PROTECTED B

NRC·CNRC

Quantifying Oxidation and Acquiring Data Pertinent to Neutralization Rates of Troilus Mine Wastes (Phase I)

Volume: 1

Report Number: NRC-EME-56511

Date: June 23, 2023

Author(s): Nadia Zavala, Kidus Tufa, Eben Dy, Simon Liu, Cheng Huang, Liang Ma

CBI: Energy, Mining and Environment

National Research Council Canada
Conseil national de recherches Canada

Canada

Table of Contents

Table of Figures

Introduction

Background

The Troilus Gold Project is located in Quebec, approximately 120 kilometers north of Chibougamau, where Inmet Mining Corporation operated a large mine/concentrator complex from 1996-2010. The Troilus Gold site is composed of several ore zones, including the J4 ore zone partially mined in the past as a pit. A Drainage Monitoring Station STP-9 is located nearby, which monitors drainage chemistry from the existing J4 waste-rock pile.

Troilus is conducting environmental assessment studies on existing waste rock piles at the Troilus mine site and planning the management of new waste rock piles generated from future operations. Troilus is also interested in the carbon dioxide (CO_2) absorption and emission from these waste piles.

Many studies involving acid-base accounting (ABA) have been conducted for decades on the J4 ore zone waste rock—for example, prior to mining (e.g., 1992 and 1993), during mining from ~1996-2010 (e.g., 2003, 2004, and 2009), and after mining (e.g., 2011 and 2019). All these acid rock drainage (ARD) studies reached the conclusion that the rock from J4 were almost entirely net acid generating (“PAG”) and would release ARD. [Acid is formed by the reaction of sulfide minerals, such as pyrite, in the waste rock with oxygen (O_2) in the air and water.] Only the most recent studies addressed issues like lag times and intensities. These studies found that pyrite in J4 waste rock oxidizes slowly relatively,[1] and that the lag time to ARD would be 100 to 1000 years. However, rinse pH as low as 3.7 has already been detected in the existing J4 waste rock.

Troilus would like to find answers to the following questions:

- Why did nearly all ABAs done from 1992 to 2019 say that the existing J4 waste rock is almost entirely net acid generating (“PAG”), but acidic pH has not been measured at the Drainage Monitoring Station STP-9?
- Why have a few acidic rinse pH values been measured in existing J4 waste rock, but acidic pH has not been measured at STP-9?
- Are predictions that ARD will appear in 100 years or 1000 years reasonable, or will ARD ever appear?

---

[1] Kinetic Tests on Selected Samples of Waste Rock from the J4 Rock Pile, Lawrence Consulting, November 30, 2021.

- What are the current and future CO_2 uptake and emission profiles from these waste rock piles?

Troilus would also like to resolve these questions through full-scale modeling of the existing J4 waste rock pile and future J4 waste rock pile.

The NRC's research team has developed the modeling, characterization and data analysis capabilities for ARD prediction to study the kinetics of sulfide minerals oxidation reactions and neutralization reactions inside mine waste materials, water/gas transport coupled with geochemical reactions and metal leaching (ML) inside waste rock piles and unsaturated tailings. These capabilities enable the NRC's research team to tackle the request.

In addition to sulfide minerals, carbonates and silicates are also contained in the waste rocks. The carbonate minerals can neutralize the acidity produced by the oxidation of sulfide minerals producing CO_2 while silicate minerals can take up CO_2. Hence this research service project provides a great opportunity for the client and NRC research team to explore about the potentials of CO_2 storage by mine-site components.

The proposed project was originally planned in three phases as detailed below:

> Phase I: Quantifying Oxidation and Acquiring Data Pertinent to Neutralization Rates of Troilus Mine Wastes is the subject of this report.
>
> Phase II: Customized metal leaching testing and full-scale modeling of J4 waste rock pile will be the subject of a future research proposal.
>
> Phase III: Pile operational monitoring for full-scale modeling validation and data analysis for long term prediction will be the subject of a future research proposal when field measurements and instrumentation are available.

Only Phase I is the scope of this report. The objectives of this Phase I project are: 1) to quantify the oxidation rate of J4 waste rock through the oxygen consumption (OxyCon) test, 2) to acquire data associated neutralization reactions rates from CO_2 generation (CO2Gen) and effluent water quality monitoring, and 3) to study the neutralization products' passivation potential through mineralogical characterization. In consultation with Troilus, the scopes of Phase II and III may change based on the results of Phase I.

The purpose of this report is to provide the final results of this project year as well as to make recommendations for the next phase.

Experiments

Troilus provided representative freshly crushed rock samples from their J4 waste rock pile. They were freshly crushed into two sizes: 4-6 mm (course) and <1 mm (fine).

The course rock were loaded into three 4” (diameter) x 8” (height) test cells [Figure 1 (a)] and the fines were loaded into three 8” (diameter) x 2” (height) cells [Figure 1 (b)]. A total of six test cells were setup.

Water was flushed through and collected from these cells for a total of 43 cycles on a weekly basis except when OxyCon tests, which took additional days, were inserted between flushing cycles. For each flushing cycle, the effluents from each column were tested for pH, conductivity, sulfate, acidity, alkalinity, total inorganic carbon (TIC) and concentration of acid forming/neutralizing elements: Na, Ca, Mg, K, Al, Fe and Si.

After flushing cycles 6, 12, 18, 24, 27, 33 and 39, OxyCon and CO2Gen rates of the samples in the test cells were measured using NRC’s proprietary OxyCon testing equipment. O_2 consumption is a direct measure of the rate of sulfide oxidation, the main source of acid generation. CO_2, on the other hand, is a direct measure of acid neutralization by carbonates.

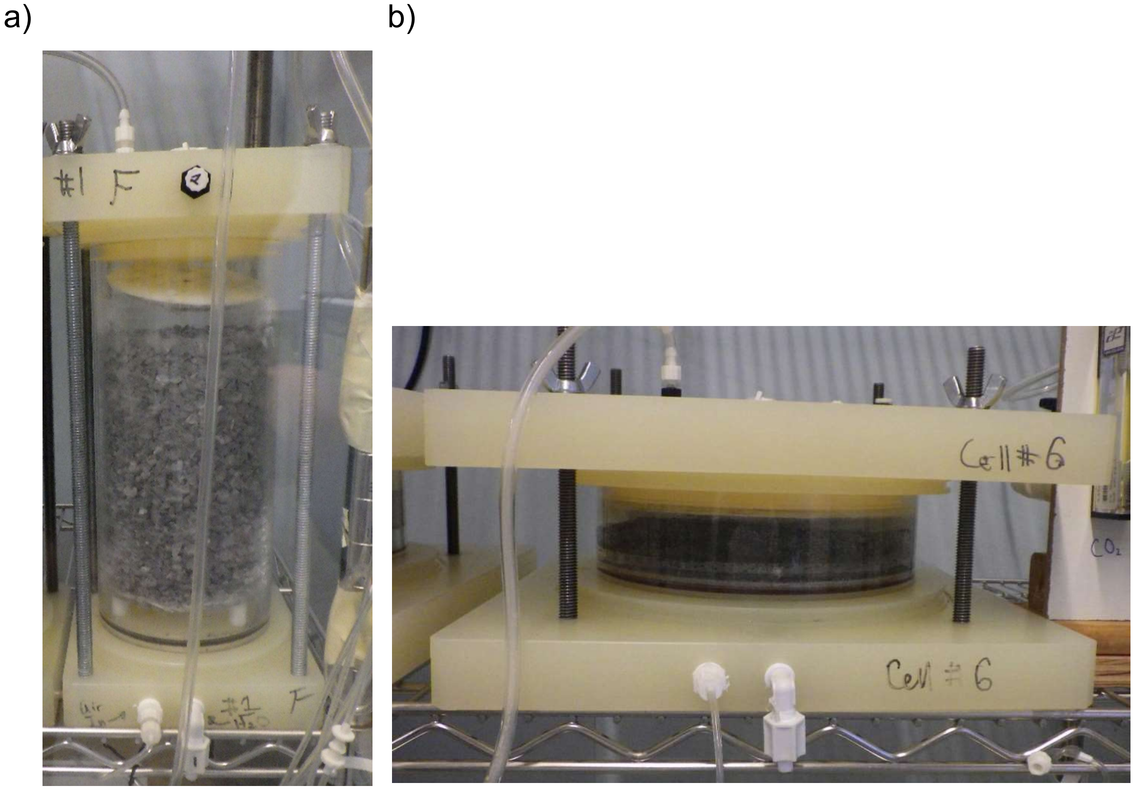


Figure 1. Reaction cells for OxyCon test and effluent water analysis. Cells are equipped with connectors for supplying and draining water, purging with humid or dry air, and enclosing the chamber for recirculating air to O_2 and CO_2 sensors. The dimensions of the sample compartment for course (4-6 mm) rock (a) are 4“(diameter) x 8” (height) while those for < 1mm fines (b) are three 8” (diameter) x 2” (height).

