

TECHNICAL MEMORANDUM

То:	Nevada Environmental Response Trust
From:	Dana Grady, Jenny Dabbs, Tetra Tech, Inc.
Date:	July 19, 2024
Subject:	Treatability/Pilot Study Modification No. 10 – Las Vegas Wash ZVI-Enhanced Bioremediation Treatability Study

This Treatability/Pilot Study Modification No. 10 – Las Vegas Wash Zero-Valent Iron (ZVI)-Enhanced Bioremediation Treatability Study (Treatability Study) technical memorandum (Modification) has been prepared on behalf of the Nevada Environmental Response Trust (NERT) to present a modification to the scope of work for the Treatability Study that is currently in progress within Operable Unit 3 of the NERT Remedial Investigation (RI) Study Area (**Figure 1**). As presented in the Nevada Division of Environmental Protection (NDEP)-approved Las Vegas Wash ZVI-Enhanced Bioremediation Treatability Study Work Plan Addendum (Work Plan Addendum) (Ramboll US Consulting, Inc. [Ramboll], 2021), the Treatability Study evaluates the effectiveness of ZVI to degrade perchlorate, chlorate, and nitrate in groundwater with the ZVI acting as both the reactive media and source of hydrogen to support biological degradation of perchlorate.

Subsurface emplacement of ZVI in both continuous and discontinuous walls was completed in March 2023. Following construction of the ZVI walls, the injection and performance monitoring well network was installed, and a one-time injection event of an inoculum culture was completed in April 2023 in an effort to reduce lag time associated with perchlorate biodegradation. After completion of the construction phase in April 2023, a 16-month performance monitoring program was implemented in accordance with the Work Plan Addendum to determine effectiveness of ZVI-enhanced bioremediation. The performance monitoring program began in May 2023 and is ongoing.

As documented in monthly progress reporting provided since the inception of the Treatability Study, notable reductions of chlorate and nitrate concentrations in groundwater up to 99% and 97%, respectively, have been observed in several of the test areas. However, reductions in perchlorate concentrations in groundwater have been less pronounced during the initial year of performance monitoring. These results were generally expected as the bench-scale study indicated that the removal of nitrate and chlorate is rapid and primarily an abiotic process occurring primarily on the ZVI surface, while the reduction of perchlorate is slower and performed predominantly by perchlorate-reducing bacteria using hydrogen generated by ZVI corrosion. Based on performance monitoring results to date indicating the perchlorate degradation is starting to occur, an extended performance monitoring period and technical evaluation of this additional data is recommended to develop a more thorough understanding of perchlorate degradation and longevity of the ZVI technology for potential long-term applications of ZVI-enhanced bioremediation, which is an important component of the forthcoming Feasibility Study (FS). This Modification defines objectives for continuation of the Treatability Study and provides a proposed path forward for additional field activities to be conducted prior to the conclusion of the study.

1.0 TREATABILITY STUDY MODIFICATION

The proposed modifications as part of Treatability/Pilot Study Modification No. 10 are as follows:

- Treatability Study Extension Extension of the performance monitoring period will allow for additional data collection to:
 - Provide a better understanding of the performance of ZVI-enhanced bioremediation with respect 0 to nitrate, chlorate, and perchlorate degradation in groundwater;
 - Continue to assess long-term production and distribution of hydrogen and the associated 0 biologically active zone generated by the ZVI both within and downgradient of the reactive zones; and
 - Further assess the longevity of ZVI with respect to hydrogen production, ZVI mass loss, 0 passivation, and precipitation of inorganic species over time.
- Post-Treatment Borings Longevity of ZVI in the subsurface is an important component for evaluation of ZVI-enhanced bioremediation in the forthcoming FS. As a result, the advancement of post-treatment borings within both the continuous and discontinuous ZVI walls and collection of cores for both visual observation and laboratory analysis will provide valuable information to update the groundwater and geochemical models and assist in characterizing potential precipitation and/or biofouling effects within the subsurface.
- Dissolved Hydrogen Analytical Method Revision The Work Plan Addendum specifies dissolved hydrogen will be analyzed by AM20GAX Bubble Strip Method, which is a method specific to Pace Analytical Laboratories in Baton Rouge, Louisiana (Pace) that has been discontinued. Groundwater samples collected during all remaining performance monitoring events will be analyzed using the new RSK175 Bubble Strip Method offered by Pace or an alternative field method utilizing sensors developed by Unisense (Aarhaus, Denmark).

