

Challenges in Prediction of Acid Rock Drainage Potential for Skarns – Use of Modified Testing

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ABSTRACT

The Hilarion Mining Project, located in the Peruvian Andes, is anticipating the use of thickened tailings as disposal method for the projected QuenhuaRagra tailings storage facility. A comprehensive geochemical program of tailings samples was performed to characterize them in terms of acid mine drainage (AMD) and metal leaching potentials. Two samples representative of the Zn-Ag-Pb polymetallic skarn-type deposit were used.

Skarn deposits typically pose a challenge for traditional kinetic testing programs. High neutralization potential and high sulfur contents can lead to extended testing times, as the high content of each extends the depletion times. This makes it difficult to evaluate uncertain materials or potential lag times. In this case mineralogical results indicated the presence of high concentrations of neutralization minerals and high concentrations of acid generation minerals. Acid base accounting tests confirmed high neutralization potential, together with a high acidic potential.

Humidity cell tests (HCT) were performed to confirm static test results and to determine lag time for the onset of acidic conditions. After a first stage of testing (89 and 54 cycles), the results reported circum-neutral pH conditions and low release of sulfate and metal concentrations. This result combined with depletion calculations predicting acid generation, the static tests results, and uncertainties from the net acid generating test made the AMD potential classification a challenge.

To better understand the skarn tailings geochemistry, hydrogen peroxide was used as lixiviant for the HCTs in a second stage of the testing. After a decrease in pH, both samples returned to their previous pH values; however, sulfate and metal release did react to the change. After 21 and 18 HCT cycles with hydrogen peroxide, acidic conditions were not reached.

Accelerated kinetic test provided useful information for waste management. While acidic conditions are doubtful, oxidation of sulfides will produce release of metals and sulfate.

Keywords: skarns, extended lag time, hydrogen peroxide

INTRODUCTION

The geologic characteristics of mineral deposits exert important controls on the natural environmental signatures that could result from mining and mineral processing. A good understanding of the environmental geology of mineral deposits is therefore crucial to the development of effective mining-environmental prediction, mitigation, and remediation practices (Plumlee 1999).

Skarns are coarse-grained metamorphic rocks formed when magmatic-hydrothermal fluids are expelled from the magmas and react chemically with sedimentary rocks. The skarn alteration frequently introduces calc-silicate minerals replacing carbonate-bearing rocks. The skarn ores may include massive sulfide lenses and veins occurring within and/or replacing the sedimentary host rocks (Plumlee *et al.* 1999). This type of replacement increases the acid generation capacity by increasing the content of acid-generating sulfides in rocks and may decrease the acid-neutralizing capacity by removing carbonate minerals (Plumlee 1999). However, the original host rocks frequently still retain a high carbonate content. This results in geochemical model signatures of circum-neutral pH values, and low metal concentrations with a few exceptions, including copper and zinc (Plumlee *et al.* 1999).

Evaluation of a material with high contents of sulfides and high carbonate content poses a challenge for the geochemical characterization programs and the determination of the acid generation potential because an extended kinetic testing time may be required to deplete one or the other, even in an accelerated test. The long lag times to acid generating conditions or to depletion of the neutralization potential are impractical compared to other aspects of mine planning and permitting and do not allow useful decisions to be made during the design process.

The Hilarion project in Peru is a Zn-Ag-Pb skarn-type deposit hosted in a contact zone of the calcareous sedimentary sequence of the Chulec-Pariatambo-Pariahuanca Formations (early Cretaceous) and an acidic intrusive stock (likely Tertiary). The calcareous sedimentary sequence ranges from predominantly claystone in the Pariatambo formation to limestones in the Chulec formation. The intrusive rocks present in the zone are a potential source of mineralization and are characterized as dioritic, feldspar porphyry, quartz monzonitic porphyry, and granodioritic types, affected by hydrothermal alteration mainly of the kaolinite and sericite into plagioclase and chloritic in amphiboles.

Compania Minera Milpo S.A.A. (Milpo) is currently developing the Hilarion project, which is located in the Peruvian Andes at an altitude varying between 4,500 and 5,200 meters above sea level, approximately 230 kilometers north of Lima and 80 kilometers southeast of the city of Huaraz. Milpo is considering the use of thickened tailings as a disposal method in the planned tailings storage facility (TSF).