Samples from one of the cells (#4) were collected during the later cycles to observe if secondary minerals are forming. To gain a baseline understanding of primary minerals originally present for comparison, fresh course rock samples were also studied by thin section petrography, Raman spectroscopy, XRD, SEM/EDX and combustion-IR (LECO) C/S analysis.

Experimental Task 1. Oxygen consumption and carbon dioxide generation (OxyCon) Test

The O_2 and CO_2 concentration were measured for each of the six cells as a function of time using NRC's proprietary OxyCon testing equipment after flushing cycles 6, 12, 18, 24, 27, 33 and 39.

Prior to the start of every OxyCon test cycle, six sets of O_2 and CO_2 sensors were calibrated versus nitrogen (0% O_2 and 0% CO_2, blank), a 4% CO_2 certified gas standard, and air (20.98% O_2).

Each of the six cells were then connected to their respective pump, O_2 sensor, CO_2 sensor and back to the cell in a closed loop. The air in the cell was recirculated by the pump to the CO_2 and O_2 sensors. The CO_2 and O_2 concentration in the cells were logged as a function of time every 30 seconds for five days (except for cycle 27 which was extended to two weeks).

At the end of each OxyCon test cycle, the cells were disconnected from the sensors and the pumps. The sensors were validated against the same set of standards for quality control after each test. The sensors are purged with nitrogen for drying and put away. Data from the loggers were downloaded for processing. The cells then continued on with their flushing cycle: purged with dry air for three day and humidified air for another three days and flushed with one Liter of water.

Experimental Task 2. Water solubility of reaction products

The OxyCon cells were flushed with one Liter of DI water at the start of the experiment. The effluents from the cells were collected for water quality analysis.

Effluents from each cell were immediately filtered through 0.45-micron MCE filters and collected in polypropylene bottles. pH and conductivity were measured within one hour after filtration of the collected samples. A 50-mL portion of each effluent were preserved by adding drops of concentrated HNO_3 acid to pH 2 and stored in a refrigerator for analysis of dissolved ions. Another 50-mL portion of the effluent were kept in the refrigerator for sulfate analysis. The total inorganic carbon (TIC), acidity and alkalinity were measured within three hours after filtration

The TIC was analyzed with a Skalar Fromacs HT TOC analyzer following manufacturer procedures. pH and conductivity were measured with a PCE Instruments PHD-1 combination meter. Acidity was analyzed with a Hanna HI84530U-01 auto-titrator and alkalinity by manual titration following APHA Standard Methods for the Examination of Water and Wastewater.

On the next day, the cells were purged with dry air for three days and then purged with water-saturated air for another three days. This flush-dry-humidify cycle was repeated weekly except with one variation: after flushing cycles 6, 12, 18, 24, 27, 33 and 39 where OxyCon tests were inserted prior to the dry air purging step.

Within 30 days after sample collection, the dissolved Ca, K, Na, Mg, Fe, Si and Al ion contents of the collected samples were analyzed following manufacturer recommended conditions with a PerkinElmer PinAAcle 900F flame atomic absorption spectrometer (AAS). Sulfate contents were analyzed by barium precipitation following the manufacturer's procedure with Millipore 1018120001 sulfate test kits on a Millipore Move 100 Photometer.

Experimental Task 3. Mineralogical characterization and microscopic observation of reaction products

The objective of this task is to observe the secondary minerals (oxidation/neutralization products) by microscopy in order to understand any possible passivation effect.

As a first step, it is important to know the primary minerals originally present in the freshly crushed rock. Samples of fines were mounted on ten sample holders with epoxy, polished and analyzed for bulk mineral composition by powder XRD using a Bruker AXS D8 Advance X-Ray Diffractometer. Five samples of fines were also analyzed for bulk carbon and sulfur content by a LECO furnace combustion-infrared detection carbon and sulfur analyzer. Course rock specimens were mounted in epoxy and polished into thin section for petrographic microscopy. Minerals as identified by petrographic microscopy were observed under a Hitachi S-3500N Scanning Electron Microscope (SEM) with an Oxford Instrument X-Max energy-dispersive x-ray fluorescence detector (EDX) in backscattering mode. Elemental analysis by EDX is particularly important for knowing the possible sources of acid neutralizing ions, such Ca, Na, Mg and K, in the effluents.

Thin section petrography and SEM/EDX in backscattering mode only works for samples that are well-polished. Thin sections petrography also requires that rocks be cut to 30 microns thick. Unfortunately, these techniques are not applicable to fines obtained from flushing and drying of test cell effluents, which are by nature irregular in shape. The approach chosen to study the minerology of particles obtained from test cells is Raman microscopy. Raman spectra of minerals identified by thin section petrography and SEM/EDX were compared to a commercial Raman mineral library supplied with a Renishaw InVia Raman Microscope. A Raman library of Troilus minerals was also created to improve the match quality of minerals as compared to those from commercial libraries.

Samples were taken from Cell #4 starting cycle number 30. Particles were studied by Raman microscopy.

Results and Discussions

Experimental Task 1. Oxygen consumption and carbon dioxide generation (OxyCon) Test

Figure 2 shows the raw O_2 and CO_2 data downloaded from the loggers for Cells 1, 2 and 3 containing course (4-6 mm) crushed rock while Figure 3 shows the raw O_2 and CO_2 data obtained for Cells 4, 5, and 6 containing fine (<1mm) crushed rock.

