Evaluation of Lag Times for Tailings in Extreme Arid Climates by Long-Term and Delayed-Rinse Kinetic Tests

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ABSTRACT

For operations and closure planning, understanding lag times to the potential development of acidic conditions is critical for management of a tailing storage facility (TSF). While this is important for many mines, for the site presented herein (and similar projects) the climatic and hydraulic conditions expected for TSFs in the extreme arid climate of the Atacama Desert present specific challenges for prediction of lag times to acidic conditions and subsequent metals leaching.

Long term humidity cell testing (up to 151 total cycles) was undertaken for several fractions of pilot plant tailings for a copper porphyry deposit. Modified humidity cell tests were also utilized with weekly cycles of humid and dry air and rinses every 20 cycles. The delayed rinse cells were used to provide insight for conditions where wetting of tailings will occur very infrequently following deposition.

Tailings evaluated had total sulfur contents near 1.0% and low neutralization potential. While predicted to be acid generating by static testing, extended lag times were observed. Long term humidity cell testing indicated a lag time of 40 cycles to significant acid generation and a slow process of acidification (reaching stable final pH values near 2.5 took almost 115 cycles). Metals leaching, as expected, increased with acidic conditions. The delayed rinse cells indicated longer lag times to acidification and reduced loading rates for key metals.

Evaluation of the potential development and timing of onset of acidic conditions in the TSF considered the results of the long-term and delayed-rinse testing, pre- and post-testing mineralogy, as well as the hydraulic conditions expected in the TSF under the extreme climate conditions. These include: high evaporation rates, salt migration, and hardpan formation. This paper describes the test work, results, and how the results were used to guide design efforts for both operations and closure planning.

Keywords: Closure planning, arid climate, humidity cell lag time, prediction

INTRODUCTION

While mine wastes may be predicted to be potentially acid generating (PAG), the lag time to the generation of acidic conditions in the field has important implications for mine and closure planning. The lag time may dictate how the material may be handled, stored, or treated prior to acidification. Understanding lag times, and the factors that affect them, is critical in order to effectively design, operate, and prepare for closure of a mine. There are a number of factors that may affect a lag time, including geochemical factors (such as sulfide content, sulfide mineral availability and morphology, secondary mineral coating, available neutralization potential) and physical factors (such as exposure time, grain size and surface area, and moisture content).

Understanding the timing to the onset of acidic conditions is important for facility design, operation, and closure because once acidic conditions are initiated they can persist over the long term. Acidic conditions may require a spectrum of water management practices, water treatment needs, or mitigation strategies, all of which may also evolve with time from operations to closure. For tailings storage facilities (TSFs), these measures may include: seepage capture systems, water treatment facilities, water management for run-on and runoff, amendments, and closure covers. Implementation of these strategies is generally more costly and difficult to perform without preparation or in a retroactive fashion; therefore, it is important to understand these needs as early as possible in the design of a TSF (INAP 2009).

For tailings, the overall dynamics for acid generation are generally well understood. Highest oxidation generally occurs shortly after tailings deposition ends (Blowes et al. 2003). Oxidation rates are generally the highest at the initiation of oxidation and the majority of acid generation occurs during the early stages of acid generation (e.g., MEND 1997). Oxidation occurs at the surface of the TSF and an oxidation front typically progresses downward from the TSF surface. This process results in a profile that includes an upper oxidized zone where sulfides have oxidized, an oxidation zone, where oxidation is occurring, and an un-oxidized layer underneath (e.g., Blowes et al. 2003). The location of an actual acidic front within this profile is dependent on the infiltration rates and the balance of acid generation versus neutralization potential. The acidic front will either remain within the upper zones of the profile or be carried downward by infiltration and, if it overwhelms the neutralization potential below, acidic seepage can result.

The depth and development of the oxidation profile and acidic front is dependent on a range of factors, such as the tailings' acid-base characteristics, saturation state, oxygen diffusion, and age of the facility. Saturation state of the tailings is considered a key parameter for tailings facilities, as higher saturation will restrict oxygen entry, limit oxidation, and subsequently control the development and location of acidic conditions.

