DRAFT CHEMICAL OXIDATION CONTINGENCY PLAN
CORRECTIVE ACTION FOR SOURCE AREA SOIL
MARYLAND SQUARE PCE SITE
3661 SOUTH MARYLAND PARKWAY
LAS VEGAS, NEVADA

SUBMITTED TO
NEVADA DIVISION OF ENVIRONMENTAL PROTECTION
BUREAU OF CORRECTIVE ACTIONS
901 SOUTH STEWART STREET, SUITE 4001
CARSON CITY, NEVADA 89701-5249

PREPARED FOR
HERMAN KISHNER TRUST
C/O MR. TOM VANDENBERG, ESQ.
707 WILSHIRE BOULEVARD, 45TH FLOOR
LOS ANGELES, CALIFORNIA 90017

PREPARED BY

TETRA TECH
639 Isbell Road, Suite 390
Reno, NEVADA 89509
775.322.0555

July 5, 2011

TABLE OF CONTENTS

1.0 INTRODUCTION 1
2.0 CHEMICAL OXIDATION 1
2.1 Oxidant Dosing 1
2.2 Oxidant Application 1
3.0 IN-SITU OXIDATION PERFORMANCE MONITORING AND CONTINGENCY MEASURES 2
4.0 SAFETY AND ENVIRONMENTAL CONCERNS AND CONTINGENCY MEASURES 2
4.1 Desorption and Mobilization of Contaminants 2
4.2 Displacement of Contaminated Groundwater into Previously Clean Areas 3
4.3 Alteration and Mobilization of Naturally Occurring Constituents 3
4.4 Precipitation of Mineral Phases that Occlude Porosity and Permeability of the Soil 4
4.5 Explosive Exothermic Reaction 4
4.6 Unexpected Breakthrough of Injectate 4
4.7 Damage to Utilities and Buried Infrastructure 4
5.0 REFERENCES 5

Table
1 SUMMARY OF BENCH-SCALE TEST METALS MOBILITY RESULTS

Appendix
A Calculations

Attachment
1 Bench-Scale Test Report

1.0 INTRODUCTION

This contingency plan has been prepared in response to a Nevada Division of Environmental Protection (NDEP) letter dated October 27, 2010, on the subject of the Draft Soil Corrective Action Plan for the Maryland Square Shopping Center.

The remedial design for corrective action of source area soils at the Maryland Square PCE site was prepared in accordance with the final corrective action plan (CAP) for source area soils (Tetra Tech 2010). The CAP specifies excavation of tetrachlorethylene (PCE)-impacted source area soils above the water table, and application of a chemical oxidant to the bottom of the excavation. NDEP has asked that this contingency plan evaluate and respond to some of the common problems resulting from in situ treatment using a chemical oxidant.

NDEP's letter (NDEP 2010) and a subsequent email (NDEP 2011) indicated that the contingency plan should:

- Outline how the success of the remedy will be evaluated against specific criteria, and what additional remedial measures could be taken if cleanup goals are not achieved.
- Address safety and environmental concerns including:
  - Desorption and mobilization of contaminants
  - Displacement of contaminated groundwater into previously clean areas
  - Alteration and mobilization of naturally occurring constituents
  - Precipitation of mineral phases that occlude porosity and permeability of the soil
  - Explosive exothermic reaction
  - Breakthrough of injectate
  - Damage to utilities and buried infrastructure.

2.0 CHEMICAL OXIDATION

The chemical oxidant will be applied to the bottom of the excavation after impacted soil above the water table has been removed. Based on the most recent groundwater elevations, the excavation is expected to be 20 feet deep.

2.1 Oxidant Dosing

According to the bench-scale test (Attachment 1), the permanganate natural oxidant demand of these soils is 0.4 grams per kilogram. Appendix A presents dosing calculations. Approximately 205 pounds of potassium permanganate will be applied to a 1,280-square-foot targeted treatment area over a 3-foot vertical interval. This is more than enough oxidant to satisfy the natural and contaminant oxidant demand of a 4-foot-thick layer of soil. The remaining oxidant will migrate downgradient and treat any dissolved PCE in its path.

2.2 Oxidant Application

Permanganate will be mixed with 820 gallons of water to produce 828 gallons of a 3 percent solution. Half of it (414 gallons) will be applied to 1,280 square feet of open excavation and mixed into the top 1 foot of saturated soil. Permanganate in this layer will diffuse into the soil below and treat at least 1 more foot of saturated soil. Soil mixing is being limited to 1 foot because it will be difficult to compact saturated soil, and poorly compacted soil can lead to long-term settlement that would be detrimental to future structures.

The other half of the permanganate solution (414 gallons) will be applied to the overlying 2 feet of fill material. If seasonal effects cause the water table to rise, the permanganate in the fill material will react with the PCE in groundwater and reduce the potential for re-contamination of clean fill material.