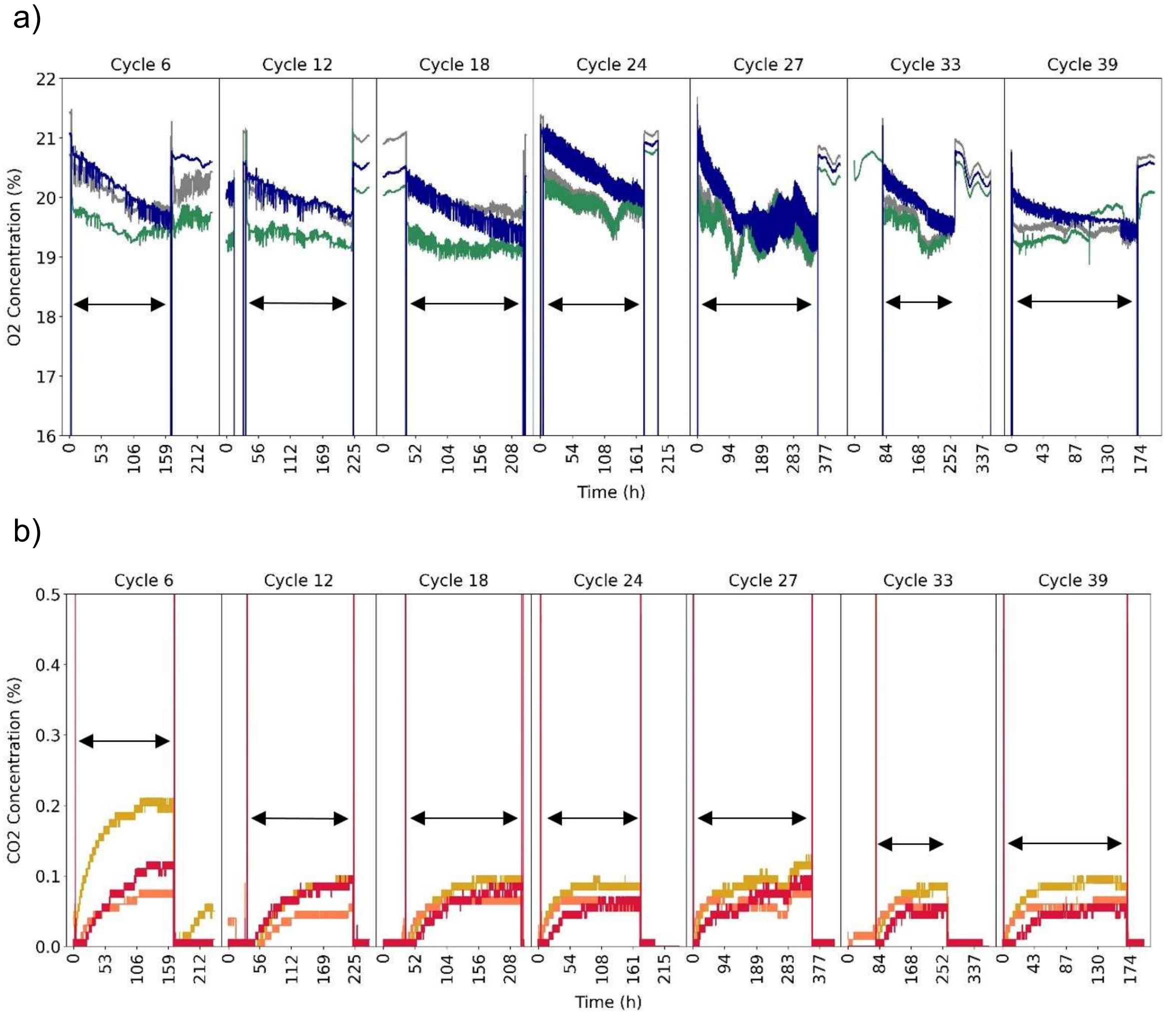


Figure 2. OxyCon test raw data logged from cells containing course (4-6 mm) particles of Troilus J4 rock. Oxygen sensor readings for cells 1(gray), 2(green) and 3(blue) cycles (a) 6, 12, 18, 24, 27, 33 and 39 were recorded as $\%O_2$ versus time interval (30 seconds per data point). Carbon dioxide sensor readings for cells 1(yellow), 2 (orange) and 3(red) cycles (b) 6, 12, 18, 24, 27, 33 and 39 were recorded as $\%CO_2$ versus time interval (30 seconds per data point).

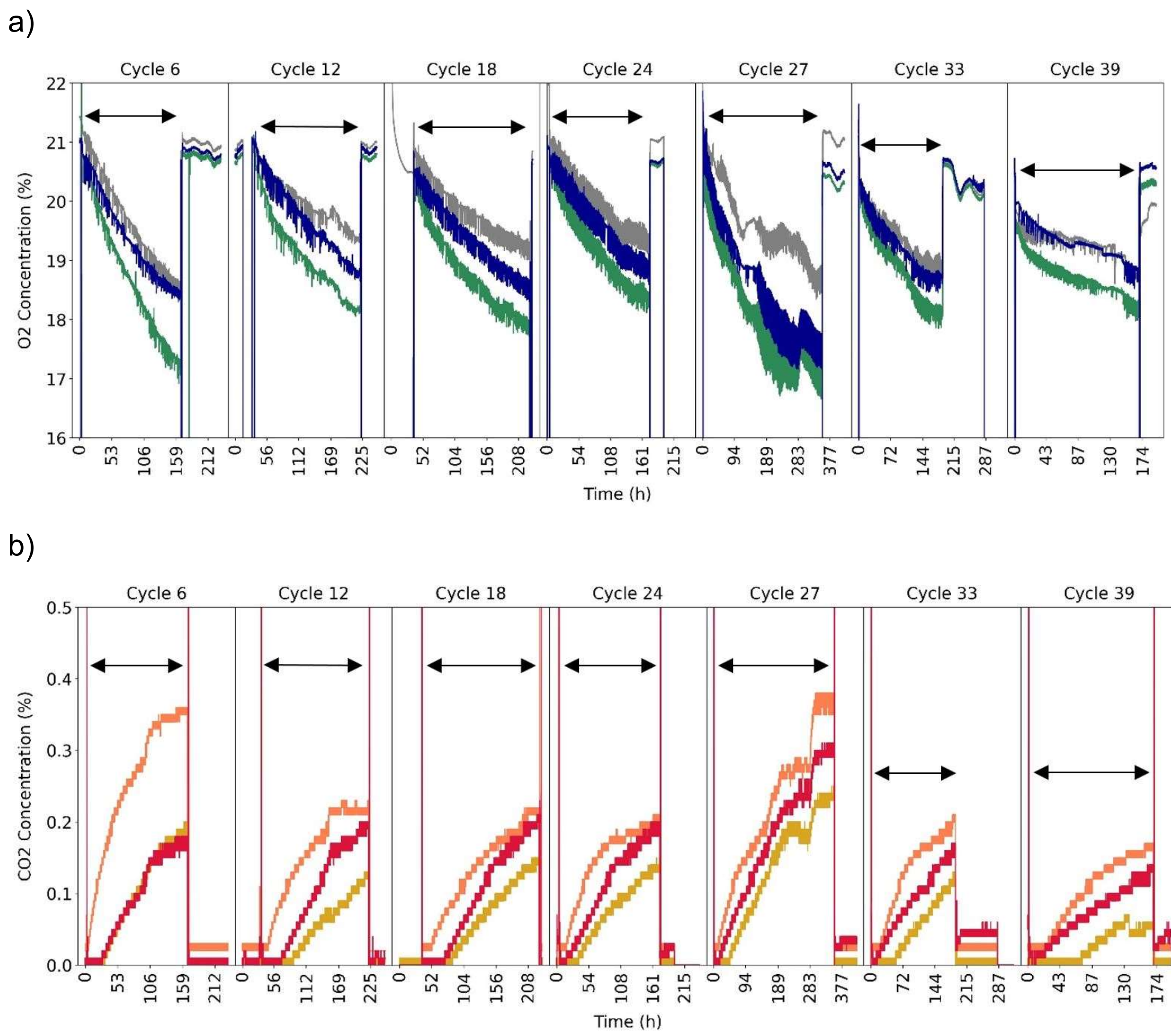


Figure 3. OxyCon test raw data logged from cells containing fine (<1mm) particles of Troilus J4 rock. Oxygen sensor readings for cells 4(gray), 5(green) and 6(blue) cycles (a) 6, 12, 18, 24, 27, 33 and 39 were recorded as %O_2 versus time interval (30 seconds per data point). Carbon dioxide sensor readings for cells 4(yellow), 5 (orange) and 6(red) cycles (b) 6, 12, 18, 24, 27, 33 and 39 were recorded as %CO_2 versus time interval (30 seconds per data point).

The data was processed for calibration, drift correction and smoothing, and curve fitted. Where the standards deviated before and after the test cycle, the data were either corrected for drift or, in cases where the detectors malfunctioned (cycle 39, cells 2,3, and 4), rejected. Figure 4 shows the best fit lines for oxygen consumption while Figure 5 shows the best fit lines for CO_2 generation.