In the Atacama Desert, the saturation state of the tailings is an important parameter for consideration of the generation of acidic conditions. The Atacama Desert is one of the driest places in the world with annual average precipitation under 15 millimeters (mm) for an average year and on the order of 100 millimeters per year for a 100 year return period. Coupled with this, evaporation is high, with an annual average evaporation near 2500 mm per year. In addition, precipitation is infrequent with many successive years registering zero precipitation. When precipitation does occur it is typically concentrated in one larger event. The extreme arid climate will affect geochemical and hydraulic factors of the oxidation profile and warrant consideration in the design, management, and closure planning for TSFs in arid climates.

As a part of permitting and design of a TSF in the Atacama Desert for development of a copper porphyry deposit, a kinetic testing program was undertaken for several fractions of pilot plant tailings. The kinetic testing program included long-term (up to 151 cycles) humidity cells and modified humidity cells with extended time between rinse cycles. The objective of the modified humidity cells was to evaluate the lag time under dry conditions with infrequent wetting and rinsing, as found at the climate of the site. The testing program was designed to meet both permitting requirements and informational needs to provide inputs to engineering design, operations planning, and closure planning activities.

METHODOLOGY

Three tailings samples were included in the kinetic testing program, including whole tailings, underflow tailings, and overflow tailings. The whole tailings sample represents materials from a process plant mill that will then be cycloned to produce the overflow (two stages, combined for this sample) and underflow materials. The underflow sample represents the sands that will be used to build the dam for the TSF. A combination of whole tailings and overflow tailings are planned to be placed in the TSF. All tailings samples were produced by a metallurgical pilot plant.

A standard and complete static testing program (e.g., INAP 2009, MEND 2009) was performed on all tailings samples, including acid base accounting (ABA), mineralogy by x-ray diffraction (XRD) with Rietveld refinement, elemental content, grain-size distribution, net acid generation testing (NAG), and short term leach testing. Pertinent ABA and mineralogy results are provided in Tables 1 and 2, respectively. All tailings have moderate amounts of sulfur (0.78 to 1.1 wt. %) and are estimated to be potentially acid generating (PAG) from the results of both ABA and NAG testing (using criteria presented in INAP (2009) and MEND (2009)). These results are confirmed by the mineralogical testing that indicates moderate pyrite content (between 1.3 and 2.0 %) and limited minerals with neutralization potential.

Kinetic testing was performed utilizing two types of humidity cells. The first was based on the standard humidity cell test (ASTM D5744-07), utilizing standard cycles of humid air and dry air during a week, followed by a week-end leach. However, these humidity cells were run for extended periods, including 60, 130, and 151 cycles for the overflow, underflow, and whole tailings samples, respectively.

The second test was a modified humidity cell, referred to herein as a delayed humidity cell. In this test, the standard procedure was modified so that that leach cycle was performed every 20 cycles rather than weekly. The weekly dry and wet air cycles were still performed. Delayed humidity cells were performed for two samples, the whole tailings and the underflow tailings. Delayed humidity cells were run for 80 cycles and were leached 4 times during the testing period.

At the termination of the humidity cell tests, splits from the humidity cells were tested for post-testing ABA and mineralogy (Tables 1 and 2, respectively). Post-testing ABA results indicate a depletion of sulfides and neutralization potential during kinetic testing. Post-testing mineralogical results indicate depletion of sulfides and the presence of reaction products such as jarosite and gibbsite, as expected. This is also consistent with post-testing ABA results as well. An increase in carbonates (calcite and ankerite) was detected in the post-testing XRD analysis, inconsistent with both the expected depletion and the ABA results; this result is considered likely due to heterogeneous materials.