As part of the permitting efforts, Milpo and Golder developed a geochemical characterization program to assess the acid generation and metal leaching potential of tailings samples representative of the polymetallic skarn-type deposit present at the Hilarion project following standard phased geochemical programs, including static and kinetic testing. However, given the

difficulties and extended time required to evaluate materials with high carbonate and high sulfide contents, the latter was modified through the addition of an oxidizing agent for further evaluation of the materials.

This case study provides an overview of the geochemical characterization program and its results, including the challenges presented by the nature of the material investigated and the modifications applied to a standard kinetic test to better understand the geochemical behavior of the Hilarion tailings samples.

METHODOLOGY

Tailing samples from pilot scale metallurgical work were tested as a part of the geochemical characterization program. The samples represented tailings from the ore material, following all metallurgical processes, that will be mined from the skarn deposit and that are expected to be deposited in a valley fill tailings storage facility (TSF). This study evaluated the expected environmental behavior of the tailings in the TSF, after metallurgical leaching processes. The study was designed to provide information for future waste management and water management strategies for the TSF, including water management strategies for runoff water and seepage, water management strategies for the tailings pond, water balance, and recirculation requirements, and whether and when treatment might be required.

Three tailings samples were evaluated. For sample 1 and sample 2, a complete geochemical testing program, including static and kinetic testing by humidity cells, was performed following standard guidance (*e.g.*, INAP 2009, MEND 2009). The geochemical testing program for these samples is summarized in Table 1. As part of confirmatory efforts during the static testing phase, an additional sample (sample 3), was sent to the lab to perform confirmatory analyses with respect to mineralogy and with respect to oxidation potential of the sulfides (*i.e.*, the sequential net acid generation procedure).

The focus of this study was to better understand the geochemical behavior of the samples in the long term; as such, a second phase of kinetic testing was undertaken for samples 1 and 2. This second phase of testing was a modified kinetic test as described below. Given the interest in the long-term behavior, this paper focuses on the kinetic test results; however, the results of the static testing phase are also summarized to provide the context for the interpretation of the kinetic test results.

Table 1. Summary of complete geochemical testing program

Program	Analysis	Sample 1	Sample 2	Sample 3
Static	Elemental content by acid digestion	X		
	Acid base accounting	X	X	
	Net acid generation	X	X	
	Net acid generation test effluent analysis	X	X	
	Short term leaching procedure	X	X	
	Sequential net acid generation test			X
	X-ray diffraction with Rietveld refinement	X	X	X
	Acid base accounting after humidity cell test	X	X	
Kinetic	Humidity cell test	X	X	
	Modified humidity cell tests	X	X	

The humidity cell test (HCT) method (based on ASTM 2007) was used as the kinetic test in this project. The ASTM HCT, a cyclic kinetic test, was selected primarily given its common use and regulatory acceptability. For the modified kinetic testing, the original HCTs were continued into a second phase of testing with a modified procedure. In this phase, the lixiviant was changed from deionized water to hydrogen peroxide. The second phase of testing was initiated at cycles 89 and 54 for samples 1 and 2, respectively. After the lixiviant change, the modified HCTs were continued for additional 21 and 18 cycles (to 110 and 72 cycles, respectively).

Hydrogen peroxide is commonly used as a part of the net acid generation (NAG) test developed by AMIRA (AMIRA 2002) and is intended to accelerate oxidation of sulfides and challenge the neutralization potential present in the sample. The objective of using hydrogen peroxide in this case was to attempt to reach acidic conditions predicted by the static test results and depletion calculations.

After kinetic tests were terminated acid base accounting (ABA) testing was performed on the sample remaining in the humidity cells to confirm the depletion calculations based on the HCT results and to evaluate changes to the original acid generation potential classification following kinetic testing.

Laboratory testing, with the exception of the mineralogical analysis, was performed by a commercial laboratory in Lima, Peru. The laboratory has its own quality control, and quality

assurance program and experience performing ASTM HCT method. The mineralogical analysis was performed by the University of British Columbia, Vancouver, Canada.