Sections 1.1 through 1.3 provide additional details on the proposed modifications to the Work Plan Addendum.

1.1 Treatability Study Extension

The 16-month performance monitoring program, which began in May 2023 and is currently scheduled to end in August 2024, includes monthly synoptic gauging events to evaluate hydrologic changes over time and groundwater sampling events approximately one month after completion of the construction phase and quarterly thereafter. In addition, real-time transducer data collection is being performed to evaluate changes in horizontal and vertical gradients, assess the potential for groundwater mounding upgradient of the ZVI reactive zones, assess hydraulic effects of seasonal precipitation, and evaluate potential non-uniform flow.

The original 16-month duration of the performance monitoring period was selected to account for a 4- to 6-month acclimation period to allow for the onset of biological perchlorate reduction and a subsequent 10- to 12-month steady state performance monitoring period. Based on results to date, perchlorate concentration reductions ranging from 23 to 46 percent have been observed in groundwater samples collected from the alluvium, while perchlorate concentration reductions up to 99 percent have been observed in groundwater samples collected from the UMCf. These results indicate that although some biological reduction of perchlorate is occurring in the alluvium, extending the performance monitoring program will provide the necessary data to evaluate the Treatability Study objective of determining the extent to which perchlorate can be degraded in the field using ZVI. Section 8.3 of the Work Plan Addendum indicates that the monitoring duration may be extended, if necessary, to achieve the objectives of the field test. As part of this Modification, the performance monitoring program will be extended to include three additional quarterly groundwater sampling events in November 2024, February 2025, and May 2025, resulting in collection of two years of performance monitoring data for the Treatability Study. Both the parameters and monitoring frequency (monthly synoptic events, real-time transducer data collection, and

guarterly groundwater sampling events) will continue to be implemented in accordance with the Work Plan Addendum during the Treatability Study extension, with the exception of the hydrogen testing as described in Section 1.3.

1.2 Post-Treatment Borings

As detailed in the Work Plan Addendum, longevity of a ZVI wall is primarily based on the rate of mass loss due to corrosion, rate of ZVI passivation, and reductions in porosity and hydraulic conductivity. Mineral precipitation and, to a lesser extent, biological fouling could reduce the porosity and reactivity of the ZVI walls. In addition, the high dissolved oxygen, nitrate, and alkalinity concentrations in groundwater within the Treatability Study area can lead to formation of ferrous carbonate (siderite), oxide precipitates, and accumulation of ammonium, which contribute to passivation of the ZVI surface. Precipitation reactions are common to all ZVI systems, and the preliminary geochemical modeling effort completed during preparation of the Work Plan Addendum estimated a loss in total porosity of about 0.7% per year.

Concurrent with field-scale implementation of the Treatability Study, precipitate samples from previous benchscale testing were analyzed by x-ray diffraction and ramen spectroscopy, and an additional bench-scale study was performed to examine potential passivation rates. Although the laboratory bench-scale data are useful in assessing ZVI longevity, the extension of the performance monitoring period (described in Section 1.1) provides a unique opportunity to assess ZVI longevity in a field setting. Collection and analysis of cores from the continuous and discontinuous ZVI walls at the conclusion of the Treatability Study will help characterize potential changes to porosity through precipitation of inorganic species and/or biofouling effects that can impact the performance and longevity of ZVI-enhanced bioremediation. The actual field conditions of the continuous and discontinuous ZVI walls after being in-place for two years can also be compared to bench-scale testing results related to precipitation and passivation as well as provide valuable data to inform the updated geochemical and groundwater models.