Table 1 ABA results

Parameter	Units	Whole		Overflow		Underflow	
		Pre	Post(1)	Pre	Post(1)	Pre	Post(1)
Paste pH	s. u.	8.2	3.7	8.0	5.1	8.3	6.1
Total S	wt.%	1.04	0.44	0.86	0.77	0.78	0.73
Sulfide-S	wt.%	0.99	0.27	0.77	0.65	0.69	0.60
TIC	% CO_2	0.02	<0.01	0.03	<0.01	0.01	<0.01
NAG pH	s. u.	2.7	--	2.9	--	2.9	--
NP	kg $CaCO_3$/ton	4.8	<0.1	4.9	1.3	3.4	2.0
CO3-NP	kg $CaCO_3$/ton	0.50	<0.8	0.70	<0.8	0.20	<0.8
NNP	kg $CaCO_3$/ton	-26.1	-7.94	-19.2	-19.0	-18.2	-16.8
NPR	--	0.16	0.06	0.20	0.06	0.16	0.11

(1) Post-testing results shown for standard humidity cell sample.
(2) NNP and NPR based on standard NP and AP calculated from sulfide sulfur.

Table 2 XRD results

Mineral	Ideal Formula	Weight Percent					
		Whole		Overflow		Underflow	
		Pre	Post(1)	Pre	Post(1)	Pre	Post(1)
Quartz	SiO_2	34.6	31.5	32.9	28.6	41.4	36.4
Chlorite/Clinochlore	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$	2.5	7.1	2.5	6.9	1.5	4.4
Muscovite	$KAl_2AlSi_3O_{10}(OH)_2$	16.0	15.7	18.2	17.7	11.6	13.2
Biotite/Phlogopite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	4.4	4.9	4.4	5.9	3.2	5.2
K-Feldspar	$KAlSi_3O_8$	17.8	16.4	17.6	14.8	18.5	15.7
Plagioclase/Albite	$NaAlSi_3O_8$ – $CaAl_2Si_2O_8$	20.8	20.2	21.6	19.6	21.0	19.5
Pyrite	FeS_2	2.0	0.3	1.6	1.1	1.3	0.7
Chalcopyrite	$CuFeS_2$	0.5	--	--	--	--	--
Magnetite	Fe_3O_4	0.3	--	--	--	0.2 (2)	--
Halite	NaCl	0.5(3)	0.2(3)	--	--	--	--
Rutile	TiO_2	0.7	--	0.6	--	0.5	--
Calcite	$CaCO_3$	--	0.6	0.8	1.8	0.8	0.7
Ankerite	$CaFe(CO_3)_2$	--	0.8	--	0.8	--	1.0
Jarosite	$KFe_3(SO_4)_2(OH)_6$	--	1.8	--	1.9	--	2.1
Gibbsite	$Al(OH)_3$	--	0.4	--	0.8	--	0.6
Total	--	100.1	99.9	100.2	99.9	99.8	99.5

(1) Post-testing results shown for standard humidity cell sample.
(2) Mineral quantity at methods detection limit, mineral not confirmed.
(3) Halite is an artifact of the pilot plant test solutions and is not associated with tailings mineralogy.

RESULTS OF THE KINETIC TESTING PROGRAM

Results for the leachate pH values with time for all kinetic test types are shown in Figure 1a. Concentrations of sulfate are shown on Figure 1b and concentrations of copper are shown on Figure 1c. The humidity cell leachates initially have near neutral pH values for all tests and a typical first flush of elevated sulfate concentrations and metals is observed. Following the first flush, an extended lag time to acidic conditions is observed for all tailings samples under the test conditions, during which pH values remain above 7 and sulfate concentrations steadily decrease.

Following the lag period, sulfide oxidation and subsequent acid generation occurs. For the whole tailings sample in the standard humidity cell, increasing sulfate concentrations (indicating sulfide oxidation) and increasing calcium concentrations (indicating dissolution of calcite) are observed starting at cycle 35. The pH begins a steady decline following this in cycle 40. The pH continues to drop with subsequent cycles to cycle 116 when the pH stabilizes near a value of 2.5, which is maintained for the final 35 cycles of testing (151 cycles total). During the final acidic phase, calcium concentrations decrease (likely indicating depletion of carbonate) and a decrease in sulfate concentrations to between 300 and 450 mg/L occurs. Concentrations for metals are elevated, including: aluminum, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, lithium, manganese, nickel, thallium, uranium, and zinc.