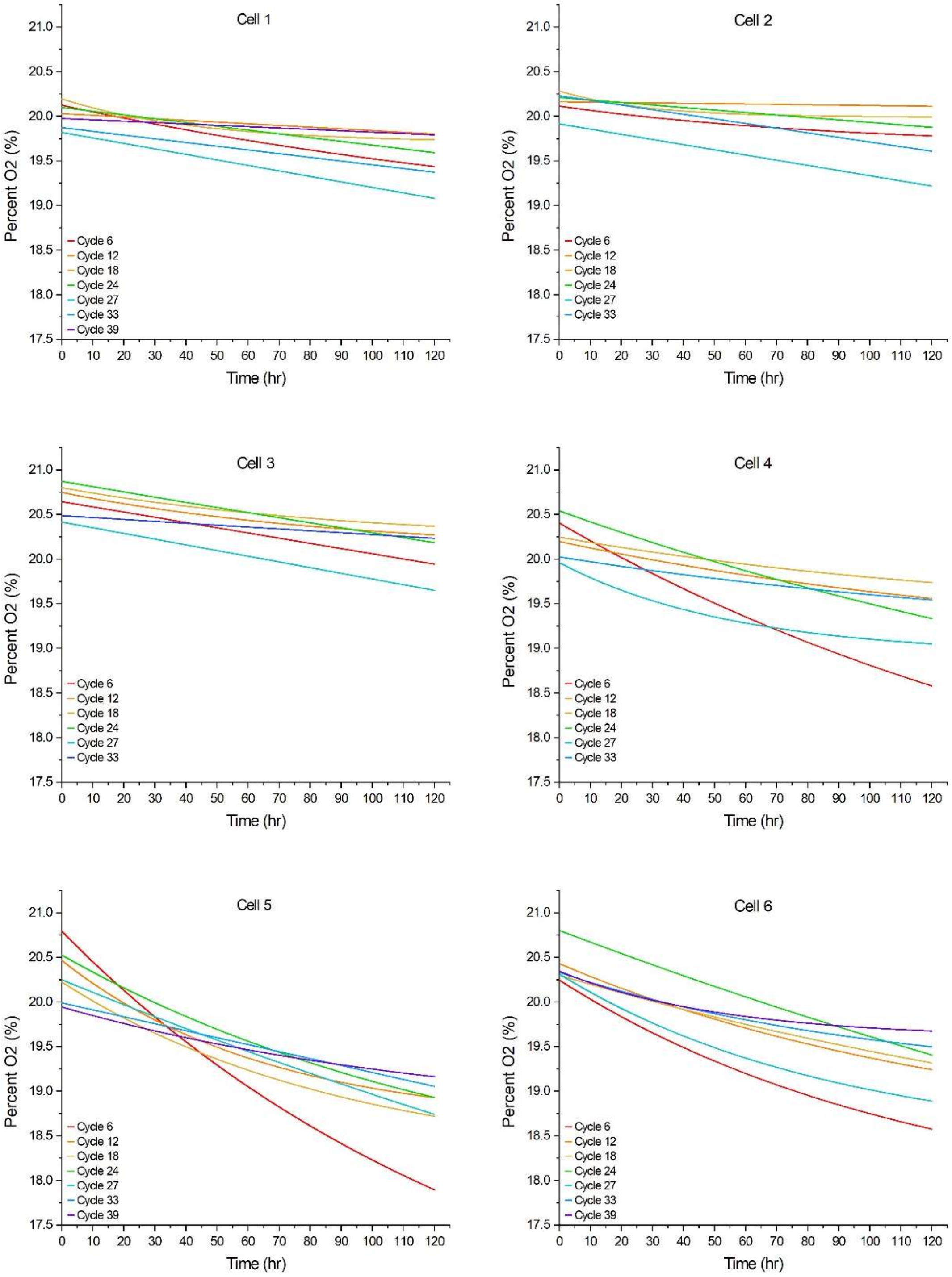


Figure 4. Processed oxygen consumption test data for Troilus J4 rock.

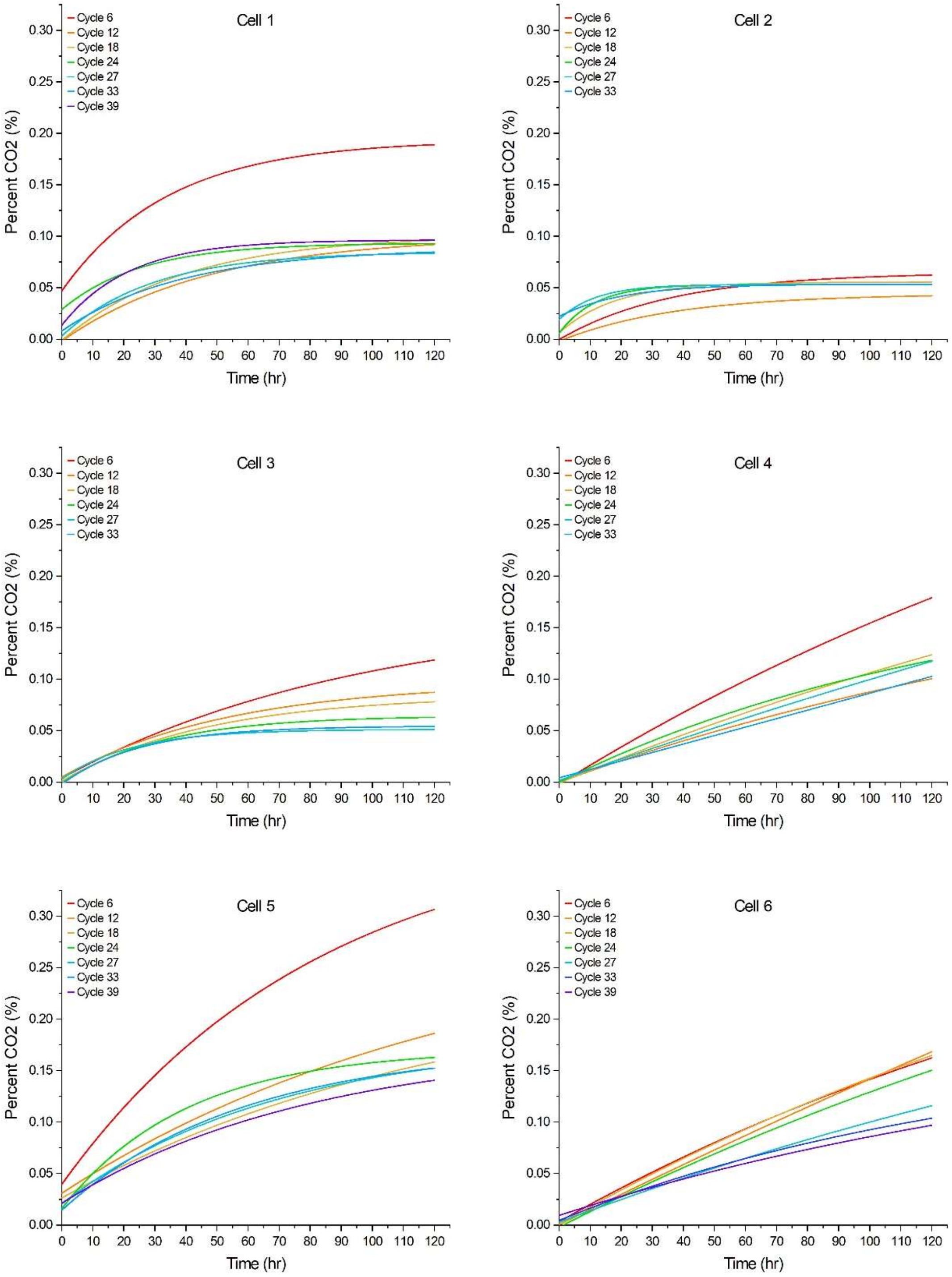


Figure 5. Processed oxygen consumption test data for Troilus J4 rock.

It can be seen that the oxygen consumption rate for Troilus rock is very small. The first OxyCon test (performed after wetting Cycle #6) shows faster reaction kinetics than the subsequent tests (Cycles #12, 8, 24, 27, 33 and 39) for cells #4, 5 and 6. The subsequent OxyCon tests yielded essentially the same results.

