MEMO

To:

Steve Clough
Remediation Director
Nevada Environmental Response Trust

Copies:

Rich Royer, PhD

Arcadis U.S., Inc.
1140 N. Town Center Drive
Suite 320
Las Vegas, NV 89144
Tel: 702.485.6000

From:

Jeff McDonough, PE

Justin Provolt, PE

Date:

April 16, 2020

Arcadis Project No.:

30018143

Subject:

Ex-situ Zero Valent Iron (ZVI) Technology Evaluation for Nevada Environmental Response Trust Site

INTRODUCTION

At the request of the Nevada Environmental Response Trust (NERT or the Trust), Arcadis U.S., Inc. (Arcadis) respectfully submits this technical memorandum (memo) evaluating the feasibility of groundwater treatment using ex-situ zero valent iron (ZVI) for the NERT site located in Clark County, Nevada (Site). This evaluation was requested to assess the potential viability of this technology to provide a cost-effective alternative to NERT's current chemical treatment process.

Based on the existing groundwater treatment plant (GWTP) treatment flow rate, the influent chemistry, and the associated stoichiometric consumption of the ZVI media, Arcadis has calculated a Best Case and a Most Likely Case ZVI utilization rate. Stoichiometric ZVI demand calculations suggest that approximately 1,200 pounds of ZVI per day and 1,600 pounds of ZVI per day are anticipated to be required under a Best Case and a Most Likely Case, respectively. These ZVI demand calculations suggest that several hundred thousand pounds of ZVI will be consumed per year at a cost of several hundred thousand dollars per year due to ZVI consumption, solids management, and waste disposal. This memo provides an overview of the ZVI technology, a description of the stoichiometric ZVI demand calculations, and a commentary on ZVI for this application.

TECHNOLOGY OVERVIEW

Zero Valent Iron

ZVI is a manufactured elemental iron (Fe^0) material in the zero-valence state (i.e., solid metallic state) commonly used in water treatment applications. ZVI is commercially available in a granular or powdered form and is a highly reactive chemical reductant. The familiar formation of rust is an iron oxidation reaction that has water treatment applications for environmental contamination. When iron forms rust, it is oxidized, and that oxidation reaction always occurs with a paired chemical reduction reaction. In water treatment applications, the oxidation of the iron can be used to chemically reduce a range of contaminants, destroying them or rendering them less mobile in the environment. ZVI reacts with a range of different chemicals and therefore is **non-specific**.

Oxidation of ZVI results in the generation of ferrous (Fe^{2+}) and/or ferric (Fe^{3+}) iron. ZVI oxidation may be directly coupled to the reduction of a chemical of interest or may generate other reactants (such as ferrous [Fe^{2+}] iron or dissolved hydrogen), which may participate in further chemical or biological reduction reactions. Ferric (Fe^{3+}) iron generated due to ZVI oxidation primarily precipitates as oxyhydroxide minerals. Ferrous (Fe^{2+}) iron generated may precipitate directly, be co-precipitated with the oxyhydroxide minerals, be adsorbed, or remain as dissolved ferrous (Fe^{2+}) iron depending on the pH and other constituents that are present in the water being treated. Lastly, the dissolved hydrogen generated may facilitate biological reactions that provide an additional mechanism of treatment.

Fundamentally, the practical usefulness of ZVI to treat a chemical of interest has three primary considerations. If all three of these considerations are not satisfied, it is unlikely that ZVI will be practical in the application of interest. The considerations are:

1. Will the ZVI react with the chemical of interest?

The first question is a thermodynamic evaluation of the reactivity between ZVI and the chemical of interest. Thermodynamics gives a “yes” or “no” answer as to whether a reaction can occur under a given set of conditions independent of how fast the reaction will occur. Many thermodynamically possible reactions are too slow to be of practical use in environmental remediation. Thermodynamic calculations are possible using widely available data for most chemicals of interest. All reactions described in this memo are thermodynamically favorable.

2. How much ZVI will be required to meet the demand of the chemical of interest?

The second question is answered by evaluating the chemical and biological reactions that apply to the chemical of interest. This is a basic accounting of the mass of ZVI required to react with the chemical of interest over a specified duration. Under the most favorable conditions, these calculations provide insight as to whether or not the use of ZVI is feasible. These calculations can then be modified to account for real-world inefficiencies. This analysis requires no additional laboratory data and serves as an excellent preliminary feasibility evaluation. This basic accounting of ZVI mass is the primary means of evaluation used in this memo.

