

Mineral Reaction and Solute Loading Rates from Field ARD Test Pads at the Bagdad mine in Arizona

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Abstract

Standard lab tests are critical tools to predict the acid rock drainage (ARD) and metal leaching (ML) potential and hence, the long-term seepage water quality from mine stockpiles. Due to differences in lab testing and actual field conditions, field testing is likely to represent more closely the internal conditions within a rock pile as well as the various mechanisms controlling ARD/ML generation. The objective of the field test pad study at the Bagdad mine in Arizona is to improve the prediction of ARD/ML potential and long-term seepage water quality from development rock and previously acid-leached ore materials under field conditions. To supplement the natural precipitation received at the relatively semi-arid site, water is applied via a network of driplines installed on the top surface and upper side slopes of the test pads.

For the development rock test pads, seepage pH and EC values have remained relatively constant throughout the study thus far at ~ 7.5 - 8.5 and ~ 2000 - 4000 $\mu\text{S}/\text{cm}$, respectively. Sulfate loading rates in the seepage have been used to estimate the reaction rates of the two acid generating minerals present in the test pad materials - pyrite and chalcopyrite. Calcium and magnesium loading rates in the seepage have been used to estimate the reaction rates of the acid neutralizing minerals calcite and biotite, respectively. Calculations using the mineral contents and average reaction rates predict that the acid neutralizing minerals, especially calcite are likely to remain available after the acid-generating minerals are consumed. Findings from this study indicate that seepage from the development rock materials is not likely to develop acidic pH levels in the future due to excess alkalinity provided by calcite and the reactive silicate minerals.

Introduction

Acid rock drainage (ARD) is a natural phenomenon that is primarily caused by the oxidation of sulfide minerals. It is characterized by acidic waters and is typically, but not always, associated with metalliferous

and sulfate-rich waters. Standard lab tests are critical tools to predict the ARD and metal leaching (ML) potential. However, there are wide differences in parameters that control ARD/ML generation, including - particle size distribution, temperature, microbial activity, air-flow and water movement within the materials in the lab vs in the field (Kempton 2012; Pearce et al. 2015). Lab tests also have the limitation of testing small amounts of materials that may have appreciable variability in mineralogy and ARD/ML potential. Hence, lab tests may provide a limited representation of future seepage water quality from these materials. A multi-pronged approach which includes field-testing of larger amounts of materials using constructed test pads is likely to provide a more representative demonstration of ARD and ML generation from mine stockpiles under normal field conditions.

A field test pad study is underway at the Bagdad mine in Arizona to evaluate ARD/ML potential and long-term seepage water quality from future development rock and leached ore stockpiles under field conditions. The Bagdad mine is an open-pit copper and by-product molybdenum mine operated by Freeport-McMoRan Bagdad Inc., a subsidiary of Freeport-McMoRan Inc. (FCX) located in Yavapai County approximately 210 km northeast of Phoenix, Arizona, USA. Average annual precipitation rate at the site is approximately 380 mm/year (WRRC 2016). Average summer high temperature approaches 36 degrees Celsius (°C) in July, and the average winter low is just above 0 °C in January. The results obtained from the study will be utilized in support of the on-going mine planning and permitting processes, and to provide guidance for developing any necessary measure(s) to control and/or mitigate ARD and ML from future stockpiles. The objective of this paper is to (i.) estimate reaction rates for sulfide mineral oxidation and dissolution of neutralizing minerals, (ii.) estimate the acid generation-neutralization balance based on solute loading rates, and (iii.) understand the long-term ARD potential from future stockpiles constructed with the development rock materials.

Test Pad Construction, Operation and Sampling

Error! Reference source not found. shows an aerial drone image of the six test pads (five development rock and one previously leached material) constructed as part of the Bagdad ARD Test Pad Study. These rock types represented significant tonnage in the projected mine plan and were typically classified as having an uncertain ARD potential based on static testing namely - Porphyry Quartz Monzonite (PQM), Quartz Monzonite (QM), and Precambrian Undifferentiated (pCundiff). Results from the leached ore test pad (TP8) will not be discussed here, as the focus for this test pad is to evaluate drain-down of previously leached material and is different from that of the five development rock test pads (TP3-TP7). The final test pad shape resulted in the following configuration (plan view dimension): 9-m by 9-m top, 21-m by 21-m bottom, 5-m height from center of the stockpile, and side slopes of 1.5H:1V.

