Mine Closure 2023 - Behrooz Abbasi, Jeff Parshley, Andy Fourie & Mark Tibbett (eds)

doi:10.36487/ACG_repo/2315_065

Laboratory test for confirmation of natural attenuation in groundwater

T Patterson *SLR International Corporation, United States*

T Tesfay *SLR International Corporation, United States*

Abstract

A large, inactive copper mine near Kingman Arizona that started operations in the 1960's has historical groundwater impacts extending beyond the limits of mining facilities. Field investigations and engineering evaluations performed from 2016 to the present defined the conceptual hydrogeologic and hydrogeochemical site model as well as a corrective action program to address the impacts. A Corrective Action Monitoring Program (CAMP) is part of the corrective action program ultimately accepted by state regulators. The CAMP includes development of performance objectives that demonstrate that the geochemical natural attenuation mechanisms described in the conceptual site model are active and effective in protecting downgradient beneficial uses of groundwater.

This paper describes the conceptual hydrogeochemical site model and geochemical attenuation mechanisms that are based on neutralizing the acidic conditions in groundwater using the native aquifer materials and the concomitant precipitation and adsorption of metals that occurs when pH increases. The paper also describes a sequential batch leach test specifically designed to confirm the attenuation mechanisms and to develop quantitative or semi-quantitative performance objectives for the CAMP. The regulator has approved the special batch leach test procedure for demonstration of the attenuation model.

Keywords: *groundwater, remediation, impact management, acid mine drainage, natural attenuation, leach testing*

1 Introduction

Impacts to groundwater quality at mines located in historical mining districts are difficult to characterize because of typically poor baseline water quality data and because of impacts that pre-existed the operating modern mines in these areas. This in turn creates difficulties in establishing clean-up objectives for remediation of impacts to groundwater. Further, changes to hydrology and hydrogeology are caused by mine construction and operation which makes it difficult to establish whether water quality changes have occurred due to releases from mining waste units or if they are due to changes in the hydrologic setting. Also because of the scale of mining projects and the nature of the changes caused by mining, mine-related groundwater quality impacts are difficult to address with regulatory programs that were developed for facilities like landfills, surface impoundments, and waste piles/stockpiles. As a consequence, mine owners often must work with regulatory agencies to develop non-traditional strategies and objectives for groundwater remediation that rely on the flexibility typically contained in the regulatory program, are protective of human health and the environment, and are feasible and effective.

We present herein a case study for a copper mine located in northwestern Arizona within a historic mining district which began operation in the 1960's. The mine has been under a Consent Decree for cleanup of groundwater that threatened to prevent future operations. A groundwater remediation strategy was developed that involved several source control measures, but ultimately relies on monitored natural attenuation (MNA) to address groundwater impacts. The MNA program is based on a hydrogeologic and geochemical conceptual site model (CSM) that is somewhat unique to mines.

Because the regulators lack experience and expertise in mine waste geochemistry and because of the need to confidently satisfy external stakeholders that the MNA approach protects human health and the environment, the approved MNA program includes a laboratory test to validate and confirm the CSM as an early step in implementation of the groundwater remedy.

In this paper, we describe the hydrogeologic and geochemical CSM with supporting information that was used to develop the CSM, as well as the laboratory test we developed that was approved by the regulators to simulate and confirm the CSM. The results of the testing will be used to establish the details of the compliance strategy for the cleanup program (e.g., points of compliance, parameters to demonstrate the effectiveness of MNA, timeframes for remediation, etc.). The CSM and laboratory test may have applicability at other mines in similar or related situations.

2 Background

Mining in this historical mining district in northwestern Arizona began in the 1870's. The area produced silver, gold, copper, lead, zinc and turquoise. Large scale open pit mining of copper began in the early 1960's and has continued under several owners to the present. Current facilities include open pits, dump leaches, a tailings storage facility, waste rock piles, ponds and impoundments, a mill, and a solvent extraction/electrowinning plant.

There are mountains east of the mine and a pediment to the west that thickens toward the west into a wide valley where the groundwater is used for drinking water and farming. Natural groundwater recharge occurs in the mountains and groundwater flows through bedrock from the mountains through the mine area and out to the pediment and valley. There is no groundwater recharge in the area of the pediment or to the west in the alluvial valley.