Following completion of the extended performance monitoring period, up to 10 post-treatment borings will be installed at strategic locations within both the continuous and discontinuous ZVI walls. Post-treatment borings will be installed by a licensed drilling contractor using sonic drilling techniques and will be advanced through the entire targeted treatment interval, and up to five feet into the underlying formation. Continuous cores will be collected and logged by the field geologist from ground surface to total depth using the Unified Soil Classification System. Because it is important to minimize exposure of the samples to air to avoid precipitation of minerals not representative of the actual subsurface conditions, a polycarbonate liner system known as Lexan liners will be used during the collection of cores, with the liners sealed upon extraction from the core barrel. Samples for laboratory analysis will be collected in laboratory-supplied containers, labeled, placed in plastic bags, and stored in a cooler on ice for transport to the project analytical laboratory. Up to five samples will be collected from each boring and analyzed for the parameters listed in Table 1. Additionally, up to five cores will be submitted for analysis of physical parameters including moisture content, porosity, soil density, and permeability. Lastly, up to five cores will also be analyzed by X-ray diffraction and Ramen spectroscopy to determine the composition of mineral precipitation within the ZVI walls.

Parameter	Analytical Method	Purpose
Total Inorganic Carbon	Walkley Black	Assess available inorganic carbon for biological cell growth
Soil pH	SW846 9045D	Assess geochemical conditions/microbial conduciveness
Alkalinity	SM2320B	Assess geochemical conditions
Nitrate as N	SW846 9056A	Assess a competing electron acceptor expected to be removed within the ZVI

Table 1 Sampling Protocol

Parameter	Analytical Method	Purpose
		reactive zone; Evaluate passivation potential
Ammonium as N	E350.1	Estimate the byproduct of abiotic nitrate degradation
Sulfate	SW846 9056A	Assess a competing electron acceptor; excessive reduction which can cause loss of permeability
Iron	E3050B and SW6010	Estimate the mass of iron present
Phospholipid Fatty Acids	Microbial Insights Method ¹	Examine microbial characteristics
Perchlorate Reductase and	Quantitative polymerase	Examine microbial perchlorate degradation
Chlorite Dismutase Genes	chain reaction (qPCR)	characteristics
Notes:		

White, D. C., H. C. Pinkart, and A. B. Ringelberg. (1995). Biomass measurements: Biochemical approaches, p. 91-101. In C. J. Hurst, G. R. Knudsen, M. J. McInerney, L. D. Stetzenbach, and M. V. Walter (ed.), Manual of Environmental Microbiology. ASM Press, Washington.

1.3 Dissolved Hydrogen Analytical Method Revision

Dissolved hydrogen, generated by the corrosion of ZVI in groundwater, is the electron donor used by perchloratereducing bacteria to reduce perchlorate in groundwater as it migrates through the ZVI walls. The performance monitoring program in the Work Plan Addendum includes analysis of dissolved hydrogen in groundwater collected from monitoring wells located upgradient, within, and downgradient of the ZVI reactive zones to assess the distribution of dissolved hydrogen and evaluate the extent of the hydrogen-enriched zone where perchlorate reduction would be expected to occur. The Work Plan Addendum specifies dissolved hydrogen will be analyzed by AM20GAX Bubble Strip Method, which is a method specific to Pace Analytical Laboratories in Baton Rouge, Louisiana (Pace). During the May 2024 sampling event, Pace indicated that the AM20GAX Bubble Strip Method is being discontinued and will be transitioned to the RSK175 Bubble Strip Method in August 2024. Because there are no other commercial laboratories in the United States that can analyze for dissolved hydrogen via the method prescribed in the Work Plan Addendum, groundwater samples collected during all remaining performance monitoring events will be analyzed using the new RSK175 Bubble Strip Method offered by Pace. RSK175 Bubble Strip Method is an established method for measuring dissolved gases in groundwater, which include hydrogen, methane, ethylene, ethane, propane, butane, acetylene, nitrogen, nitrous oxide, and oxygen. RSK175 Bubble Strip Method involves displacing 10% of the sample volume with high purity helium, shaking the sample for 5 minutes and injecting the headspace of the sample into a gas chromatographic column where the gaseous components are detected by a thermal conductivity detector, a flame ionization detector, or an electron capture detector. The only difference between the RSK175 Bubble Strip Method method and the approved AM20GAX Bubble Strip Method method is the use of helium instead of nitrogen during analysis.