Eight 210-liter (L) barrels of material from each test pad were collected prior to pad construction and processed (composited/split) for geochemical and mineralogical analyses. Post-construction Operation, Monitoring and Maintenance (OM&M) activities, including seepage sampling and analysis, began in 2019 and will conclude in 2022. Due to the relatively semi-arid conditions at the site, drip-line systems supplying water on the top surface and upper slopes of the test pads were installed to augment water received via natural precipitation. Supplemental water application is expected to accelerate the natural ARD/ML development, ensure sufficient toe seepage for water quality analyses, and facilitate a future water quality evaluation within the relatively short study duration of 3 years. A target application rate of ~3800 L per week per test pad has been used. This is approximately three times the annual precipitation volume. Seepage from each test pad reports to a seepage collection system at the toe of the pad via a seepage collection pipe buried underneath the pad and collected into a 19-L sampling container. Test pad seepage has been collected and analyzed for field parameters and selected water quality constituents on a monthly/bimonthly basis. Detailed descriptions of test pad construction, material characterization, and OM&M activities are provided in Raghav et al. (2021).



Figure 1. Aerial drone images of the test pads constructed as part of the Bagdad ARD Test Pad Study. Note: QM – Quartz Monzonite; PQM – Porphyry Quartz Monzonite; pCundiff – Precambrian Undifferentiated; Mineral Creek – material from Mineral Creek leach stockpile.

Results

Test Pad Seepage Chemistry

Test pad seepage pH and electrical conductivity (EC) values have remained relatively constant throughout the study at 7.5-8.5 and 2,000-4,000 $\mu\text{S}/\text{cm}$, respectively. Fluctuations outside this pH range were observed from April through August 2021 (Figure 2), which have been attributed to unreliable readings due to normal wear-and-tear of the probe. Measurements obtained using a new pH probe since September 2021 have remained more stable. A sharp, but short-lived decrease in pH has also been observed on selected occasions when pH measurements were obtained during or immediately following high-intensity precipitation events (e.g., late January 2021 and early December 2021). Higher water content in the test pads can result in higher internal carbon dioxide levels and decrease in pore water pH. However, the test pad seepage pH increased to the typical range within a week after draindown and increased carbon dioxide degassing to the atmosphere as has been observed in other studies (Peterson 2014).