3. Is the reaction of the ZVI and the chemical of interest kinetically favorable that a reasonably sized treatment system can be constructed?

An analysis of rate kinetics is typically the last step in evaluating the feasibility of a treatment chemistry. Reaction kinetics can be determined through experiments in laboratory trials, small-scale field tests, or extrapolated from literature reviews and practical experience. ZVI reaction kinetics associated with those chemicals of interest at the Site are sufficiently understood to make general comments about their applicability to the NERT Site.

ZVI UTILIZATION CALCULATIONS

The calculations evaluating ZVI as a treatment media to address perchlorate (ClO_4^-), chlorate (ClO_3^-), and/or hexavalent chromium (CrO_4^{2-}) are summarized in Attachments 1 and 2 as Best Case and Most Likely ZVI utilization calculations. The flow rate and associated influent chemistry were obtained from the Groundwater Extraction and Treatment System (GWETS Operation Monthly Report – June 2019 (Envirogen Technologies, Inc. 2019) and are presented below in Table 1.

For this evaluation, it was assumed that a ZVI reactor would replace the current chemical treatment system for hexavalent chromium at the existing GWTP. The GWTP operates at 70 gallons per minute (gpm) and utilizes hexavalent chromium reduction with ferrous iron, precipitation, and clarification treatment processes. The treatment flow rate and available influent chemistry summarized in Table 1 are representative of the influent to the GWTP. It is noteworthy to mention that GWTP-specific nitrate and chlorate data were not available. Therefore, a similar nitrate concentration and chlorate to perchlorate ratio as measured in the influent for the existing Fluidized Bed Biological Reactor was used as a practical approximation. There is no pre-treatment to remove chlorate or nitrate ahead of the GWTP and, therefore, the selected influent concentrations represent reasonable assumptions.

Table 1: GWTP treatment flow rate and associated influent chemistry

Parameter	GWTP influent conditions
Treatment Flow Rate	70 gpm
Dissolved Oxygen	8 mg/L
Nitrate (as N)	10 mg/L
Chlorate	425 mg/L
Perchlorate	500 mg/L
Hexavalent Chromium	7 mg/L

Notes: GWTP = Groundwater Treatment Plant, gpm = gallons per minute, mg/L = milligrams per liter

Because ZVI is a **non-specific** reactant, nontargeted electron acceptors (such as oxygen and nitrate) must be considered to understand ZVI consumption. Thermodynamics notwithstanding, the rate kinetics of ZVI reactivity with dissolved oxygen (DO) are such that this highly relevant reaction will consume ZVI in parallel with chemicals of interest. One of the hypothesized mechanisms for nitrate and chlorate treatment with ZVI is abiotic (i.e., non-biological) reduction (Westerhoff 2003). In contrast, the hypothesized mechanism for perchlorate treatment involves a ZVI corrosion reaction to generate hydrogen, which subsequently facilitates an autotrophic metabolism (a biological reaction) using perchlorate as an electron acceptor (Yu et al. 2006). Nitrate and chlorate are thought to be reduced by a similar biological mechanism. The rate kinetics associated with this indirect biological reduction are comparatively slower than organic carbon mediated biological reduction. Therefore, while the abiotic ZVI reaction mechanism for hexavalent chromium will proceed, there are clearly multiple scavenging reaction mechanisms (i.e., reactions consuming ZVI that do not reduce the contaminants of interest) that will reduce the efficiency of ZVI. This is demonstrated in Attachments 1 and 2 in which the stoichiometry of DO, nitrate, chlorate, perchlorate, and hexavalent chromium is all presented with respect to the flow rate and influent chemistry. The mass of ZVI per mass of chemicals of interest under Best Case conditions (those presented in Attachment 1) is summarized in Table 2.