The lag time under testing conditions was greater for the cyclone fractions. The underflow fraction sample had the greatest lag time to initiation of sulfide oxidation and to initiation of acidic conditions (starting at approximately 83 cycles with a drop in leachate pH below 7 and an increase in sulfate concentrations). Additionally, the final stable pH for the underflow humidity cell test was higher, at a value near 5. For the overflow sample, sulfate concentrations followed a similar trend as the whole tailings sample, with increasing concentrations beginning near cycle 40 and an initiation of a decrease in pH beginning in cycle 58. Given similar behavior to the whole tailings, this test was terminated at this time.

For the delayed humidity cells, the lag time was not exhausted during the testing period. The pH values for the entire duration of testing were greater than 7. Additionally, a change in sulfate and overall metals mass loading was not generally observed in the leachate over time. Leachate sulfate and metals concentrations were generally elevated in the delayed humidity cell test relative to that of the standard test because removal of mass load from the cells only occurred every 20 cycles. Calculation of mass flux from the standard humidity cell compared to that of the delayed humidity cell at cycles 20, 40, 60, and 80 are presented for sulfate, copper, arsenic, and antimony on Figures 2a through 2d (results shown for whole tailings samples only).

DISCUSSION

The majority of the geochemical characterization data indicate that the tailings (whole and cycloned fractions) have potential to be acid generating under appropriate conditions, such as assuming the presence of sufficient moisture following desaturation of the tailings. With the onset of acid generation, pore water quality would be expected to have low pH values between 2.5 and 3 with elevated concentrations of sulfate and metals. For a copper porphyry deposit with sulfide tailings this is not an unexpected result. From a planning perspective for design, operations, and closure, the most pertinent results are those from the kinetic testing with respect to the lag time. A significant lag time is expected based on the results of the standard humidity cell test. The lag time was observed to vary between the different tailings fractions, with the shortest lag time for initiation of acidic conditions observed for the whole tailings (40 cycles) and longest for the underflow (80 cycles). For this site, translation of laboratory lag times to the field is significant. One equivalent cycle under field conditions could take many years to occur as there can be successive years without precipitation or without precipitation sufficient to wet more than the surface of the tailings due to the high evaporation rate.