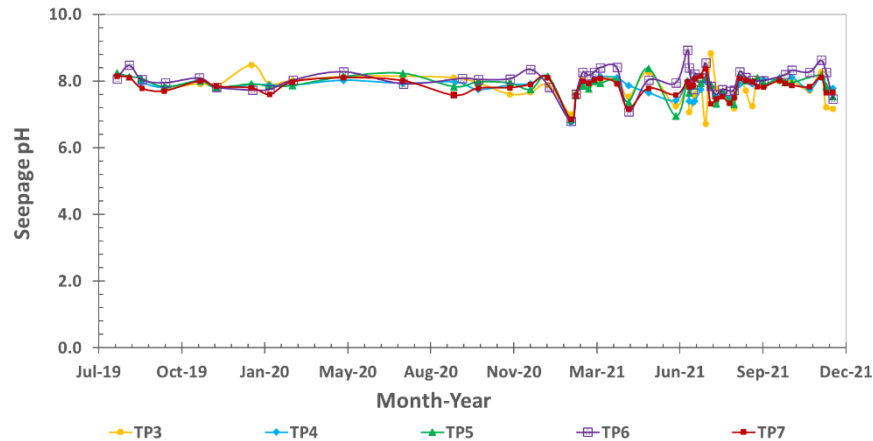


Figure 2. Test Pad Seepage pH

The degree of water saturation and flushing frequency can influence sulfide oxidation rates and solute loading in seepage (Herasymuik et al. 2006; Hollings et al. 2001). Water application was paused during periods of high-intensity precipitation to prevent constant flooding of pore spaces, which could slow down sulfide oxidation by limiting oxygen supply. Conditions within the pads are not oxygen limited based on consistently positive oxidation-reduction potential (ORP) data and moderate-high dissolved oxygen (DO) measurements (typical DO percent saturation of 50-80%). Additionally, seepage sulfate concentrations have typically remained in the 1,000-2,000 mg/L range. Hence, the volume and frequency of water application are generally appropriate to promote sulfide oxidation by flushing out built-up oxidation products and exposing fresh mineral surfaces for further oxidation.

Test Pad Mineralogy

Based on X-ray Diffraction (XRD) test results, chalcopyrite and pyrite are the two most likely sulfide

minerals that upon oxidation can release acidity, sulfate and metals into the seepage (Table 1). For TP5 and TP6, pyrite was not reported, but the total S data are consistent with pyrite being present below the XRD detection limit (0.3%). Hence, a pyrite concentration of 0.29% is assumed for these materials. No sulfate minerals were detected in any of the development rock types. However, based on total S data, it is possible that sulfate minerals may be present below the XRD detection limits in some or all the test pads. For the purposes of this evaluation, all sulfate loading in the seepage is assumed to be a result of sulfide mineral oxidation. No sulfate minerals are considered to be dissolving or precipitating.

Calcite, biotite, and chlorite are the minerals present in all test pads that are most likely to provide neutralization potential in the short- to medium-term (Table 1). Calcite is a ‘fast dissolving’ carbonate that is most likely involved in the neutralization of the acidity generated from sulfide mineral oxidation. Biotite is a silicate mineral known to weather faster than other silicate minerals such as feldspars, plagioclase, etc. (Karlsson et al. 2018). Chlorite is another silicate mineral with intermediate weathering rate that may provide neutralization capacity but has not been considered because the indicator solute in seepage (magnesium) is the same as for biotite. For this evaluation, all the magnesium in the test pad seepage is assumed to result from biotite dissolution.

Table 1: Pre-test rock characterization – XRD Mineral Content (weight%)

Description	TP3	TP4	TP5	TP6	TP7	Detection Limit
Quartz	28.2	31.3	23.3	23.5	30.1	0.1
Plagioclase	21.0	19.0	24.4	28.3	16.7	0.5
K-Feldspar	27.3	25.8	34.5	29.1	22.0	0.5
Muscovite	6.2	6.8	5.5	6.0	9.9	0.5
Biotite	2.6	1.7	2.4	2.2	2.8	0.5
Chlorite	2.7	3.0	0.8	2.1	4.1	0.5
Kaolinite	2.4	3.6	2.4	1.6	2.6	0.5
CEC SC	6.2	5.2	4.6	5.1	6.6	0.01
Calcite	2.2	2.0	1.2	1.5	3.5	0.5
Pyrite	0.46	0.70	0.00	0.00	0.94	0.3
Chalcopyrite	0.68	0.74	0.87	0.75	0.80	0.3
Molybdenite	0.0	0.0	0.0	0.0	0.1	0.01
Gypsum	0.0	0.0	0.0	0.0	0.0	0.5
Jarosite	0.0	0.0	0.0	0.0	0.0	0.7
Sum	100	100	100	100	100	-

Note: Minerals listed but reported as 0.0 did not have peaks above background levels (or above peak overlaps) and may be present below XRD detection limits. CEC SC refers to ‘Cation Exchange Capacity from Swelling Clays’.