Table 2: Mass of ZVI per mass of chemicals of interest under Best Case conditions (Attachment 1)

Compound	Pounds of iron per pound of chemical reduced under ideal conditions
Dissolved Oxygen	2.33
Nitrate (as N)	6.65
Chlorate	0.45
Perchlorate	0.75
Hexavalent Chromium	1.07

In Attachment 1, the Best Case conditions for the ZVI reactivity are presented. Namely, all electron transfer is focused on chemically or biologically reducing the chemicals of interest and the ZVI is completely oxidized to ferric (Fe^{3+}) iron. Assuming all electron transfer facilitates biotic or abiotic reduction of the chemicals of interest is a Best Case condition because some percentage (as high as 50 percent) of electrons will be used for cell synthesis by the bacteria. Cells investing energy into cell synthesis is a universal process carried out in all biological systems. Further, assuming all of the ZVI is completely oxidized to ferric (Fe^{3+}) iron is a Best Case condition because, in practice, inefficiencies do occur; therefore, incomplete oxidation of ZVI to ferric (Fe^{3+}) iron is likely to occur and will result in some percentage of ferrous (Fe^{2+}) iron, which is soluble and may flow out of the reactor (i.e., lost treatment capacity). Under these Best Case conditions, the calculated ZVI consumption is approximately 1,200 pounds per day (Attachment 1).

In Attachment 2, the Most Likely conditions for the ZVI reactivity are presented. In these calculations, three changes were made. First, the entirety of the perchlorate and chlorate reduction is not attributed to electron transfer and the benefits of the dismutase enzyme discount the stoichiometric demand of the perchlorate and chlorate on the ZVI. Second, ZVI is assumed to incompletely oxidize to ferrous (Fe^{2+}) iron instead of fully oxidize to ferric (Fe^{3+}) iron. Third, the consumption of ZVI via nitrate, chlorate, and perchlorate reduction was multiplied by 2 to represent 50 percent of the energy from the reaction being diverted to cell synthesis. Under these Most Likely conditions, the calculated ZVI consumption is approximately 1,600 pounds per day.

The analysis of ZVI consumption for treatment of the extracted water at the Site illustrates the amount of ZVI that would be required. For example, the calculations summarized in Attachments 1 and 2 suggest ZVI estimates ranging from over 0.4 to 0.6 million pounds of ZVI per year with an associated ZVI cost of $241,000 to $321,000 per year (at an assumed cost of $0.55 per pound). These costs only represent the annual ZVI media cost and do not consider the holistic system operation, solids management, and/or disposal costs. Additionally, market demands for iron drastically change the price and are largely unpredictable.

SUMMARY AND RECOMMENDATION

At the request of the Trust, Arcadis conducted a focused feasibility assessment of using ZVI in place of the existing chemical treatment at the GWTP to specifically address hexavalent chromium. ZVI is a well established treatment media that has been extensively studied. The general treatment capabilities of ZVI are well understood. The utility of ZVI for a given application comes down to site-specific considerations. With respect to the three primary considerations for practical usefulness of ZVI to treat a chemical of interest at the Site, ZVI may be feasible for full-scale implementation and no further study (laboratory-scale or field-scale) is recommended at this time. If ZVI is to be considered as a leading candidate for full-scale treatment, additional evaluation could be performed as part of the feasibility study.

ENVIRONMENTAL CERTIFICATION JURAT

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 provided 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.

Description of Services: Ex-situ Zero Valent Iron (ZVI) Technology Evaluation for the Nevada Environmental Resource Trust Site.

Yun Y. Wang
Principal Environmental Engineer
CEM No. 2125 (expires 10/18/2021)

ATTACHMENTS

Attachment 1. Best Case Zero Valent Iron Utilization Calculations

Attachment 2. Most Likely Zero Valent Iron Utilization Calculations

REFERENCES

Envirogen Technologies, Inc. 2019. Memo to NDEP Nevada Environmental Response Trust titled NERT – GWETS Operation Monthly Report – June 2019. July 20.

Westerhoff, Paul. 2003. Reduction of Nitrate, Bromate, and Chlorate by Zero Valent Iron (Fe0). Journal of Environmental Engineering-asce - J ENVIRON ENG-ASCE. 129. 10.1061/(ASCE)0733-9372(2003)129:1(10).

Yu, Xueyuan, Christopher Amrhein, Marc Deshusses, and Mark Matsumoto. 2006. Perchlorate Reduction by Autotrophic Bacteria in the Presence of Zero-Valent Iron. Environmental science & technology. 40. 1328-34. 10.1021/es051682z.