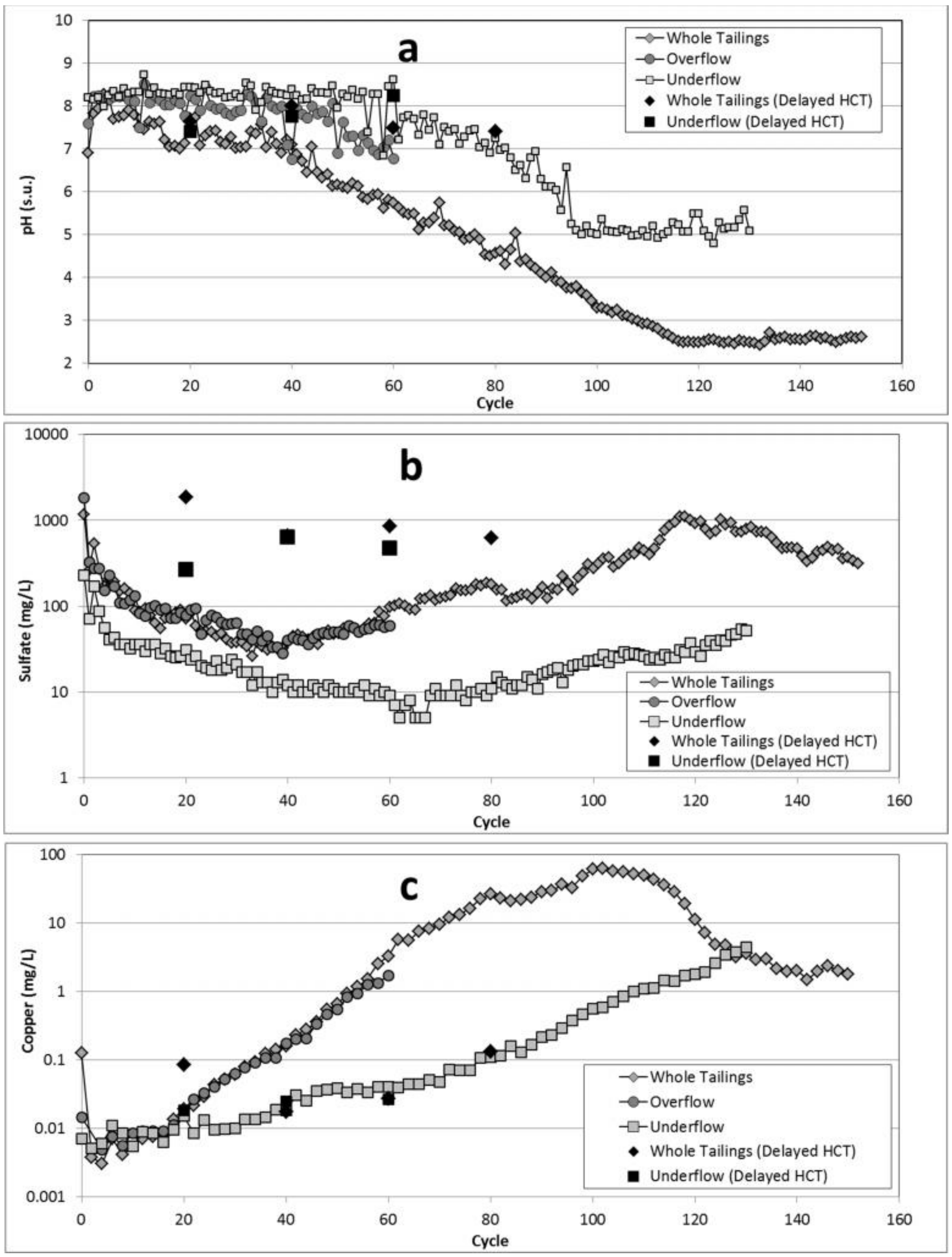

Figure 1 Leachate a) pH, b) sulphate and c) copper concentrations with time

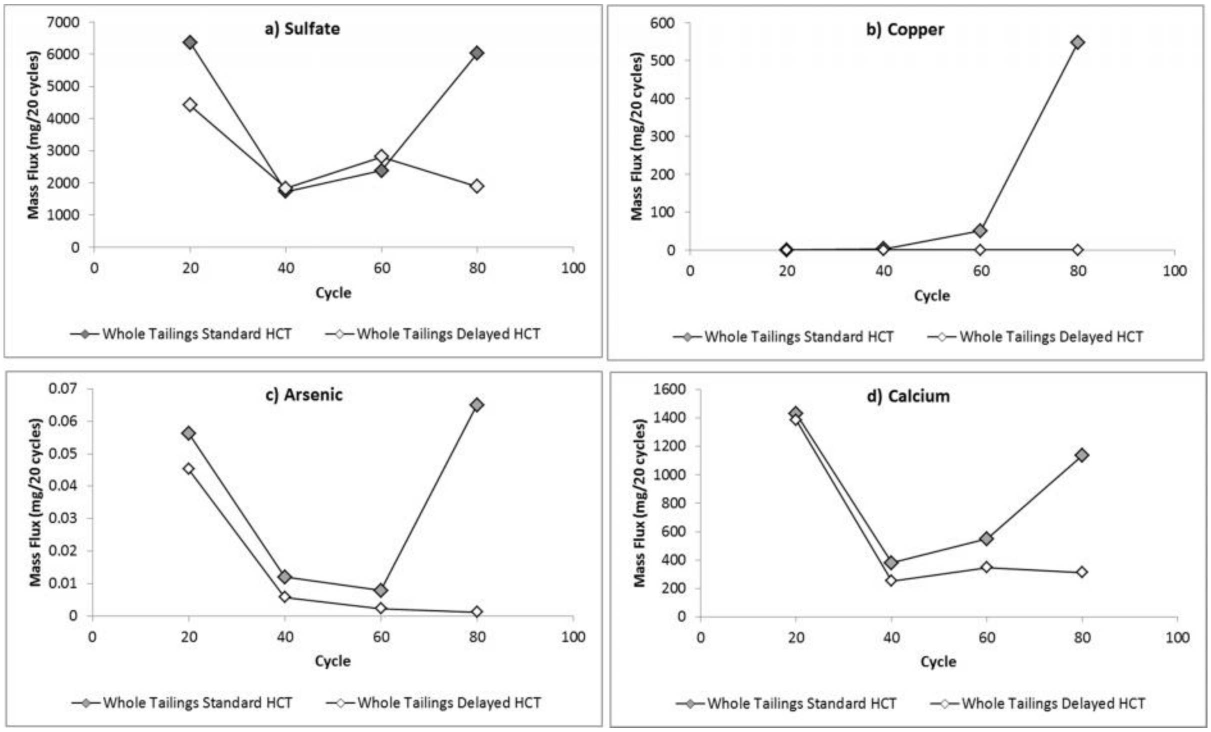

Figure 2 Mass flux from standard and delayed humidity cells over 20 cycles for: a) sulfate, b) copper, c) arsenic, and d) calcium

The results of the delayed humidity cells confirm the lag time and indicate that the lag time may be extended further with less frequent wetting as expected in drier conditions. The pH of the delayed humidity cells remained constant through testing (80 cycles) and no increase in sulfate or metals concentrations is observed. This indicates that initiation of sufficient oxidation to affected leachate water quality is postponed in the absence of weekly rinsing cycles.

Trends of mass flux from the standard humidity cells compared to that of the delayed humidity cells provide greater insight into the oxidation behavior. Mass flux for sulfate (Figure 2a) and most metals (similar to that of copper and arsenic, as shown on Figures 2b and 2c) are similar for the standard and delayed humidity cells for the first 40 cycles, indicating similar rates of oxidation and metals release up to this time. Following the initiation of sulfide oxidation just before 40 cycles in the standard humidity cells, a slight increase in cumulative loading is observed for the standard humidity cells, resulting in higher loading rates compared to the delayed humidity cells at 60 cycles. At 80 cycles, the pH values of the standard humidity cells have dropped below 5, sulfate and metals mass flux increases dramatically. In comparison, mass flux of metals and sulfate from the delayed humidity cells remains relatively constant between cycles 40 and 80.

The mass flux trends indicate that whole tailings in both the standard and delayed humidity cells had similar oxidation and metals release during the initial phases of the test (i.e., the first 40 cycles). Because the mass flux changes for the standard cells, but not the delayed humidity cells, this implies that the initiation of significant oxidation is delayed by less-frequent wetting and it is not a mechanism of neutralization that delays acid generation. Calcium mass flux (Figure 2d), which would provide an indication of calcite dissolution, is also similar between the standard and delayed humidity cells until significant oxidation and acidic conditions are apparent in the standard cell.