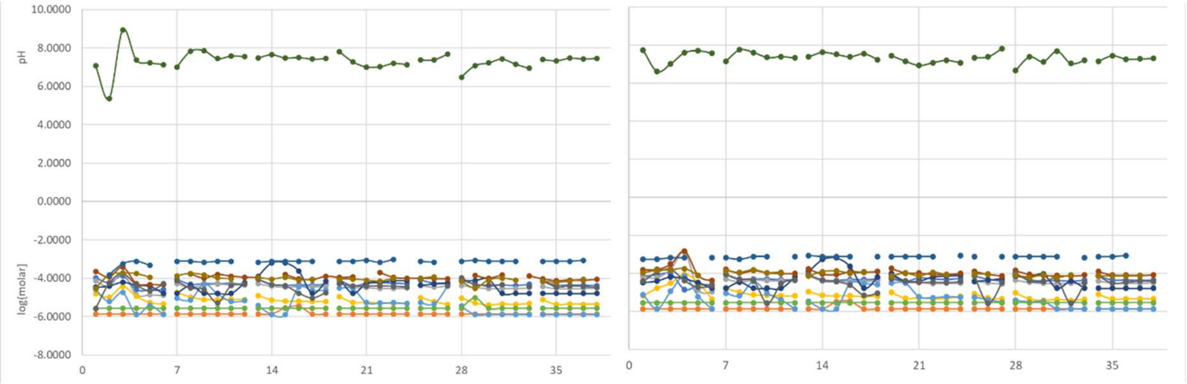
CO_2 generation rate is proportional to oxygen consumption. It is not clear at this point if CO_2 is generated from primary carbonates (pre-existing in the crushed rock) or from carbonates generated in-situ between flushing cycles from CO_2 in the atmosphere and dissolved alkali/earth ions from the rock. Presuming that the CO_2 is from pre-existing carbonates, it may take a long time before CO_2 generation decline given the slow oxygen consumption rate. But eventually, the carbonate minerals would deplete with time and the effluent will turn acidic. On the other hand, if the CO_2 were generated from CO_2 in the atmosphere trapped by dissolved alkali/earth ions, it is quite possible that the acid generating sulfides deplete before the alkali/earth elements in the rock are completely consumed. The elemental contents and mineralogy of the rock will be discussed in subsequent sections.

A key parameter for pile scale modeling is K, oxygen consumption rate, where $dP_{O2}/dt = -KP_{O2}$. These tests showed that the rate of oxygen consumption is about 0.186 mole O_2 per ton of fine crushed rock per day and about 0.056 mole O_2 per ton of coarse rock per day. These tests showed that the rate of CO_2 gas production is about 0.018 mole CO_2 per ton of fine crushed rock per day and about 0.007 mole CO_2 per ton of coarse rock per day.

Raw data and details of the calculations can be downloaded from the Troilus Project shared folder in NRC's NextCloud. The NRC will use oxidation and neutralization rates derived from these tests for full-scale modeling of J4 pile in the next phase. These reaction rates are approximations that can be used for the first iteration of modeling. These rates, however, could change with conditions such as moisture content and temperature, so field testing is recommended for Phase II. Due to possible changes in chemical reaction rates, the continuation of laboratory OxyCon testing and monitoring of effluent water quality is also recommended for Phase II.

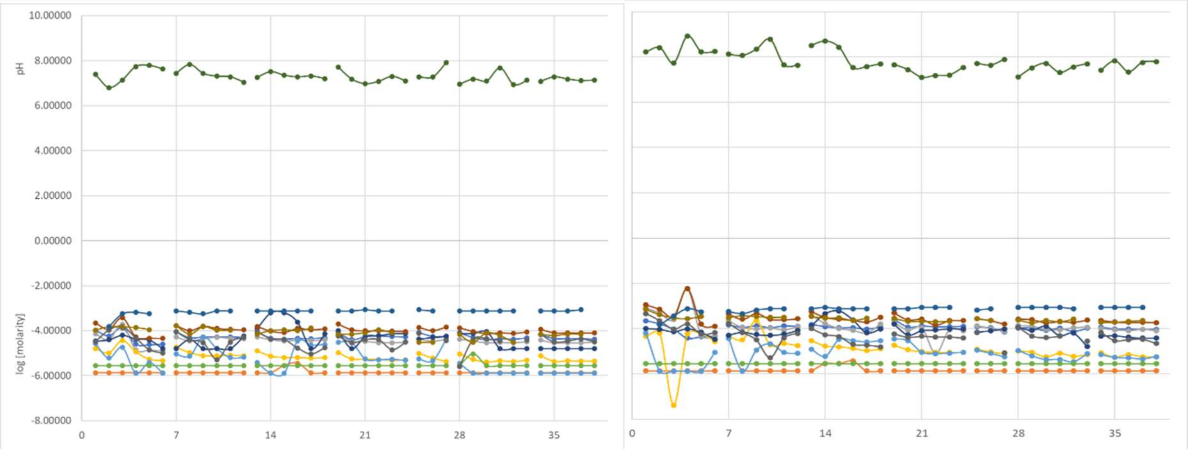
Experimental Task 2. Water solubility of reaction products

For each flushing cycle, the effluents from each column were tested for pH, conductivity, sulfate, acidity, alkalinity, total inorganic carbon (TIC) and concentration of acid forming/neutralizing elements (Na, Ca, Mg, K, Al, Fe and Si). The results are compiled and plotted as pH or log molar concentration versus flushing cycle as shown in Figure 6.



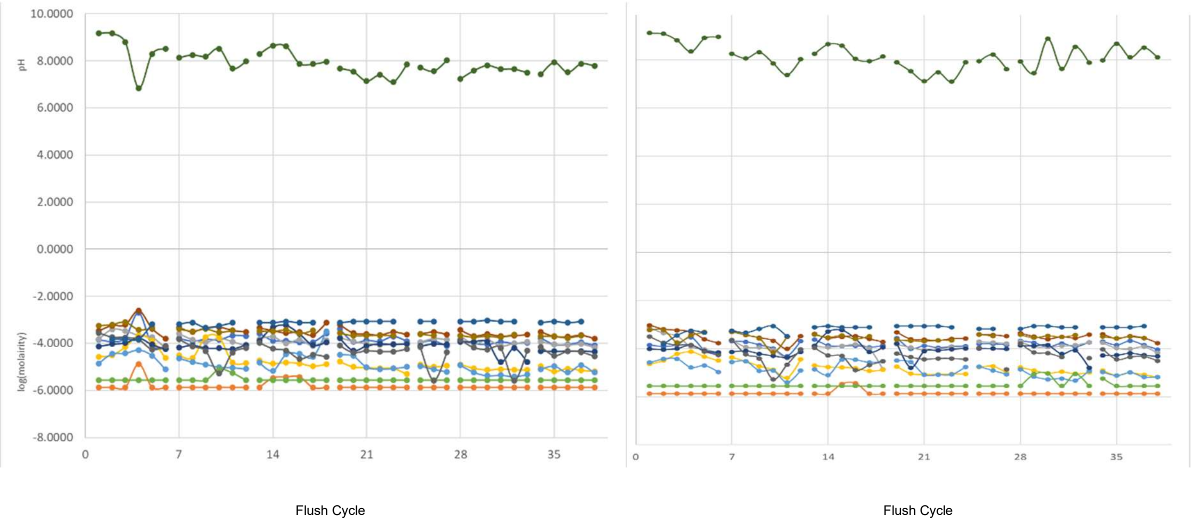
a) Cell # 1

b) Cell #2



c) Cell #3

d) Cell #4



e) Cell # 5

f) Cell #6

Figure 6. Water quality analysis results for cells 1(a), 2(b), 3(c), 4(d), 5(e) and 6(f) plotted as log of molar concentration (—●—Ca —●—Fe —●—K —●—Mg —●—Na —●—Al —●—Si —●—Ca+K+Mg+Na —●—SO4 —●—Alk —●—Acid)and pH (—●—) as a function of flushing cycle.