Estimation of solute loading

Test pad seepage flow measurements typically included peak and low flow periods during the weekly water application cycles and hence, provide a reasonable estimation of seepage volumes. To estimate monthly seepage volume, an average of all the seepage flow rate measurements in the corresponding month was used. Solute concentrations in seepage have been measured on a monthly basis from August 2019 to March 2020 and every other month thereafter. Hence, solute loading rates, mineral reactions rates, and acid generation-neutralization balance are estimated on a monthly basis. The monthly solute loadings (moles) in seepage are calculated for sulfate, calcium, and magnesium using molar mass (g/mol), monthly seepage concentrations ($C_{Seepage}$, mg/L) and monthly test pad seepage volumes (L). In order to use sulfate loading in the seepage to estimate sulfide oxidation rates, the sulfate contribution from ‘water applied’ on the test pads is subtracted. Similarly, the calcium and magnesium contribution from ‘water applied’ on the test pads is subtracted when estimating calcite and biotite dissolution rates, respectively. This is important because a significant fraction of the ‘water applied’ is stored within the test pads and not reported as seepage. To account for this, the fraction of ‘water applied’ to the total water received is calculated ($f_{Water\ Applied} = \frac{Water\ Applied}{Water\ Applied + Precipitation}$). For the purposes of this evaluation, the same fraction is assumed to apply to the seepage volume. In other words, the monthly seepage volume is multiplied by this fraction to estimate the volume of ‘water applied’ that will contribute to the seepage. This adjusted volume is multiplied by solute concentrations in the ‘water applied’ ($C_{Water\ Applied}$) to estimate the contribution of ‘water applied’ to solute loading in the seepage.

Adjusted solute loading in seepage (moles)

$$= Seepage\ Volume\ (L) \times \left[C_{Seepage} \left(\frac{moles}{L} \right) - C_{Water\ Applied} \left(\frac{moles}{L} \right) \times f_{Water\ Applied} \right]$$

Figure 3 shows the adjusted loading of sulfate, calcium, and magnesium in seepage from TP3. Other development rock test pads show similar trends for adjusted loading of these solutes in seepage.

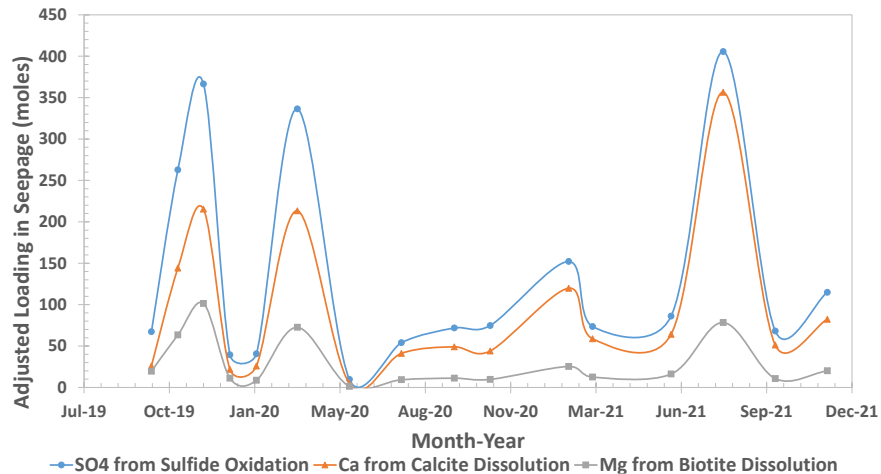
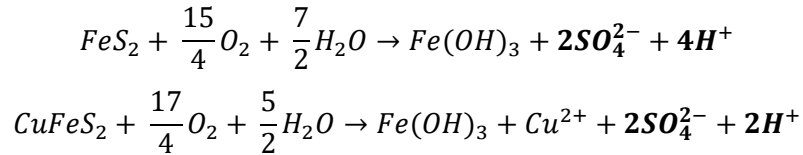


Figure 3. Adjusted solute loading in test pad seepage

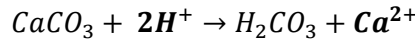
Estimation of acid generation-neutralization balance

Based on pyrite and chalcopyrite oxidation reactions below, two moles of sulfate are released per mole of pyrite or chalcopyrite oxidized. Two moles of H^+ are released per mole of sulfate released from pyrite oxidation, as opposed to one mole of H^+ released per mole of sulfate released from chalcopyrite oxidation. Based on test pad seepage chemistry observed, only abiotic sulfide mineral oxidation by oxygen is considered in this evaluation. Biotic sulfide oxidation by ferric iron is dominant only at low pH conditions (pH < 4.5) due to the dependence of ferric iron solubility on pH.