The delay in the initiation of oxidation could be due to factors such as an initial surface coating of sulfide surfaces with secondary minerals that may form during initial processing (e.g., Jambor 1994; Thomas et al. 1998) or throughout the testing, sulfide mineral availability, initially available neutralizing minerals, or buffering capacity of initial process solutions. The limited flushing in the delayed humidity cell test may not sufficiently remove oxidation products from the pyrite surface, thereby further limiting initiation of significant oxidation (e.g., Blowes and Ptacek 1994, Jerz and Rimsdit 2004, Huminicki and Rimstidt 2009).

A second pertinent result from a TSF design and planning standpoint is that following initiation of sulfide oxidation and depletion of the neutralization potential, the development of fully acidic conditions was gradual under the test conditions. While terminal pH values were near 2.5 with elevated metals concentrations, it took greater than 75 cycles to reach these conditions after sulfide oxidation initiated between cycles 35 and 40 (based on the increasing sulfate concentrations at this time). Peak sulfide oxidation rates (based on sulfate release) are reached in cycle 116, as a pH of 2.5 is reached, and then sulfide oxidation rates decrease through the conclusion of the test at 151 cycles. The greatest sulfide oxidation rates are expected for tailings at the beginning of acidic conditions (e.g., MEND 1997). In this case, a similar result is observed, but only after fully acidic conditions were attained (i.e., at the start of consistent pH values near 2.5). While the neutralization potential of the tailings was expected to be limited based on initial ABA and XRD analyses, sufficient available neutralization potential from the tailings (and possibly process solutions) was available to slow the acidification process.