As can be seen from the results, the water quality is unremarkable with low sulfate content and circumneutral pH (except for cycle 2 of cell 1, which is slightly acidic). Water quality normalized after the first few cycles suggesting that the ions flushed out during the first few cycles were partly generated from reactions prior to cell testing. The results are consistent with slow oxidation of sulfides and neutralization by carbonates.

The pH has remained between 6.5 to 7.9 for cells 1-3 (course rock) and 7.1 to 8.9 for cells 4-6. The sulfate contents are mostly in the 10^{-4} M range with some in the 10^{-3}M range for fine crushed rock. Effluents show low to sub ppm levels of calcium, potassium, silicon, sodium and magnesium. Iron and aluminum were not detected, which is expected under circumneutral pH condition. Acidity and Alkalinity were consistently low.

When compared with field data, the OxyCon cell effluents contain less dissolved ions. This can be attributed to the difference in water-to-rock ratio as well as time periods between flushing. Potassium (K) concentration in the water from OxyCon test cells is closer to calcium (Ca) concentration while it was about an order of magnitude less than Ca in the field data.

It is inconclusive if dissolved ions and pH from flushing cycles with OxyCon tests were higher due to longer reaction time. The results suggest that weekly flushing cycles as required by standard procedures for humidity cell testing may not be ideal for this type of slow reacting rock. For changes in dissolved ion concentration and pH to become more significant, it is recommended that the reaction time (dry-wet air purging) between flushing be extended to once every four weeks

Raw data and details of the calculations can be downloaded from the Troilus Project shared folder in NRC’s NextCloud.

Experimental Task 3. Mineralogical characterization and microscopic observation of reaction products

Powder X-Ray Diffraction

X-Ray Diffractometer (XRD) observes the diffraction pattern of x-ray by caused surface atoms, which varies with atomic arrangements within the crystal structure of different minerals. XRD is used to determine minerals component present in the bulk rock sample and their relative quantity.

Samples of finely crushed Troilus J4 rock were mixed with a small amount of (amorphous) epoxy, casted into ten sample holders and polished (Figure 7).

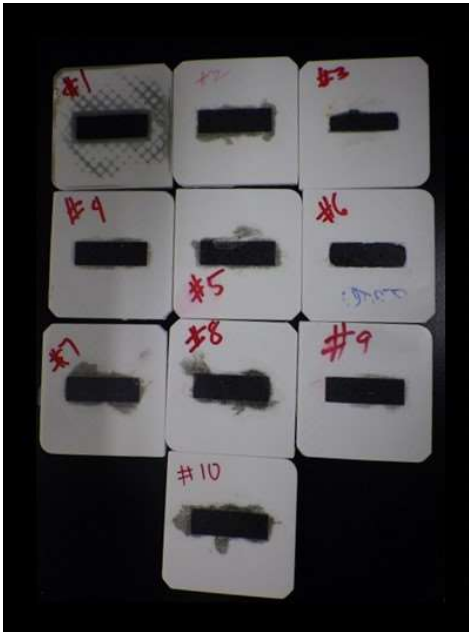


Figure 7. Fine (<1mm) Troilus J4 rock samples mounted on epoxy and polished for XRD analysis.

The ten samples were analyzed by XRD. The diffractograms obtained were processed by the PowdR full pattern summation algorithm using the USGS RockJock 2021 library. The quantitated mineralogical composition from ten samples were averaged and reported below as percentage by mineral groups (Table 1) and percentage by individual minerals (Table 2).

Table 1. X-Ray Diffraction Results of Troilus J4 Rock Samples by Mineral Groups.

Mineral Group	**% Composition**
plagioclase	54.35
Quartz	26.56
mica	10.71
amphiboles	7.05
pyrite	0.60
Titanite	0.28
balance of unknown	0.44

Table 2. X-Ray Diffraction Results of Troilus J4 Rock Samples by Minerals.

Mineral	% Composition
Plagioclase group	
bytownite	4.32
labradorite	3.35
andesine	11.69
oligoclase	25.50
albite	9.51
Quartz	26.56
Mica group	
muscovite	1.07
phlogopite (magnesium rich biotite)	1.39
biotite	8.26
Amphibole group	7.05
tremolite	5.29
actinolite-tremolite	1.76
Pyrite	0.60
Titanite	0.28
balance of unknown	0.44

XRD analysis provides a bulk description of rock mineral composition and is one of the many useful tools for characterizing mineralogy. It is not without limitations: a mineral in the sample but not in database will not be matched correctly, minerals at lower concentration are less accurate. The results give a good picture of what is in the rock, especially for major minerals groups, but must also be compared with results obtained from other analytical methods.

Carbon and Sulfur analysis

Five samples of fines were analyzed for bulk carbon and sulfur content by a LECO furnace combustion-infrared detection carbon and sulfur analyzer. The results are summarized in Table 3.

Table 3.Troilus crushed rock carbon and sulfur analysis results.

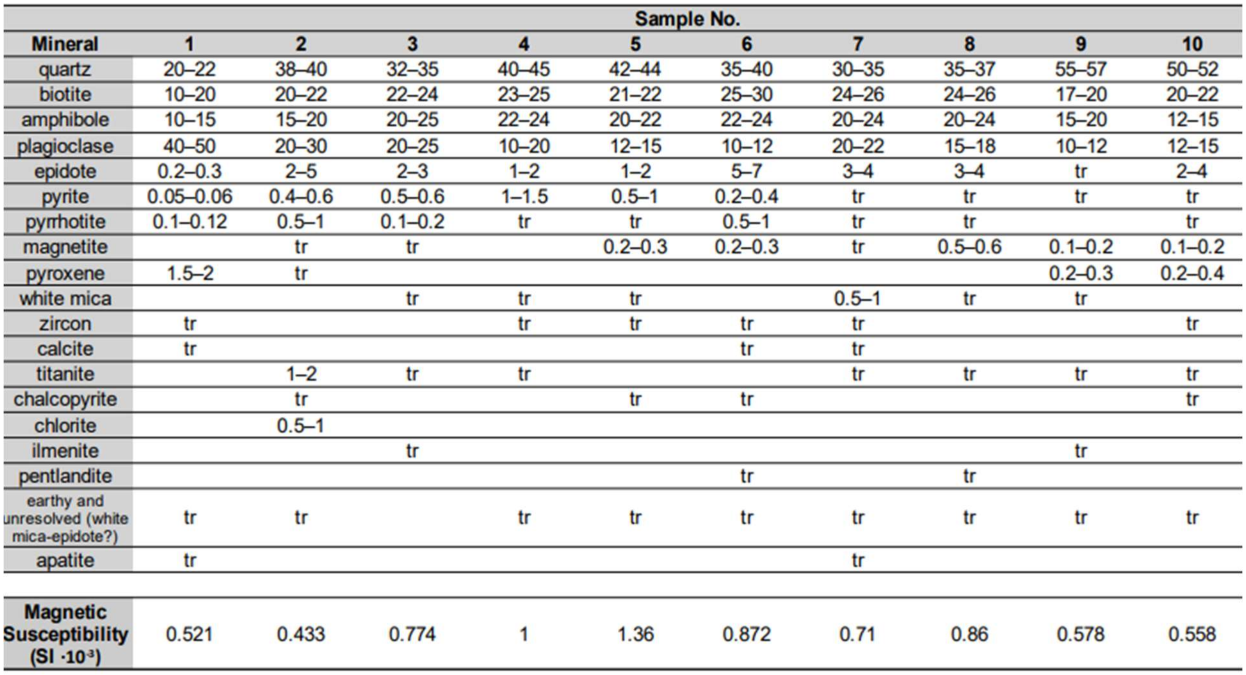
	%S	%C
Bag 1	0.361215	0.114529
Bag 2	0.449005	-0.00945
Bag 3	0.485634	0.065263
Bag 4	0.540879	0.081595
Bag 5	0.481442	0.074836
Mean	0.48708	0.058415
std. Dev	0.033364	0.039661

The results for carbon and sulfur are consistent with previous ABA reports. The deviation between samples is as expected. The average sulfur and carbon contents confirm that the slow reactivity observed in the OxyCon cells is not a result of accidental sampling of rock with low sulfur content.