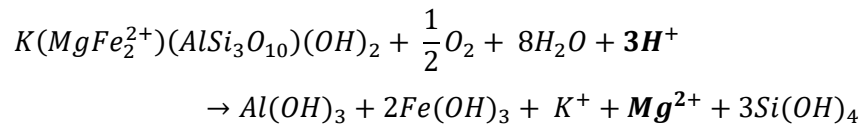


$$\text{Total } H^+ \text{ released} = (H^+ \text{ moles released})_{\text{Pyrite}} + (H^+ \text{ moles released})_{\text{Chalcopyrite}}$$

Two moles of H^+ neutralization is available for every mole of calcium released from calcite dissolution.



Based on the oxidative weathering reaction of biotite, one mole of magnesium is released per mole of biotite dissolved. Three moles of H^+ neutralization are available for every mole of magnesium released from biotite dissolution.

**Total H^+ neutralization available**

$$= (H^+ \text{ neutralization available})_{\text{Calcite}} + (H^+ \text{ neutralization available})_{\text{Biotite}}$$

Alkalinity in the ‘water applied’ is also a likely contribution to H^+ neutralization. However, alkalinity is reported based on lab titrations to a standard pH endpoint of 4.2. The $(H^+ \text{ neutralization available})_{\text{Water Applied}}$ cannot be accurately estimated using the lab reported alkalinity in the ‘water applied’. Assuming two moles of H^+ neutralized for every mole of alkalinity, results in the contribution of ‘water applied’ to ‘total H^+ neutralized’ to be minimal. Figure 4 for TP3 shows that the ‘net H^+ neutralization available’ in seepage is predominantly positive (excess neutralization available) when considering only calcite and biotite dissolution. Findings from other test pads are similar and consistent with the near-neutral pH and moderate alkalinity values (~60 mg/L as $CaCO_3$) of the seepage.

$$\text{Net } H^+ \text{ neutralization available} = \text{Total } H^+ \text{ neutralization available} - \text{Total } H^+ \text{ released}$$