RESULTS

Static tests results summary.

Mineralogical results for the three samples are presented in Table 2. The results of the XRD were consistent with the general understanding of the site geology, with a polymetallic skarn type mineralization of Zn-Ag-Pb. A high concentration of calcite was determined with a range between 8.1 and 10.4% by weight. Sulfide presence was highly dominated by pyrrhotite (15.8 to 18.0% by weight), followed by lower concentrations of pyrite and sphalerite.

Results of the static testing program indicated inconsistent results for sample 01. This sample is considered to have the potential for acid generation based on standard ABA calculations (both net neutralizing potential ratio (NPR) and net neutralization potential (NNP) calculations). While the neutralization potential (NP) of the sample was high (156 kg CaCO₃/t, consistent with the 10 % by weight calcite content), this sample has a high acid potential (227.5 kg CaCO₃/t) consistent with an elevated sulfide content (20.3% by weight sulfides, including 17.7 % by weight pyrrhotite and 1.9% by weight pyrite). In contrast, the net acid generation (NAG) test did not confirm this classification for sample 1, reporting neutral pH values after the procedure. However, the NAG test is subject to complications for samples with high sulfide contents; insufficient hydrogen peroxide may have been added to oxidize all of the sulfides present.

Results of the static testing program indicated that sample 02 is considered to have an uncertain potential for acid generation based on the NPR result (i.e., 1.8), while the NAG result reported a circum-neutral pH value. This uncertain classification is again due to the high NP (207 kg CaCO₃/t, consistent with the 10.4 % by weight calcite content), this sample has a high acid potential (115 kg CaCO₃/t) consistent with an elevated sulfide content determined by mineralogical analysis (18.4% by weight sulfides, including 15.8 % by weight pyrrhotite and 1.6 % by weight pyrite).

Due to the inconsistency between the NAG test and the ABA results, a sequential NAG test (AMIRA 2002) was performed over a confirmatory sample (sample 3). A three step sequential NAG test was performed over the sample. The results after the three cycles reported a pH of 2.3 and elevated metal concentrations. This test confirmed that the one step NAG test performed over the original samples was inadequate to completely oxidize all the sulfide material present and confirmed the acid generating potential of the tailings samples.

Table 2. Tailings samples mineralogical test results (% by weight)

Minerals	Formula	RE-HI10-01	RE-HI10-02	RE-HI10-04
Quartz	SiO ₂	5,8	6,5	6,0
Clinocllore	(Mg,Fe ²⁺) ₅ Al (Si ₃ Al)O ₁₀ (OH) ₈	3,4	4,4	3,1
Muscovite	KAl ₂ AlSi ₃ O ₁₀ (OH) ₂	1,9	--	--
Biotite	K(Mg,Fe) ₃ (AlSi ₃ O ₁₀)(OH) ₂	--	0,8	--
Actinolite	Ca ₂ (Mg,Fe) ₅ Si ₈ O ₂₂ (OH) ₂	--	--	1,0
K-Feldspar	KAlSi ₃ O ₈	18,5	20,5	14,8
Andradite	Ca ₃ Fe ₂ ³⁺ (SiO ₄) ₃	--	--	4,1
Calcite	CaCO ₃	10	10,4	8,1
Siderite	FeCO ₃	0,7	0,4	0,3
Clinozoisite	Ca ₂ Al ₃ (SiO ₄) ₃ (OH)	6,6	6,4	5,8
Diopside	CaMgSi ₂ O ₆	12	14,2	11,7
Grossular	Ca ₃ Al ₂ Si ₃ O ₁₂	20,9	17,7	22,5
Sphalerite	(Zn,Fe)S	0,7	1,0	1,6
Pyrrhotite	Fe _{1-x} S	17,7	15,8	18,0
Pyrite	FeS ₂	1,9	1,6	3,1
Ilmenite	FeTiO ₃	--	0,4	--
Total		100	100	100

Kinetic test results

The objectives of the kinetic test were to:

- Address the uncertainties provided by the initial static test results,
- Evaluate potential lag times to acidic conditions, and
- Evaluate the geochemical behavior of the tailings samples under acidic conditions.