The mine facilities (waste rock piles, dump leaches and tailings storage facility) are unlined and have discharged acidic, metal-laden solutions to groundwater. While mine operations collect and contain much of the solution (for recovery of copper and re-use in mine processes), some escaped into the groundwater and migrated to areas downgradient of the mine facilities.

In 2018, the Arizona Department of Environmental Quality (ADEQ) issued a Consent Order following a determination that the owners were out of compliance with their Aquifer Protection Permit because of impacts to groundwater quality. Following Consent Order requirements, the nature and extent of groundwater impacts were characterized, a hydrogeochemical CSM was developed, and site improvements and source control actions were implemented to eliminate further discharges of mine water to groundwater.

However, there were residual impacts to downgradient groundwater that need to be addressed and based on the hydrogeochemical CSM, there would be continued release of acid and metals into groundwater from in-place mineralized bedrock. Therefore, a Corrective Action Monitoring Plan (CAMP) was developed that would verify the hydrogeochemical CSM, establish points of compliance for groundwater monitoring, and develop data to support that groundwater quality was improving. The CAMP also included the protocol for a laboratory leach test to confirm the hydrogeochemical CSM and to help develop cleanup objectives for groundwater.

With approval of the CAMP by ADEQ, the Consent Order was terminated in early 2023.

3 Current geochemical conceptual model

As mentioned above, groundwater flows from areas of recharge in the mountains to the east, flows westward through the mineralized areas under the mining facilities, and then through a pediment towards a broad valley to the west. Characterization data indicate the impacted groundwater adjacent to and downgradient of the site varies from having low pH and relatively high concentrations of metals, Total Dissolved Solids (TDS), and sulfate near the boundaries of former source areas to neutral pH, relatively low metals, and elevated TDS and sulfate in areas further downgradient. This trend is illustrated in Table 1.

Table 1 Summary of groundwater quality data illustrating trend along flowline

Location	pH (field)	Sulfate (mg/L)	TDS (mg/L)	Acidity, Total (mg CaCO3/L)	Alkalinity, (mg CaCO3/L)	Manganese (mg/L)	Beryllium (mg/L)	Cadmium (mg/L)	Copper (mg/L)	Fluoride (mg/L)	Lead (mg/L)	Nickel (mg/L)	Zinc (mg/L)
HyGeo-1	7.04	877	1,495	All ND (<2)	182	0.99	0.00011	All ND (<0.00005)	All ND (<0.01)	1.9	All ND (<0.0001)	All ND (<0.008)	All ND (<0.02)
HyGeo-2	8.03	256	561	All ND (<2)	108	0.03	0.000089	All ND (<0.00005)	All ND (<0.01)	1.4	All ND (<0.0001)	All ND (<0.008)	All ND (<0.02)
HyGeo-3	6.93	804	1,383	All ND (<2)	179	3.99	0.000116	All ND (<0.00005)	All ND (<0.01)	1.2	All ND (<0.0001)	All ND (<0.008)	All ND (<0.02)
HyGeo-5	6.87	932	1,758	All ND (<2)	276	0.85	0.000098	All ND (<0.00005)	All ND (<0.01)	2.1	All ND (<0.0001)	All ND (<0.008)	All ND (<0.02)
MW-6	3.65	7,230	10,673	1,870	All ND (<1)	269	0.156	0.85	126.8	80.4	0.25	4.56	138.0
MW-19	3.54	11,028	15,500	10,218	All ND (<1)	385	0.204	1.79	221.92	150.2	0.042	4.868	255.92
MW-14	7.02	2,259	3,686	All ND (<2)	200	<0.01	All ND (<0.0002)	All ND (<0.001)	0.021	0.82	All ND (<0.0002)	0.029	0.067
MW-16	6.75	2,524	4,265	All ND (<2)	282	0.688	All ND (<0.0002)	All ND (<0.002)	All ND (<0.01)	2.1	0.030	All ND (<0.02)	0.179

🟩	- Upgradient
🟧	- Source Areas
🟨	- Downgradient
“All ND”	- All results below detection limit for this constituent.

The transition/attenuation of constituents downgradient is attributed to geochemical reactions of the mine-impacted groundwater with aquifer solids (bedrock and overburden soils) that neutralize the acids in the highly impacted water and cause the metals to precipitate or absorb. It is further hypothesized that there is a "front" or transition zone where the geochemical reactions are occurring, with the neutralizing capacity of the aquifer material being mostly exhausted behind the front (closer to the discharging facilities).