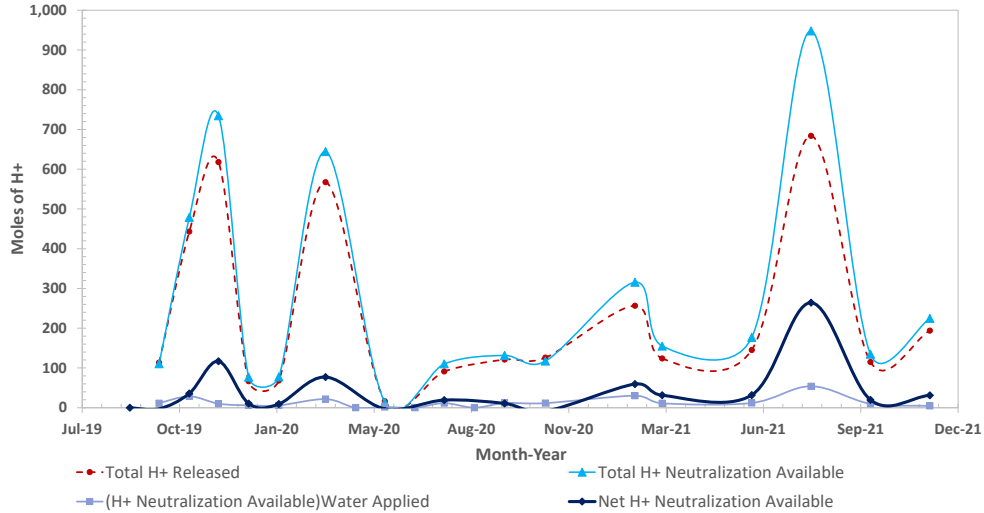


Figure 4. Estimated acid generation-neutralization balance

Estimation of mineral reaction rates

Adjusted sulfate loading is used to estimate pyrite and chalcopyrite oxidation rates in the test pads. In order to estimate the appropriate fraction of sulfate contributed by each mineral, a relationship between pyrite and chalcopyrite weathering is required. Sulfide mineral oxidation reactions are surface controlled kinetic reactions; hence, accessibility to the mineral surface strongly controls reaction rates. Steger and Desjardins (1978) showed with weathering experiments that the relative reactivity of pyrite is approximately two times that of chalcopyrite. Stromberg et al. (1994) proposed a linear dependence between mineral reaction rates for pyrite (R_{Py}) and chalcopyrite (R_{Cpy}), mineral abundance (mole/m³) for pyrite (V_{Py}) and chalcopyrite (V_{Cpy}), and relative reactivity.

$$\frac{R_{Py}}{R_{Cpy}} = \left(\frac{V_{Py}}{V_{Cpy}} \right) \times 2$$

Mineral abundance, V (mole/m³) = Pre – test mineral content (mole/kg) × Rock density (kg/m³)

The underlying assumption is that for both pyrite and chalcopyrite, the accessible surface areas for reaction are available in proportion to their relative mineral abundance in the corresponding test pad. This approach has been used in the literature to account for accessible surface areas of the sulfide minerals (Eriksson and Destouni 1997). XRD mineral content (Table 1) and mineral molar mass are used to calculate the pre-test mineral content of pyrite and chalcopyrite in mole/kg. Assuming the test pads as truncated square pyramids, the volume of each test pad is estimated as 1185 m³. Assuming a rock density of 2600 kg/m³ and porosity of 30%, the bulk density is estimated as 1800 kg/m³ and mass of rock in each test pad as 2100 metric tons. Adjusted sulfate loading from pyrite is used to calculate pyrite oxidation rate as shown below. Chalcopyrite oxidation rate is calculated similarly.

$$Sulfate_{pyrite} \left(\frac{\text{moles}}{\text{month}} \right) = \left(\frac{\left(\frac{R_{py}}{R_{cpy}} \right)}{1 + \left(\frac{R_{py}}{R_{cpy}} \right)} \right) \times \text{Adjusted sulfate loading} \left(\frac{\text{moles}}{\text{month}} \right)$$

$$Sulfate_{chalcopyrite} \left(\frac{\text{moles}}{\text{month}} \right) = \left(\frac{1}{1 + \left(\frac{R_{py}}{R_{cpy}} \right)} \right) \times \text{Adjusted sulfate loading} \left(\frac{\text{moles}}{\text{month}} \right)$$

$$R_{py} \left(\frac{\text{mole}}{\text{kg.s}} \right) = \frac{Sulfate_{pyrite}(\text{moles/month})}{\left(\frac{2 \text{ moles of sulfate}}{\text{mole of pyrite}} \right) \times (\text{kg of rock in test pad}) \times \frac{\text{days}}{\text{month}} \times \frac{86400 \text{ s}}{\text{day}}}$$

Adjusted calcium loading and the stoichiometric relationship discussed earlier (1 mole of calcium per mole of calcite) are used to estimate the calcite dissolution rate. Biotite dissolution rate is calculated via a similar approach.

$$\text{Calcite dissolution rate} \left(\frac{\text{mole}}{\text{kg.s}} \right) = \frac{\text{Adjusted Calcium Loading} (\text{mole/month})}{\left(\frac{1 \text{ mole of calcium}}{\text{mole of calcite}} \right) \times (\text{kg of rock in test pad}) \times \frac{\text{days}}{\text{month}} \times \frac{86400 \text{ s}}{\text{day}}}$$

Figures 5 and 6 show sulfide oxidation and neutralizing mineral dissolution rates, respectively. Fluctuations observed in the rates are most likely due to variability in the monthly total water received. Peaks in reaction rates correspond to periods of high-intensity precipitation or unplanned increase in water application due to major leaks (e.g., TP3 in Aug-21), which promote flushing of stored oxidation/ weathering by-products. No long-term increasing or decreasing trends are observed in the reaction rates.