Thin Section Petrography

Course rock samples were mounted in epoxy and polished into ten thin section slides for petrographic microscopy. Table 4 shows the mineral contents of the ten slides as determined by petrographic analysis and their magnetic susceptibility.

Table 4. Mineral content by petrographic analysis and magnetic susceptibility of Troilus rock samples.



	Sample No.									
Mineral	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
quartz	20–22	38–40	32–35	40–45	42–44	35–40	30–35	35–37	55–57	50–52
biotite	10–20	20–22	22–24	23–25	21–22	25–30	24–26	24–26	17–20	20–22
amphibole	10–15	15–20	20–25	22–24	20–22	22–24	20–24	20–24	15–20	12–15
plagioclase	40–50	20–30	20–25	10–20	12–15	10–12	20–22	15–18	10–12	12–15
epidote	0.2–0.3	2–5	2–3	1–2	1–2	5–7	3–4	3–4	tr	2–4
pyrite	0.05–0.06	0.4–0.6	0.5–0.6	1–1.5	0.5–1	0.2–0.4	tr	tr	tr	tr
pyrrhotite	0.1–0.12	0.5–1	0.1–0.2	tr	tr	0.5–1	tr	tr		tr
magnetite		tr	tr		0.2–0.3	0.2–0.3	tr	0.5–0.6	0.1–0.2	0.1–0.2
pyroxene	1.5–2	tr							0.2–0.3	0.2–0.4
white mica			tr	tr	tr		0.5–1	tr	tr	
zircon	tr			tr	tr	tr	tr			tr
calcite	tr					tr	tr			
titanite		1–2	tr	tr			tr	tr	tr	tr
chalcopyrite		tr			tr	tr				tr
chlorite		0.5–1								
ilmenite			tr						tr	
pentlandite						tr		tr		
earthy and unresolved (white mica-epidote?)	tr	tr		tr	tr	tr	tr	tr	tr	tr
apatite	tr						tr			
Magnetic Susceptibility (SI $\cdot 10^{-3}$)	0.521	0.433	0.774	1	1.36	0.872	0.71	0.86	0.578	0.558

Notable observations are summarized below:

- Quartz, biotite (a mica), amphibole and plagioclase (Ca-Na feldspar) are the most abundant and, therefore, most abundant on the surface. Amphibole was defined by the cleavage domain. Sample No. 1 has composition more similar to XRD which indicates more plagioclase than quartz.
- Feldspars are relatively altered. Plagioclase pitting, forming clay, flakes and fines (schistosity). These could be sericite, also described as white mica. Raman identifies the sericite/white mica as muscovite.
- Sulfides. Pyrite was the main sulfide mineral found, along with some pyrrhotite and chalcopyrite. Pyrite also found with magnetite which tends to disintegrate the pyrite (magnetite-pyrite system is not in equilibrium). Pyrite particles are well-encased, and many of the pyrites are still very fresh. Sulfides are observed as encapsulated particles and does not form veins that can lead to cracking. This can be a main factor to the slow acid generation reaction.
- Carbonates: rocks were formed under high temperature and partial-pressure of H_2O, so CO_2 was not present. Carbonates are post-metamorphic (late) precipitates which would form, on quartz veins. They would be the first to react (provide alkalinity) and mostly gone because they formed in cracks and were readily available. LECO showed an average %C (wt.) of 0.058, which is close to the detection limit of the test method. Carbonates were not found by Raman analysis of dried particles taken from Cell #4. Despite that, CO_2 generation was observed in OxyCon test.

- Epidote was observed to be overprinted on biotite. Epidote is formed with Fe from biotite (which has no Ca but Mg) and chlorite, which is formed from water and biotite.

The full report of the Petrographic analysis can be downloaded from the Troilus Project shared folder in NRC's NextCloud.

SEM/EDX and Microscopic Raman Spectroscopy

Certain areas of known mineralogy as identified by petrographic microscopy on thin section slides 1, 2, 7 and 8 were marked and labelled as shown in Figure 8 for further SEM/EDX and microscopic Raman analysis.

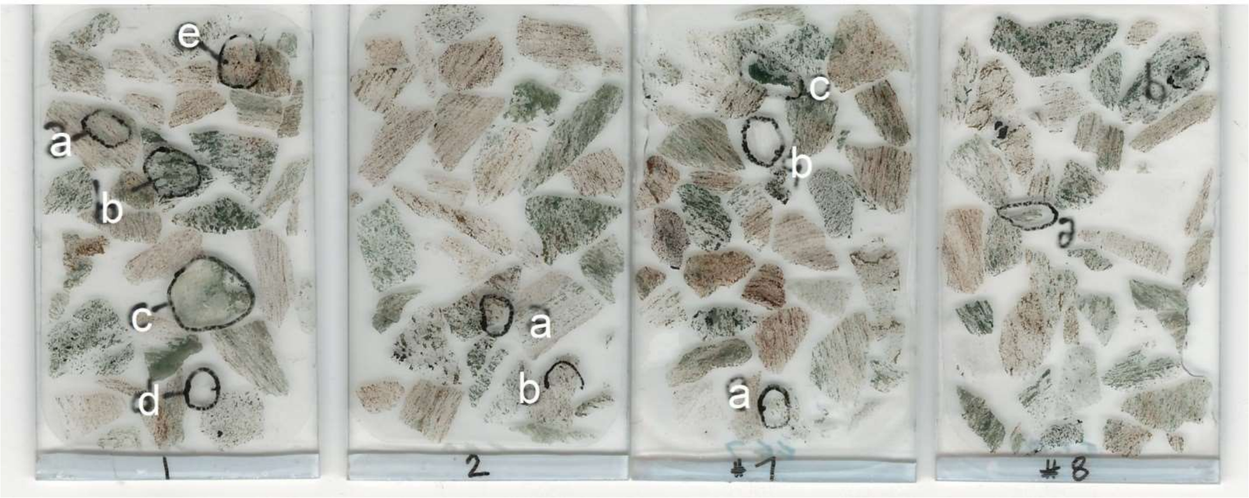
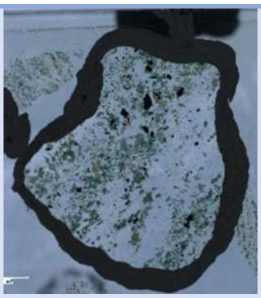
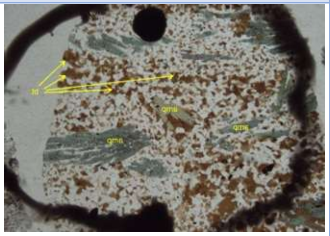
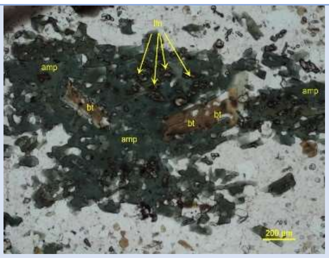
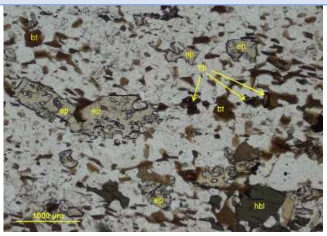
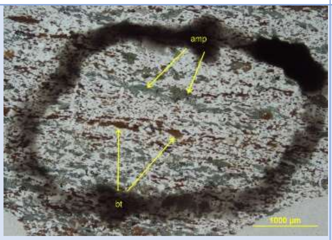
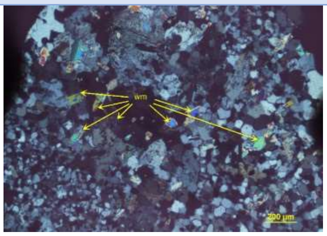
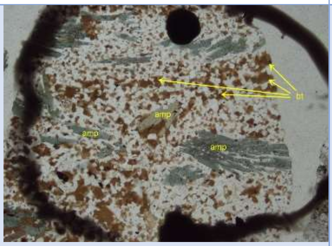


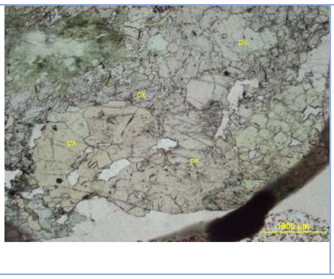
Figure 8. Thin section slides 1,2, 7 and 8 labeled for SEM/EDX and Raman analysis.

