowing from the ALD, indicating that the mine seal was sufficient as guidelines are <1 mg/L (Watzlaf et al., 2004).

However, an increase in Zn and Mn was noted in Table 4 and is possibly due to dissolution of Zn and Mn-solids in the limestone or a change in the water chemistry within the mine from the flooding of workings. Potentially, the solubilization of salts on the walls may be the cause of this water chemistry change. The water chemistry may have changed temporarily due to the wetting of new surfaces and dissolution of associated soluble salts. Long-term data collection is necessary to determine and project the performance of this ALD. Further research could include analyzing samples of the limestone used in the abandoned mine. These data may directly point to the source of the elevated levels of Zn and Mn in the outflow. Additionally, water samples and readings have been and are being taken at the site to produce monitoring data as OLD construction reaches completion.

Conclusions

The Rio Juckucha watershed is at the beginning stages of remediation from centuries of mining without environmental controls. Preliminary data suggest some minor water quality improvements; however, much construction and data collection remains to be done. Further progress should result in the removal of dissolved and total metals from Rio Juckucha to make it suitable for agricultural use. After construction is complete, robust data collection is necessary to examine the sustainability of this passive approach to Bolivian communities, government authorities, and private entities. Passive treatment of mine water has not yet been applied successfully in Bolivia; therefore it must be proven through demonstration projects to allow greater adoption.

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