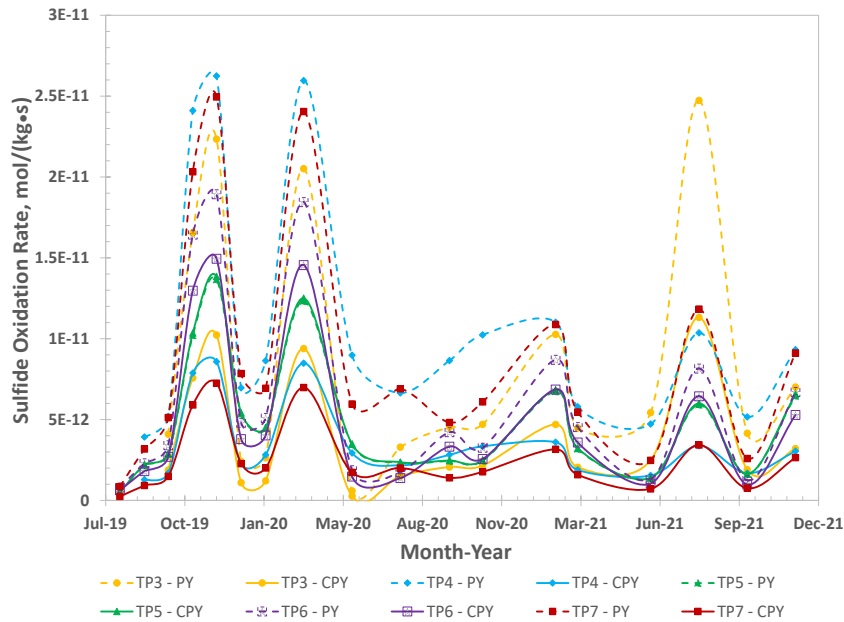


Figure 5. Estimated pyrite and chalcopyrite oxidation rates

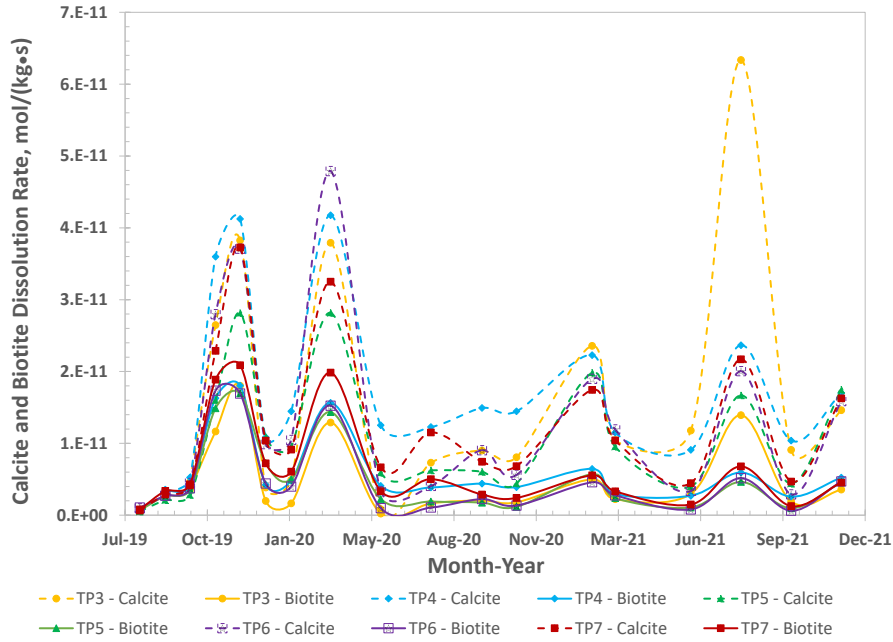


Figure 6. Estimated calcite and biotite dissolution rates

The estimated mineral reaction rates are within typical ranges reported in literature from other lab and field studies (Stromberg et al. 1994, Peterson 2014).