The results of the HCTs would then be used in predictions of water quality and tailings behavior in the TSF during operation and after closure to assist with TSF design.

Tailings samples 1 and 2 had a first phase of the kinetic testing program in HCTs based on the standard ASTM method. However, following 89 and 54 cycles for sample 01 and 02, respectively, the HCTs had maintained neutral conditions, with pH values between 7.3 and 7.6. Metals concentrations were generally low with the exception of manganese, which is mobile at these pH values. The manganese concentrations by cycles 89 and 54 reported values between 0.28 and 1.5 mg/l.

A preliminary evaluation of the results was performed midway through the first phase of testing. Based on the ABA results, sequential NAG testing, and the high concentration of sulfide minerals, it was expected that the tests would result in acidic conditions, at least for sample 01 by this time of the HCT procedure. Additionally, forward-looking depletion calculations also indicated eventual acidic conditions. However the preliminary evaluation demonstrated that leachate from both samples reported circum-neutral pH values, a sulfate concentration around 100 mg/l, and low metal concentrations. These results indicate that not only were acidic conditions not attained, but also significant oxidation was not occurring.

At this point, it was decided to modify the HCT procedure expecting to accelerate the oxidative processes in one of the samples. Starting in cycle 54, the lixiviant for sample 02 was changed from deionized water to hydrogen peroxide, capable of accelerate the sulfides oxidation rates. Sample 02 was under this lixiviation scheme until cycle 72, when the test was terminated.

The sample 01 continued to be leached using the standard procedure for comparison until cycle 89. Based on the results reported up to that cycle, it was decided to also modify this cell and start using hydrogen peroxide as the lixiviant. The sample 01 HCT was tested until cycle 110 with hydrogen peroxide.

The results after 110 and 72 cycles (including 21 and 18 cycles using hydrogen peroxide) for samples 01 and 02, respectively, can be summarized as follow:

- Acidic conditions were not generated in any of the cells, even after the use of hydrogen peroxide as the lixiviant. The pH values for both samples ranged between 6.1 and 8.3 (Figure 1).
- After the first addition of hydrogen peroxide, pH value for sample 02 reported a decrease from 7.6 down to 6.6, but returning to pH values pre-hydrogen peroxide after 5 cycles.
- Sample 01 did not report significant changes in its leachate pH value after the change to hydrogen peroxide, keeping leachate pH values between 7.3 and 8.0 until the end of the test.
- While both samples were lixiviated using deionized water sulfate and metal concentrations remained low, reporting stable or decreasing trends.
- The addition of hydrogen peroxide in both cells resulted in a significant increase in sulfate concentrations. Both samples reported a one order of magnitude increase immediately after the first hydrogen peroxide cycle. The increase of sulfate concentration remained stable in cell 02 until terminated; while cell 01 reported a decrease in sulfate concentration after ten cycles using hydrogen peroxide, but still elevated compared to the concentrations reported when using deionized water (Figure 2).
- Metals concentration also reacted to the change in lixiviant. In both cells, similar parameters reacted to the addition of the strong oxidant. In most of the cases the increases in concentration

were above one order of magnitude. The parameters that reported increases in concentration for both samples included: barium, calcium, cadmium, cobalt, chromium, copper, magnesium, manganese, molybdenum, nickel, lead, selenium, silica, strontium, and zinc. For example, Figures 3 and 4 present the results for copper and zinc, respectively.

- After the initial peak in concentrations following the change to hydrogen peroxide, most of the parameters reported decreasing concentrations; however none of them returned to the concentrations exhibited before the change in lixiviant. Only magnesium remained stable or reporting increasing trends until the cells were terminated.