Attachment 1 - Best Case Zero Valent Iron Utilization Calculations
NERT Site, Henderson, NV

Scenario #1: NERT GWTP influent conditions		
Parameter	Value	Unit
Flowrate	70	gpm
Dissolved Oxygen	8	mg/L
Nitrate (as N)[1]	10	mg/L
Chlorate[1]	425	mg/L
Perchlorate	500	mg/L
Chromate (as Cr)	7	mg/L

Scenario #1: NERT GWTP influent conditions			
Individual Electron Acceptor Load	ZVI Dose (mg/L)	ZVI Consumption Rate (lb/day)	ZVI Consumption Rate (ton/month)
Dissolved Oxygen	19	16	0.2
Nitrate	66	56	1
Chlorate	569	478	7
Perchlorate	749	630	9
Chromate	8	6	0.1
Total Electron Acceptor Load	1,410	**1,186**	18

Scenario #2: NERT GWETS influent conditions		
Parameter	Value	Unit
Flowrate	1,000	gpm
Dissolved Oxygen	8	mg/L
Nitrate (as N)	10	mg/L
Chlorate	130	mg/L
Perchlorate	150	mg/L
Chromate (as Cr)	0.03	mg/L

Scenario #2: NERT GWETS influent conditions			
Individual Electron Acceptor Load	ZVI Dose (mg/L)	ZVI Consumption Rate (lb/day)	ZVI Consumption Rate (ton/month)
Dissolved Oxygen	19	224	3
Nitrate	66	799	12
Chlorate	174	2,091	31
Perchlorate	225	2,699	40
Chromate	0.03	0.3	0.005
Total Electron Acceptor Load	484	**5,813**	87

Molecular Weight	Value	Unit
Oxygen (O_2)	32	mg/mmol
Nitrate (NO_3^-)	62	mg/mmol
Chlorate (ClO_3^-)	83	mg/mmol
Perchlorate (ClO_4^-)	99	mg/mmol
Chromate (CrO_4^{2-})	116	mg/mmol
Chromium (Cr^{6+}/Cr^{3+})	52	mg/mmol
Nitrogen (N)	14	mg/mmol
Iron ($Fe^0/Fe^{2+}/Fe^{3+}$)	56	mg/mmol

Electron Acceptor Half Reactions

Oxygen

$$\frac{1}{4}\mathrm{O_2} + H^+ + e^- \leftrightarrow \frac{1}{2}\mathrm{H_2O}$$

Nitrate

$$\frac{1}{5}\mathrm{NO_3}^- + \frac{6}{5}H^+ + e^- \leftrightarrow \frac{1}{10}\mathrm{N_2} + \frac{3}{5}\mathrm{H_2O}$$

Chlorate

$$\frac{1}{6}\mathrm{ClO_3}^- + H^+ + e^- \leftrightarrow \frac{1}{6}\mathrm{Cl}^- + \frac{1}{2}\mathrm{H_2O}$$

Perchlorate

$$\frac{1}{8}\mathrm{ClO_4}^- + H^+ + e^- \leftrightarrow \frac{1}{8}\mathrm{Cl}^- + \frac{1}{2}\mathrm{H_2O}$$

Chromate

$$\frac{1}{3}\mathrm{CrO_4}^{-2} + \frac{5}{3}H^+ + e^- \leftrightarrow \frac{1}{3}\mathrm{Cr(OH)_3} + \frac{1}{3}\mathrm{H_2O}$$

Electron Donor Half Reactions

ZVI (elemental iron to ferric [Fe^{3+}])

$$\frac{1}{3}Fe^0 + \frac{2}{3}\mathrm{H_2O} \leftrightarrow \frac{1}{3}\mathrm{FeO(OH)} + H^+ + e^-$$

ZVI (elemental iron to ferrous [Fe^{2+}])

$$\frac{1}{2}Fe^0 + \frac{1}{2}\mathrm{H_2O} \leftrightarrow \frac{1}{2}Fe^{2+} + \frac{1}{2}OH^- + \frac{1}{2}H^+ + e^-$$

Notes:

[1]Approximate value in the absence of real data. Assumed similar nitrate as Scenario #2 and a similar chlorate to perchlorate ratio as Scenario #2

gpm: gallons per minute
GWETS: Groundwater Extraction Treatment System
GWTP: Groundwater Treatment Plant
lb/d: pounds per day
mg/L: milligrams per liter
mg/mmol: milligrams per millimole

Attachment 2 - Realistic Zero Valent Iron Utilization Calculations
NERT Site, Henderson, NV

Scenario #1: NERT GWTP influent conditions		
Parameter	Value	Unit
Flowrate	70	gpm
Dissolved Oxygen	8	mg/L
Nitrate (as N)[1]	10	mg/L
Chlorate[1]	425	mg/L
Perchlorate	500	mg/L
Chromate (as Cr)	7	mg/L