Because of the fractured bedrock flow conditions, preferred flow paths for groundwater, and changes to aquifer material properties caused by the geochemical reactions (i.e., chemical weathering of the rock and soil that alters the structure and thereby changes the hydraulic properties of the aquifer material), it is very difficult to identify or designate a location of the front and the location and configuration change over time. The front is likely a network of dendritic filaments along preferred flow paths that slowly grow outward and downgradient, sometimes ceasing movement as the aquifer materials change and moving into other areas as preferred flow paths and fractures get blocked and new ones open.

Figures 1 and 2 present diagrams in plain view and section, respectively, illustrating the CSM.

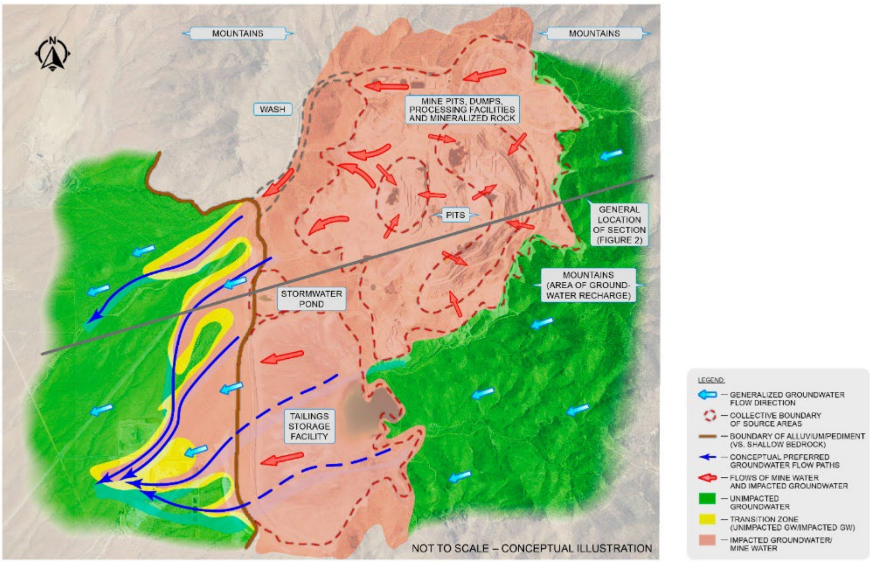


Figure 1 Diagram of groundwater conceptual site model – plan view

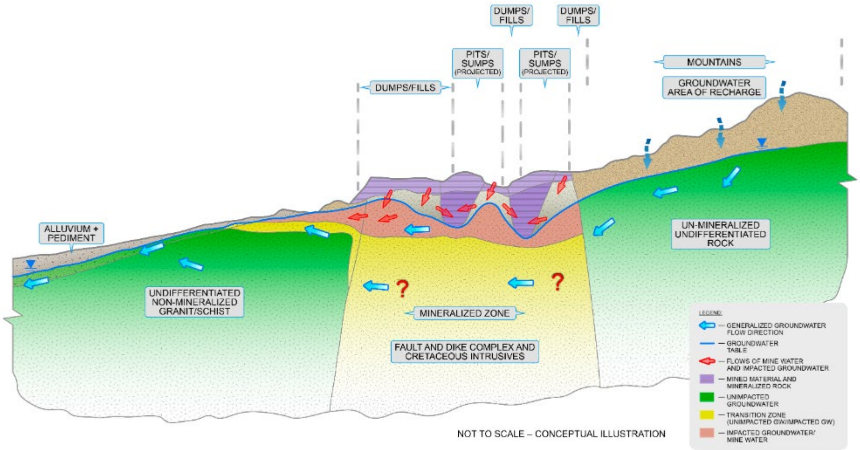


Figure 2 Diagram of groundwater conceptual model – cross sectional view

The key lines of evidence supporting this geochemical attenuation scenario are the groundwater and source-area water quality data, observations in the field, the fundamental chemistry of acid-base reactions, and the relationship between pH on metal solubilities.

Observations in the field during site characterization clearly indicate that the aquifer material is physically and chemically altered by reaction with the highly contaminated water. Figure 3 is a photograph of drill cuttings from a borehole within the highly contaminated area.