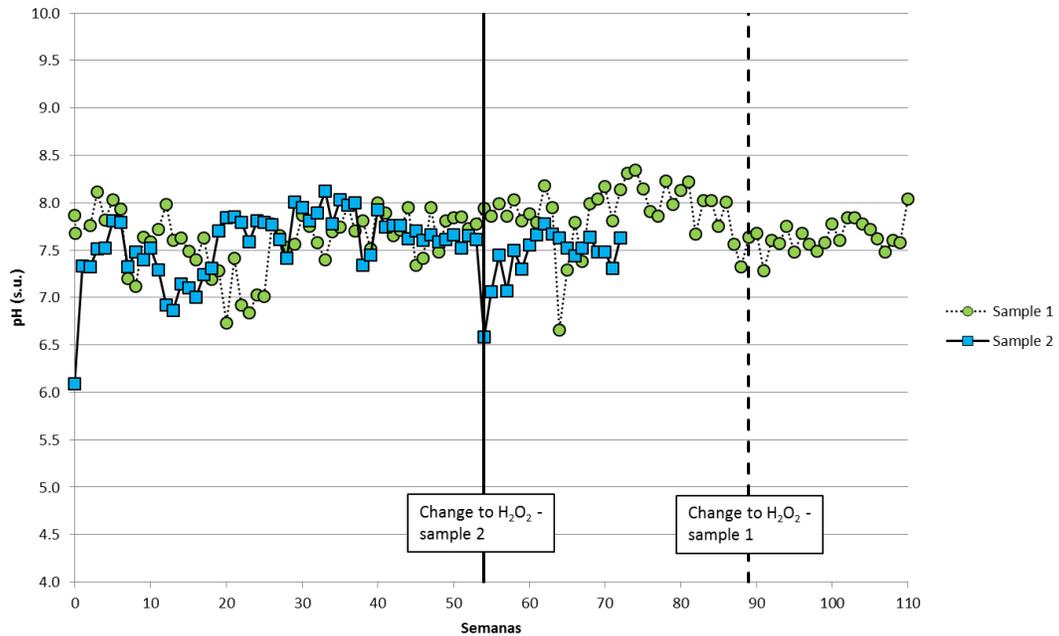


Figure 1. Kinetic test results – pH values

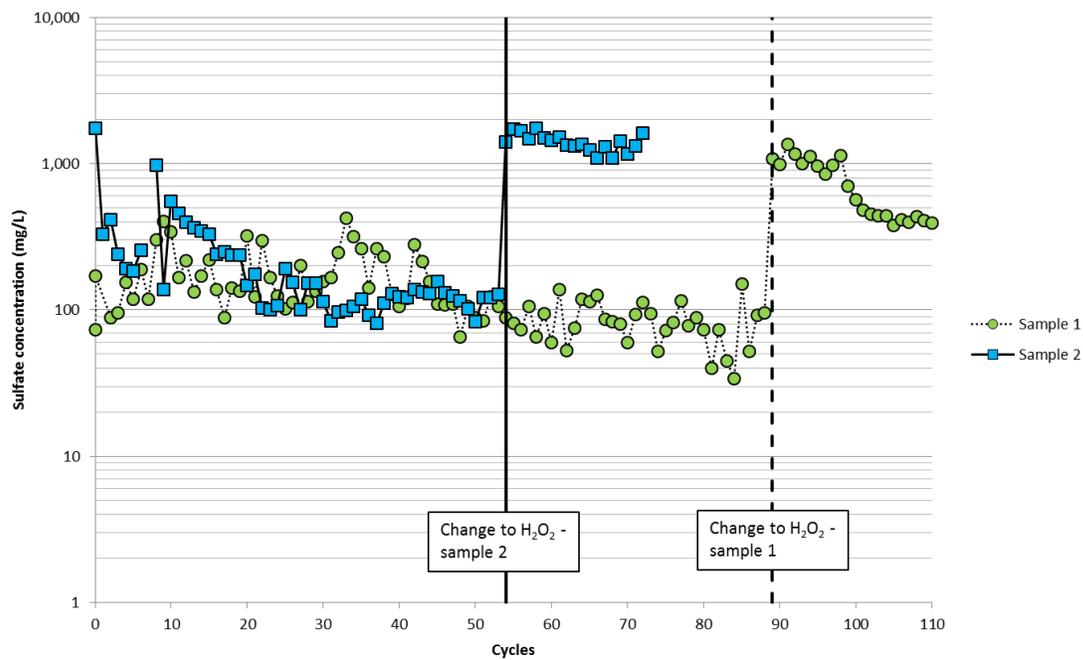


Figure 2. Kinetic test results – Sulfate concentrations

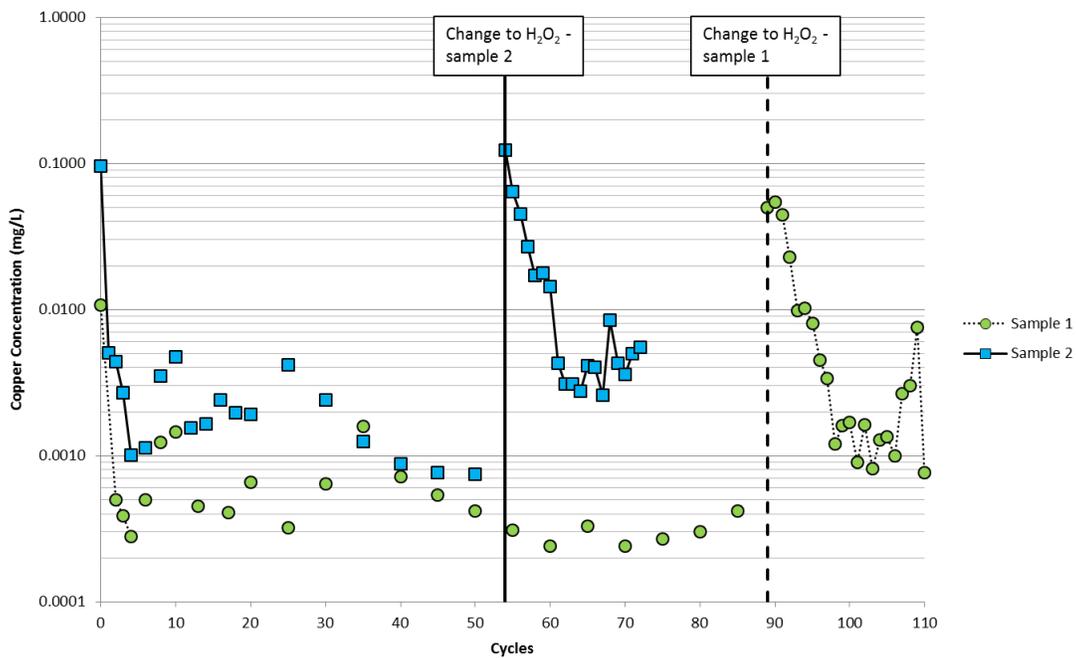


Figure 3. Kinetic test results – Copper concentrations

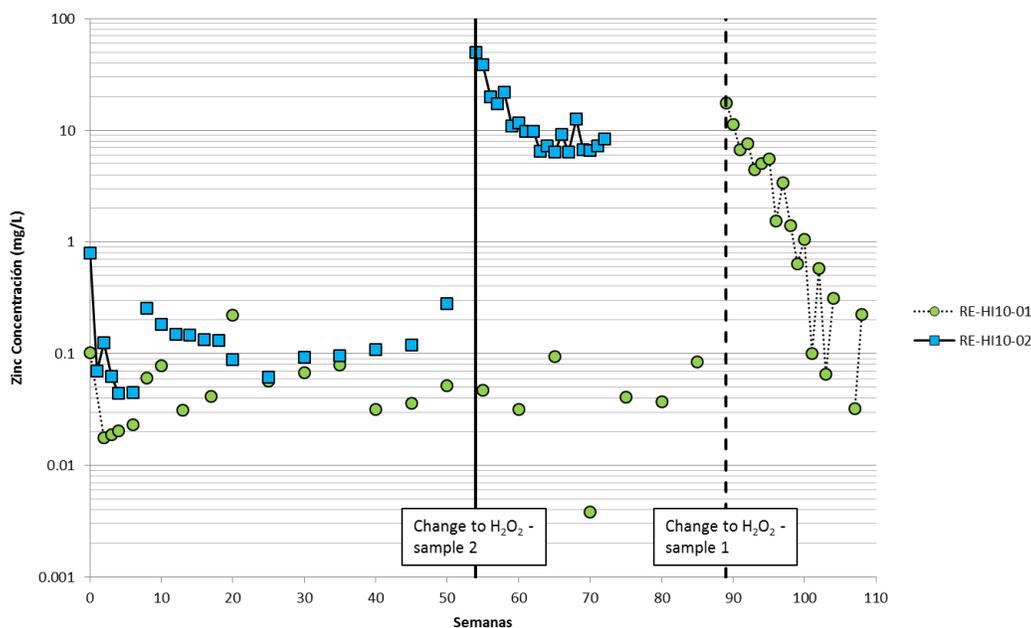


Figure 4. Kinetic test results – Zinc concentrations

DISCUSSIONS AND CONCLUSIONS

Skarn deposits pose a challenge for geochemical characterization programs. Excessive contents of carbonates and sulfides can lead to unreasonably long depletion times even in accelerated kinetic tests, resulting in uncertainty in the final acid generation behavior of waste materials.

Pilot plant tailings samples associated with the Hilarion project had high sulfide content (18.4 to 20.3 % by weight, primarily as pyrrhotite) and high carbonate content (10 to 10.4 % by weight calcite). Static ABA and sequential NAG testing resulted in predictions of potentially acid generating to uncertain. In this type of scenarios, humidity cell tests are performed to confirm the expected behavior in the future, after oxidizing conditions are applied to the samples. Humidity cell tests are used for a number of reasons, including confirmation the acid generation potential and the release rates of metals. Unfortunately, humidity cell test duration is not definitive and will depend on the results obtained, which at the same time are dependent in the type of materials studied.