Estimation of time to consume minerals

The number of years to consume the primary acid generating minerals (pyrite and chalcopryrite) and acid neutralizing minerals (calcite and biotite) are estimated to understand if the test pad materials will eventually become acid generating. The current solute loading rates are assumed to be representative of the long-term minerals reaction rates.

$$Time\ to\ consume\ mineral\ (years) = \frac{Pre - test\ mineral\ content\ (mole/kg)}{Average\ mineral\ reaction\ rate\ \left(\frac{mole}{kg.s}\right) \left(\frac{365\ days}{year}\right) \left(\frac{86,400\ s}{1\ day}\right)}$$

This calculation assumes that all the pre-test mineral content is available for reaction, not just the fraction exposed on the surface. In addition, it does not consider that only a fraction of the rock surfaces are contacted by water and are available for active mineral-water interactions. Hence, the results from this calculation do not represent the actual time to consume the minerals. No data were collected regarding ‘water to rock’ contact ratios and surface exposure, i.e., percentage of mineral exposed on the surface and available for reaction. However, assuming that all the minerals discussed have similar surface exposure, these estimates reasonably represent the relative time to consume the minerals. Figure 7 shows that for all

the development rock test pads, the acid neutralizing minerals, especially calcite are likely to remain available after the acid-generating minerals are consumed. Hence, the development rock materials are not predicted to become acid generating in the future.

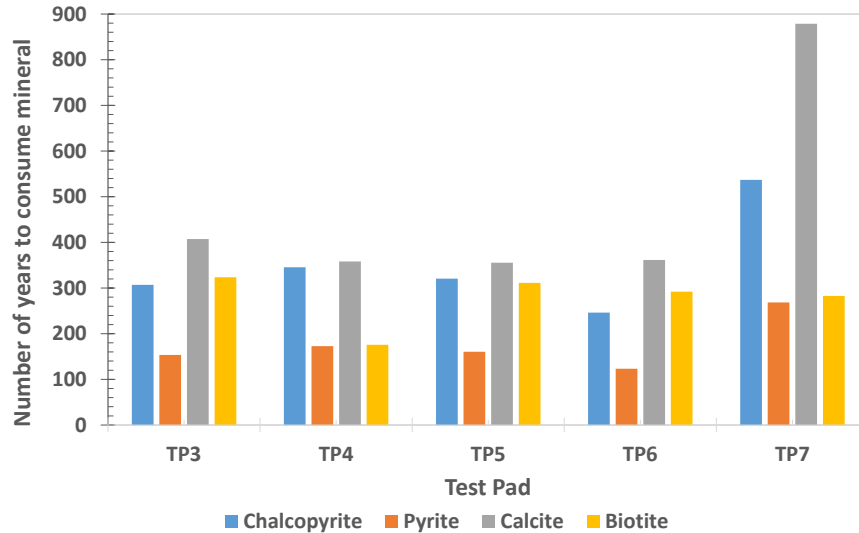


Figure 7. Estimated number of years to consume mineral

Conclusions

Field studies provide a more representative estimation of ARD potential of materials as compared to lab tests. This is especially true for mine sites in arid/ semi-arid climates such as the Bagdad mine in Arizona. After approximately 2.5 years of weekly water application and natural precipitation, seepage pH from all development rock test pads have remained near-neutral (7.5-8.5) with moderate alkalinity (~60 mg/L as CaCO_3). These observations are consistent with the estimated acid generation-neutralization balance based on seepage solute loading rates and stoichiometric solute-mineral relationships. Weekly water application employed in the study is expected to have accelerated the mineral oxidation and weathering reactions. Nevertheless, the mineral reaction rates estimated here provide a reasonable understanding of the long-term ARD potential. Future stockpiles constructed with the development rock materials included in this study are not likely to become acid generating based on the mineral contents and estimated reaction rates for pyrite, chalcopyrite, calcite, and biotite.

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