Figure 3 Drill cuttings from a borehole in the highly impacted area. The material in the left two piles comes from the saturated zone where there has been prolonged contact between the bedrock and highly acidic ground water. The other six piles are rock and overburden from the unsaturated zone. Reaction with the highly acidic groundwater has changed the brown, blocky country rock to a grey silt with clay. The leftmost pile of cuttings, from the deepest interval of the borehole, is not quite as weathered and there are still some blocks of bedrock although the color of the rock has changed throughout.

4 Specialized column testing

Although ADEQ is convinced that the CSM is sound and supported by several lines of strong evidence, they have requested additional evidence. They proposed a field program (e.g., monitoring wells or boreholes) to establish the location of the transition zone. However, the transition zone is expected to be very narrow and heterogeneous, so finding field evidence of the transition zone location is not feasible. Further, the nearly 30-year record of groundwater quality data has indicated only one monitoring location that suggests conditions that are expected in the transition zone, and those conditions have persisted for the past approximately 10 years.

A compliance framework for verifying the performance of the MNA processes is also required. Therefore, additional evaluations and analyses are required to further characterize the MNA mechanisms, e.g., to determine the rate that the natural neutralization capacity of the aquifer materials is consumed, what metals are removed and to what degree, and what is the final fate of the metals and acids. Such data can be used to establish monitoring parameters, points of compliance, and remedial action objectives for the Corrective Action Monitoring Program.

As an alternative to a field program and to gather data that can be used to develop the compliance strategy, we developed, and ADEQ approved, a specialized column test. The specialized column test is a custom test designed to evaluate the effects of the aquifer material in downgradient areas on the attenuation of constituents and acid in mine-impacted groundwater. The test protocol is outlined below. The test is essentially a sequential batch column leaching test where source water is used to saturate a column of fresh unimpacted aquifer material for a period of time, then it is drained, and another charge of source water is added and the effluent from the column is introduced into a second column of aquifer material. Up to five columns will be used.

Geochemical modeling using PHREEQC will also be performed. Results of the geochemical modeling will be used to inform details and refinements to the column tests. Similarly, the results of the column testing will be used to inform refinements to the geochemical modeling and development of corrective action performance monitoring (e.g., data evaluation procedures).

4.1 Protocol for column testing of attenuation

The analytical testing program is summarized in Table 2.

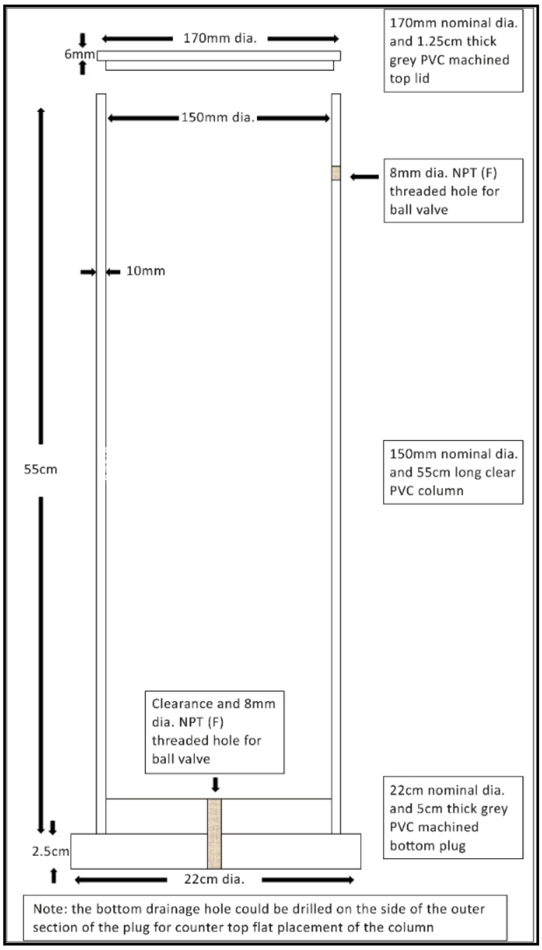
Table 2 **Summary of testing program**

Medium	Parameters
Pre-leach and post-leach chemistry of the aquifer material in each column	Static acid base accounts (ABA) Whole rock analysis for elemental composition Quantitative X-ray diffraction for relative abundances of mineral phases Short term leach testing (Meteoric Water Mobility Procedure) with analysis of the leachate for metals, pH, redox parameters, alkalinity/acidity, and dissolved mineral constituents (i.e., Ca, Na, Mg, K, Cl, SO4, and F)
Influent and effluent of each column at each stage	Volume Electrical conductivity, pH, Eh, turbidity Acidity and Alkalinity (total and bicarbonate and carbonate) Cations and anions (Ca, Na, K, Mg, SO4, Cl, F, PO4, NO3) Dissolved and total metals (including but not limited to Fe, Mn, Al, Ag, As, B, Cd, Cr, Cu, Pb, Mo, and Ni)