Implications for Design

The results of the geochemical testing program, while initially developed for permitting using standard characterization tests, were incorporated into the design and planning for the facility, considering both operations and closure. The design and planning process also considered the extreme arid climate, combined with its implications on the hydraulics of the TSF, in light of the geochemical characterization results. Additional hydraulic considerations included the high evaporation rates, salt migration, and hardpan formation which may also affect saturation state. All of these factors warrant consideration in the design, management, and closure planning for TSFs in the Atacama Desert, as well as site in other arid climates.

Operations

Given the extended lag time for the tailings and the saturation state of freshly deposited tailings, acidic conditions will not develop in the TSF during operations. Tailings will be deposited wet, in lifts by spigots. The upper portion of a lift will undergo drying; however, it will be re-wetted to a limited extent as it is subsequently covered by a fresh layer of tailings. However, due to the arid climate, limited rewetting is expected, with infiltration modeling indicated that infiltration and rewetting will be interrupted after 5 to 8 days by evaporation processes. The results of the delayed humidity cells indicate that the limited wetting and drying will further extend the already significant lag time to the initiation of significant oxidation (a minimum of 40 cycles based on the standard humidity cells) and development of full acidic conditions (a minimum of 116 cycles in the standard humidity cells). Furthermore, one cycle in the laboratory scaled to an equivalent wetting and drying cycle in the field following cessation of deposition may represent many years at the site location due to the climate conditions.

The long lag time and slow development of fully acidic conditions with peak oxidation rates has other implications for TSF management. Given acidification either may not occur at all due to the climate or it will take a very long time to develop acidic conditions, monitoring of any seepage from the tailings facility will provide a long lead time to develop and implement mitigation measures.

From an oxidation potential perspective, underflow sands in the dam can be a concern due to their grain size and position in the dam that allows for drainage and lower moisture contents. Cycloning tailings can also result in concentration of sulfides in the underflow sands. However, in this case, the latter was not observed with similar sulfide contents in the whole and underflow tailings as measured by both ABA and XRD. Additionally, the grain-size distribution for underflow sands is generally larger, resulting in a lower specific reactive surface area. The lower specific surface area and similar sulfide content resulted in less reactive underflow tailings in this case. The underflow sands exhibited a longer lag time and the terminal pH values were relatively high (values near 5) with corresponding lower concentrations of sulfate and metals. As such, significant acid generation from the underflow sands is also not expected during operations.

Given these observations, the TSF design was focused on water conservation as water quality is not expected to be a concern. These factors, combined with the expected geochemistry of the tailings, indicate a very low risk of water quality impacts during operations.

Closure

Following closure, the upper tailings will be unsaturated, allowing oxidation and acidification. However, the significance of acidification will be limited due to several factors. The most important is that following cessation of operations and deposition of tailings, the climate conditions will not provide sufficient water to mobilize seepage through the facility. Secondly, as described, a delay to acidification is expected and the dry climate will limit wet and dry cycles and mobilization of acidity. The delayed humidity cells demonstrate that persistent dry conditions and lack of flushing will increase the lag time. A lack of mobilization of constituents from the oxidized zone may also limit oxidation as secondary products may blind off reactive surfaces. Finally, while a significant unsaturated zone at the surface of the TSF is expected due to the climate, formation of a hardpan is also expected by natural and secondary salts (e.g., Coggans et al. 1999) that may limit oxidation diffusion. Natural hardpans are currently present at the site due to the climate, providing an analog for expected future conditions, and hardpan formation was observed in geotechnical laboratory studies for the tailings. Given the above considerations, limited or no water management requirements are expected following closure of the TSF to be protective of the environment.

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NOMENCLATURE

ABA	acid-base accounting
ASTM	American Society for Testing and Materials
CO3-NP	carbonate neutralization potential
HCT	humidity cell test
NAG	net acid generation test
NNP	net neutralization potential
NP	neutralization potential
NPR	neutralization potential ratio
PAG	potentially acid generating
TIC	total inorganic carbon
TSF	tailings storage facility
XRD	x-ray diffraction

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