Scenario #1: NERT GWTP influent conditions			
Individual Electron Acceptor Load	ZVI Dose (mg/L)	ZVI Consumption Rate (lb/day)	ZVI Consumption Rate (ton/month)
Dissolved Oxygen	28	23	0.4
Nitrate	100	168	3
Chlorate[2]	284	478	7
Perchlorate[2]	562	945	14
Chromate	11	9	0.1
Total Electron Acceptor Load	985	**1,624**	24

Scenario #2: NERT GWETS influent conditions		
Parameter	Value	Unit
Flowrate	1,000	gpm
Dissolved Oxygen	8	mg/L
Nitrate (as N)	10	mg/L
Chlorate	130	mg/L
Perchlorate	150	mg/L
Chromate (as Cr)	0.03	mg/L

Scenario #2: NERT GWETS influent conditions			
Individual Electron Acceptor Load	ZVI Dose (mg/L)	ZVI Consumption Rate (lb/day)	ZVI Consumption Rate (ton/month)
Dissolved Oxygen	28	336	5
Nitrate	100	2,397	36
Chlorate[2]	87	2,091	31
Perchlorate[2]	168	4,049	61
Chromate	0.04	0.5	0.007
Total Electron Acceptor Load	383	**8,872**	133

Molecular Weight	Value	Unit
Oxygen (O_2)	32	mg/mmol
Nitrate (NO_3^-)	62	mg/mmol
Chlorate (ClO_3^-)	83	mg/mmol
Perchlorate (ClO_4^-)	99	mg/mmol
Chromate (CrO_4^{2-})	116	mg/mmol
Chromium (Cr^{6+}/Cr^{3+})	52	mg/mmol
Nitrogen (N)	14	mg/mmol
Iron ($Fe^0/Fe^{2+}/Fe^{3+}$)	56	mg/mmol

Electron Acceptor Half Reactions

Oxygen

$$\frac{1}{4}\mathrm{O_2} + H^+ + e^- \leftrightarrow \frac{1}{2}\mathrm{H_2O}$$

Nitrate

$$\frac{1}{5}\mathrm{NO_3}^- + \frac{6}{5}H^+ + e^- \leftrightarrow \frac{1}{10}\mathrm{N_2} + \frac{3}{5}\mathrm{H_2O}$$

Chlorate

$$\frac{1}{6}\mathrm{ClO_3}^- + H^+ + e^- \leftrightarrow \frac{1}{6}\mathrm{Cl}^- + \frac{1}{2}\mathrm{H_2O}$$

Perchlorate

$$\frac{1}{8}\mathrm{ClO_4}^- + H^+ + e^- \leftrightarrow \frac{1}{8}\mathrm{Cl}^- + \frac{1}{2}\mathrm{H_2O}$$

Chromate

$$\frac{1}{3}\mathrm{CrO_4}^{-2} + \frac{5}{3}H^+ + e^- \leftrightarrow \frac{1}{3}\mathrm{Cr(OH)_3} + \frac{1}{3}\mathrm{H_2O}$$

Electron Donor Half Reactions

ZVI (elemental iron to ferric [Fe^{3+}])

$$\frac{1}{3}Fe^0 + \frac{2}{3}\mathrm{H_2O} \leftrightarrow \frac{1}{3}\mathrm{FeO(OH)} + H^+ + e^-$$

ZVI (elemental iron to ferrous [Fe^{2+}])

$$\frac{1}{2}Fe^0 + \frac{1}{2}\mathrm{H_2O} \leftrightarrow \frac{1}{2}Fe^{2+} + \frac{1}{2}OH^- + \frac{1}{2}H^+ + e^-$$

Notes:

[1]Approximate value in the absence of real data. Assumed similar nitrate as Scenario #2 and a similar chlorate to perchlorate ratio as Scenario #2

[2]Assumes bioreduction to chlorite; chlorite dismutase reaction requires no external electron. Also, 50% of electron transfer assumed to go to cell synthesis for biotic reactions (nitrate, chlorate, and perchlorate)

GWETS: Groundwater Extraction Treatment System
GWTP: Groundwater Treatment Plant
lb/d: pounds per day
mg/L: milligrams per liter
mg/mmol: milligrams per millimole