4.1.1 Materials

The materials used are as follows:

- 5 clear PVC columns with lids and plumbing/appurtenances (Figure 4).
- Solid aquifer material crushed to <6.35 (100% passing 6.35 mm screen). Approximately 200 kg of material is required for 5 columns.
- Source water (from pits or pregnant leach solution ponds). Assuming five cycles for the first column, 30% porosity, 40 liters (L) of solids per column, and 50% makeup, the minimum volume required is 100 L per set of 5 columns. Source water must be stored in a closed plastic container, in the dark, in a cool, preferably refrigerated location.
- Laboratory and sampling equipment (pH and Eh meters, specific conductance meter, graduated cylinders, plastic sample bottles, filtration device, scale to measure weight of solids in each column, rubber mallet, etc.).
- Sodium hydroxide to adjust pH of source water make-up for columns 2 through 5.



Note: Adapted from the Prediction Manual for Drainage Chemistry from Sulphatic Geologic Materials, MEND 2009

Figure 4 Example column design

4.1.2 Preparation

The activities that must be performed prior to initiating the leaching test are as follows:

- Perform pre-test chemical characterization of solids and source water (Table 2).
- Set up columns in an area that can be kept dark (to reduce the potential for algae growth or other biofouling) and at a constant temperature.
- Fill each column with a pre-weighed amount of crushed solid aquifer material.
- Place endcaps and close valves.

4.1.3 Procedures

The test procedure is diagramed and described in Figure 5. The procedure in general consists of source water progressing through a series of columns (with some makeup water due to holdup in the column and the volumes removed by sample collection between columns) and analyzing the chemistry of the water as it progresses through the successive columns. The volume of influent, effluent and make-up for each column is measured with each cycle.

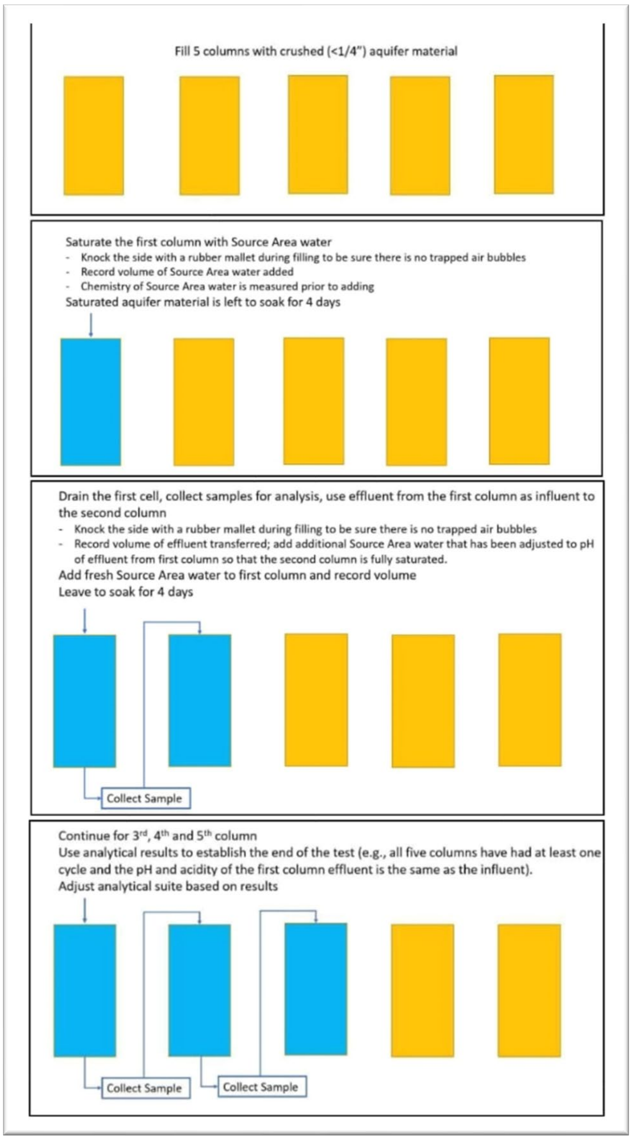
The test procedure is dynamic and there will be some refinement to the procedures based on early evaluation of the data. For example, the period of time that the source water stays in one column is initially 4 days but may be adjusted longer or shorter depending on results. Some chemical analyses may be added, and some may be eliminated. The frequency of collecting samples may also be adjusted. For example, samples of effluent may be analyzed every other or every third time that source water is circulated through a column rather than every time.