The areas analyzed were encircled with carbon paint, and lines were painted from these areas to the SEM's stainless-steel stub with carbon paint for electrical connection. SEM images, EDS and Raman results are shown below:

Table 5. Spots on thin sections further analyzed by SEM/EDX and Raman.

Sample # and sub-area	**Microscope Image**	**Identity by petrographic microscopy**	**EDX (atoms per unit), mineral**	**Raman Library Search**
1F		Plagioclase (Ca, Na feldspar)	Si 2.478 Al 1.193 Fe 0.050 Ca 0.526 Na 0.688 K 0.065 labradorite/andesine	Anorthoclase /Andesine
1G		Plagioclase (Ca, Na feldspar)	Si 2.806 Al 1.266 Fe 0.081 Ca 0.228 Na 0.545 K 0.075 Andesine-oligoclase	Labradorite Oligoclase/ Andesine
1G		Plagioclase (Ca, Na feldspar)	Si 2.673 Al 1.401 Fe 0.000 Ca 0.248 Na 0.645 K 0.033 Oligoclase	Oligoclase/ Andesine
1E		Amphibole	Mg 3.285 Al_3 2.118 Si 7.341 Ca 1.212 Fe 0.645 Gedrite-Hornblende	Hornblende /Amphibole

8B		Amphibole	Mg 2.017 Al 2.549 Si 6.652 K 0.177 Ca 1.701 Ti 0.048 Mn 0.059 Fe 1.913 Hornblende-Gedrite	Hornblende/ Amphibole
2B		Hornblende	Mg 2.945 Al 2.801 Si 7.159 K 0.139 Ca 0.994 Fe 0.471 Hornblende-Gedrite	Hornblende/ Amphibole
1A		Biotite	Mg 1.66 Al 1.74 Si 2.91 K 0.67 Ti 0.08 Fe 0.43 Biotite but richer in Mg and Al	Biotite
1D		White Mica	Al 2.60 Si 3.41 K 0.49 Fe 0.04	Muscovite
1E		Biotite	Mg 1.43 Al 1.76 Si 3.03 K 0.58 Ca 0.05 Ti 0.07 Fe 0.41 Biotite but richer in Mg and Al	Biotite

1C		Pyroxene	Si 1.971 Fe 0.209 Mg 0.775 Ca 0.969 Diopside-augite	Augite

Details of the XRD, EDX/SEM and Raman results can be found in Troilus Project folder in NRC's NextCloud.

Raman observation of particles obtained from Cell #4

The search for secondary minerals identified only Goethite coated on pyrite and on other primary minerals. No other secondary minerals were found. Most of the fines in dried effluents are primary minerals, such as feldspars and amphiboles. This finding corroborates the observation that the oxidation reaction of Troilus rock is slow. Some PMMA, the clear plastic part of OxyCon test cells more commonly known as Plexiglas, was also found in the dried effluent.

Summary and Conclusion

From this first phase, we learned that sulfide oxidation rate of Troilus rock is very slow, and the neutralization reaction has been able to keep up and keep the effluent pH near neutral.

These tests showed that the rate of oxygen consumption is about 0.186 mole O_2 per ton of fine crushed rock per day and about 0.056 mole O_2 per ton of the coarse rock per day. The slow oxidation rate of sulfides is a factor why the J4 rock pile has not been observed to generate ARD at STP-9.

These tests also showed that the rate of CO_2 gas production is about 0.018 mole CO_2 per ton of fine crushed rock per day and is about 0.007 mole CO_2 per ton of coarse rock per day. CO_2 generation and TIC in the effluent water are evidence of carbonate involvement in acid neutralization. Presuming that the CO_2 is from pre-existing carbonates, it may take a long time before the carbonates are consumed given the slow sulfide oxidation rate. But eventually, the primary carbonate minerals could deplete with time and the effluent may turn acidic. On the other hand, if CO_2 were merely released from those trapped from the purged air by dissolved alkali/earth ions, it is quite possible that the acid generating sulfides deplete before the all alkali/earth elements in the rock are completely consumed.

The effluents from the test columns were unremarkable, especially after the cycle 6, with circumneutral pH and low sulfate content, which is consistent with the slow sulfide oxidation rate. The pH has remained between 6.5 to 7.9 for cells 1-3 (course rock) and 7.1 to 8.9 for cells 4-6 (fines). The sulfate contents are mostly in the 10^{-4} M range with some in the 10^{-3}M range for fines-containing cells. Effluents show low- to sub-ppm levels of some calcium, potassium, silicon, sodium and magnesium. Iron and aluminum were not detected, which is expected under circumneutral pH condition. Acidity and Alkalinity were consistently low. The concentration of metals can give some indications as to what minerals, other than carbonates, could be a source of the effluents' alkalinity.

Fresh rock samples were confirmed to contain significant amounts of sulfur (0.49% wt.) but only trace amounts of carbonates (0.06% wt.). Metal sulfides, primarily pyrites with some pyrrhotite and chalcopyrite, were seen under the microscope but only traces of calcite were seen. Pyrite particles are well-encased, and many of the pyrites are still very fresh. Sulfides were observed as encapsulated particles and does not form veins that can lead to cracking. This can be a main factor for the slow acid generation reaction.

Petrographic microscopy and XRD both indicate that the main mineral groups in the rock are plagioclase, quartz, amphiboles and biotite. Other minor components identified include epidote, pyroxene, white mica (sericite, muscovite), titanite, chlorite and traces of other minerals. Three out of four of the major mineral groups, or 69.66% of the rock by XRD, are alkali/earth containing aluminosilicates: plagioclase (Ca, Na and some K), amphiboles (Mg, Ca and some K) and biotite (Mg, K). Considering that the feldspars were observed to be relatively altered (plagioclase pitting, forming clay, flakes and fines). It is reasonable to think that at least some of the calcium in the effluents may have originated from plagioclase and its by-products.

Some samples from cell #4 were obtained for microscopic observation. Goethite was the only secondary mineral observed.

A mid-project update meeting was held on December 21, 2022 and year-end meeting was held in May 23, 2023. This document fulfills last milestone for Phase I of this project.

Recommendations

For the next phase, we recommend continued OxyCon testing but at less frequency and with some customized modification for slow reacting samples. We recommend continued water quality monitoring for the six cells but with longer reaction time interval and less flushing frequency to increase dissolved ion concentration in the effluent. We also recommend continued microscopic observation of the samples.

New tasks recommended for the next phase are as follows:

- CO_2 was observed to evolve with oxygen consumption, indicating a that carbonate was involved in the acid neutralization process. But it is not clear if CO_2 is generated from primary carbonates or generated in-situ between flushing cycles from atmospheric CO_2 and dissolved alkali/earth ions. Therefore, we recommend experiments to clarify this for the long-term prediction of possible ARD. It is also important for understanding the potential CO_2 emission and sequestration from these waste piles.
- We obtained preliminary oxidation rates which can be used for modeling in the next phase. However, field conditions vary and so validation at the mine site is still important. We recommend installing O_2, CO_2, temperature and RH probes into Troilus' 3-meter field column #12.
- We also recommend the development of a conceptual design for a pilot-scale mine waste test pile at Troilus for (1) collecting data of O_2/CO_2/Temperature and drainage chemistry, (2) enabling scaled-up models to whole waste piles, (3) evaluating cover concepts for mine closure.

With the reduction in frequency for existing tasks and introduction of new tasks, we expect the total size of Phase II to be similar to Phase I.