If Pace (or another commercial laboratory) is unable to perform the RSK175 Bubble Strip Method by the next sampling event, an alternative field method utilizing sensors developed by Unisense (Aarhaus, Denmark) will be employed to measure dissolved hydrogen. This alternative field method involves the collection of an additional groundwater sample that will be transferred to an onsite field lab for analysis of dissolved hydrogen. The sample will be analyzed by the UniSense MicroProfiling System equipped with a hydrogen microsensor that has a detection limit of 50 nanomoles. The UniSense SensorTrace software will be used to record and automatically temperature correct the measured dissolved hydrogen concentrations.

2.0 SCHEDULE

Implementation of Treatability/Pilot Study Modification No. 10 will begin following the Month 16 performance monitoring event scheduled to be completed in August 2024. As described in Section 1.1, the extended performance monitoring period will result in continued real-time data collection via transducers and monthly

synoptic monitoring events through May 2025 as well as three additional guarterly sampling events performed in November 2024, February 2025, and May 2025. Following completion of the May 2025 performance monitoring event, final aquifer testing will be performed in accordance with the Work Plan Addendum followed by installation of post-treatment borings as described in Section 1.2. All injection and monitoring wells installed as part of the Treatability Study will be abandoned upon conclusion of Treatability Study field activities.

3.0 REFERENCES

Ramboll US Consulting, Inc. (2021). Las Vegas Wash ZVI-Enhanced Bioremediation Treatability Study Work Plan Addendum, Nevada Environmental Response Trust Site, Henderson, Nevada. September 29.

CERTIFICATION

Treatability/Pilot Study Modification No. 10 Las Vegas Wash ZVI-Enhanced Bioremediation Treatability Study Nevada Environmental Response Trust Site (Former Tronox LLC Site) Henderson, Nevada

Nevada Environmental Response Trust (NERT) Representative Certification

I certify that this document and all attachments submitted to the Division were prepared at the request of, or under the direction or supervision of NERT. Based on my own involvement and/or my inquiry of the person or persons who manage the systems(s) or those directly responsible for gathering the information or preparing the document, or the immediate supervisor of such person(s), the information submitted and provided herein is, to the best of my knowledge and belief, true, accurate, and complete in all material respects.

Office of the Nevada Environmental Response Trust

Le Petomane XXVII, not individually, but solely in its representative capacity as the Nevada Environmental Response Trust Trustee Not Individually, but Solely as President of the Trustee

Signature: Jan A Stember	Chisident	, not individually, but solely in his representative
capacity as President of the Nevada/Env	ironmental Res	sponse Trust Trustee

Name: Jay A. Steinberg, not individually, but solely in his representative capacity as President of the Nevada Environmental Response Trust Trustee

Title: Solely as President and not individually

Company: Le Petomane XXVII, Inc., not individually, but solely in its representative capacity as the Nevada Environmental Response Trust Trustee

Date: 7/19/2024

CERTIFICATION

I hereby certify that I am responsible for the services described in this document and for the preparation of this document. The services described in this document have been prepared in a manner consistent with the current standards of the profession, and to the best of my knowledge, comply with all applicable federal, state, and local statutes, regulations, and ordinances. I hereby certify that all laboratory analytical data was generated by a laboratory certified by the NDEP for each constituent and media presented herein.

Description of Services Provided: Prepared Treatability/Pilot Study Modification No. 10 – Las Vegas Wash ZVI-Enhanced Bioremediation Treatability Study.

July 19, 2024

Date

Christopher Hayes, CEM Environmental Engineer Tetra Tech, Inc.

Nevada CEM Certificate Number: EM2499 Nevada CEM Expiration Date: December 15, 2024

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