Up to 88 and 54 cycles of kinetic testing by standard humidity cells did not resolve the potential uncertainty based on the ABA results. Additionally, depletion calculations indicated that exceptionally extended testing times (up to 15 years) would have been required to resolve this issue. While it was expected that the humidity cells would reach acidic conditions, the preliminary results of the kinetic test, under standard conditions, did not provide consistency with the static test results. The change of lixiviant from deionized water to hydrogen peroxide, a strong oxidant, was

performed to accelerate the oxidation of sulfide minerals present in the samples and to reach acidic conditions.

The second stage of modified humidity cell testing provided useful information for mine design, operational planning, and closure planning. The second stage of humidity cell testing involved the use of an oxidant (hydrogen peroxide, as in the NAG test) as a lixiviant of up to 21 cycles of testing. Even after 21 and 18 cycles of leaching with the oxidant for samples 1 and 2, respectively, acidic conditions were not achieved, contrary to predictions of potentially acid generation behavior based on the ABA testing and with concentration of sulfides of up to 20.3%. However, sulfide oxidation was achieved by using the oxidant as a leachate, as shown by increases in the sulfate and metals concentrations in the leachate. Oxidation, based on sulfate generation, was greatest immediately following addition of the oxidant, and remained elevated for up to 18 cycles. For sample 1, sulfide oxidation decreased 10 cycles after the initiation of the oxidant lixiviant; however, the oxidation rates from this point through the final 110 cycles of testing (again based on sulfate release) were still elevated (4 to 5 times higher) relative to initial test conditions, indicating oxidation was still occurring despite the decrease. Even under these scenarios, available NP was sufficient to prevent development of acidic conditions.

While oxidation was occurring in the second stage of kinetic testing, significant metals and sulfate release was also observed. Increases in metals and metalloids concentrations, including Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, and Zn, were observed in the second stage of kinetic testing. It is expected these metals were released by sulfide oxidation and/or micro, localized acidic zones (even if the overall tests did not result in acidic conditions). Concentrations of Cd, Mn, Mo, SO₄, Se, and Zn, several of which are expected to be mobile even at low pH values, were elevated sufficiently to pose a risk to exceeding applicable regulatory standards based on water quality modeling for the TSF. As such, design for the TSF needed to consider potential water treatment if sulfide oxidation occurs. However, a lag time to sulfide oxidation is expected based on the first stage of kinetic testing and given that the climate and design of the TSF will keep the tailings saturated, at least through operations.

While the kinetic testing may not have definitively resolved discrepancies with respect to AMD and the static testing, the expected release of metals under neutral conditions once sulfide oxidation is initiated is significant for mine, operation, and closure planning. As such, use of this modified test to further accelerate weathering reactions provided useful information with respect to the overall expected tailings behavior.

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