Termination of the test will be based on evaluation of test results; a 3-month duration has been assumed. The column test may be extended beyond three months if the column test results at three months indicate the tests should be continued. Our initial criteria for termination of the test are that the source water has been flushed through the final column at least once and the pH and acidity of the effluent of the first column are the same as the pH and acidity of the influent.

4.1.4 Test termination

Following the decision to terminate the test:

- The columns will be drained, and the final effluent analyzed as above
- The residual solids will be allowed to dry (i.e., no free water), then weighed and analyzed as described in Table 2
- A portion of the column solids from each column will be retained by the laboratory in case the results of the post-test analyses suggest some additional analyses are needed.



Fill 5 columns with crushed (<1/4") aquifer material

Saturate the first column with Source Area water
- Knock the side with a rubber mallet during filling to be sure there is no trapped air bubbles
- Record volume of Source Area water added
- Chemistry of Source Area water is measured prior to adding

Saturated aquifer material is left to soak for 4 days

Drain the first cell, collect samples for analysis, use effluent from the first column as influent to the second column
- Knock the side with a rubber mallet during filling to be sure there is no trapped air bubbles
- Record volume of effluent transferred; add additional Source Area water that has been adjusted to pH of effluent from first column so that the second column is fully saturated.

Add fresh Source Area water to first column and record volume
Leave to soak for 4 days

Continue for 3rd, 4th and 5th column
Use analytical results to establish the end of the test (e.g., all five columns have had at least one cycle and the pH and acidity of the first column effluent is the same as the influent).
Adjust analytical suite based on results

Figure 5 Summary diagram of testing procedure

5 Performance metrics and remedy timeframe

The results of the specialized column testing and geochemical modeling will be used with site groundwater monitoring results to establish long-term performance metrics and remedy timeframe. As described above, there is no recharge in the downgradient area of the site including the pediment. Also, groundwater flow is from the higher topography areas in the east through the mine site to lower areas in the west; therefore, groundwater must flow through the area of mineralization and under the mine facilities. The source control corrective actions will enhance collection of water from the discharging facilities (i.e., reduce the release of highly impacted water to groundwater), but it is likely that groundwater flowing through the mineralized zone and under the mine site facilities will continue to show impacts from interaction with mineralized rock.

Natural baseline water quality around mineralized zones is typically poor with elevated sulfate and metals and it is common for metallic mineral deposits to be discovered by surveying water quality conditions. Therefore, there is no way to define a background or baseline condition and using water quality conditions in a nearby basin and upgradient or downgradient area would not be representative of background conditions at the site.

Considering the CSM, performance metrics cannot be based on background or baseline conditions, and it is not likely that corrective actions will achieve applicable water quality standards at locations adjacent to the mine facilities. Therefore, the proposed performance metrics will likely be based on improvement of water quality (decreasing concentration trends of Constituents of Concern [COCs]) at impacted locations and maintaining concentrations below applicable water quality standards at unimpacted downgradient locations near the property boundary.

The timeframe to observe improvements in water quality is estimated to be on the order of five years from the commencement of monitoring. This is based on the amount of time expected for the corrective actions to be effective plus the amount of time required to gather sufficient data to demonstrate a meaningful concentration trend. The timeframe for achieving applicable water quality standards at unimpacted downgradient locations is immediate since the wells are currently unimpacted.

We had hoped that the testing and modeling would have been initiated prior to publication and presentation of this paper, however it appears that the required field work will not be initiated until the end of 2023 or the beginning of 2024. We look forward to presenting the results of the testing and modeling at a future venue.