Application of a chemical oxidant in this manner is particularly appropriate and convenient for an open excavation. It will reduce the mass of PCE that might be acting as a continuing source for groundwater contamination. However, no target action level has been established for PCE concentration in saturated soil or groundwater. Information gathered from this effort will be useful in evaluating corrective action alternatives for groundwater detailed in the Draft Corrective Action Plan for Groundwater (Tetra Tech 2011).

3.0 IN-SITU OXIDATION PERFORMANCE MONITORING

After the excavation has been backfilled, a new monitoring well (MW-34) will be installed near the center of the treated excavation area. MW-34 will be screened through the upper 10 feet of the shallow aquifer. This well will be sampled 1 week, 1 month, and then every 3 months after installation. In addition, one new temporary monitoring well will be installed 40 feet downgradient of the treatment area. This well will also be screened across the upper 10 feet of the shallow aquifer. The new wells will be monitored quarterly for PCE, chromium, selenium, zinc, and field parameters including permanganate, pH, Eh, conductivity, temperature, and dissolved oxygen. Some of these parameters may be dropped from the program if they do not change significantly after 6 months of monitoring.

Change in PCE concentration versus time will serve as a measure of remedial progress. A decreasing trend will indicate that the remedy is working. PCE concentration in the treatment zone is expected to decrease initially, and then to increase gradually as oxidant concentrations decrease and PCE desorbs from the soil.

Dissolved permanganate will indicate the presence of the oxidant. Its concentration over time will indicate the rate at which oxidant is being used and will help determine the duration over which the oxidant might persist.

Elevated levels of dissolved metals will imply that metals present in the soil are being oxidized to more soluble species. Data from the downgradient monitoring well will help determine the extent of migration of the oxidant and dissolved metals.

The other monitoring parameters will provide additional information on the effect of oxidation and the extent of geochemical changes. The new wells will be monitored for 1 year following the soil corrective action.

Because no action levels are to be specified, oxidant application will be considered a success if dissolved PCE concentration decreases over time (indicating a decrease in source area mass). Moreover, generation of information that can be useful for evaluating groundwater corrective action alternatives detailed in the Draft Corrective Action Plan for Groundwater (Tetra Tech 2011) also would indicate success.

Application of oxidant to groundwater as part of corrective action for source area soil is not intended to be the final action at the site. If PCE in groundwater persists, additional action may be taken under the corrective action for groundwater (Tetra Tech 2011).

4.0 SAFETY AND ENVIRONMENTAL CONCERNS AND CONTINGENCY MEASURES

This section discusses some of the common concerns of in situ treatment with permanganate, and measures that can be adopted to mitigate negative impacts.

4.1 Desorption and Mobilization of Contaminants

Permanganate will not increase the solubility or mobility of PCE. Desorption from the soil will result primarily from a concentration gradient caused by destruction of PCE in the dissolved phase. When dissolved-phase PCE destruction stops, PCE will continue to desorb from the soil until equilibrium is reached. A sudden drop in PCE concentration in the targeted treatment area followed by a gradual increase (rebound) is common and may occur at this site. The magnitude of rebound will depend on the

amount of sorbed PCE. This should not be interpreted as an increase in solubility or mobility. No contingency measures are planned for increased solubility or mobility of PCE because the treatment will not result in these types of increases.

4.2 Displacement of Contaminated Groundwater into Previously Clean Areas

A total of 828 gallons of permanganate solution will be applied to saturated soil and coarse granular fill material. This equates to a 1-inch-thick layer of solution applied to the targeted treatment area. Half this volume (0.5-inch-thick layer of solution) will be applied to the 2 feet of clean imported granular fill material that will be placed above the saturated soil. The clean imported fill material is expected to retain the entire volume of permanganate solution applied to it. Therefore, the volume of permanganate solution introduced into groundwater will be only 414 gallons (0.5-inch-thick layer of solution). For a 10-foot-thick aquifer consisting of fine-grained material with an effective porosity of 0.35, this equates to approximately 1.24 percent of the pore volume (see Appendix A for calculations). This is 20 times less than the pore volume fraction sometimes targeted with in-situ chemical oxidation. Even with these low volumes, some displacement of contaminated groundwater is inevitable; however, this will not cause any measurable short-term increase in the size of the PCE plume. On the other hand, reduction in the mass of PCE through treatment will reduce the size of the plume in the long term. No contingency action is necessary to compensate for the small volume of PCE-contaminated groundwater that will be displaced.

4.3 Alteration and Mobilization of Naturally Occurring Constituents

Soils can contain metals that transform to more soluble species when oxidized. Permanganate applied to soil is likely to oxidize some metals, rendering them more soluble. This is evident in the results of the bench-scale test (Attachment 1), which showed that reaction with permanganate increased aqueous concentrations of chromium, selenium, and zinc, although not above their respective maximum contaminant levels (MCL) for drinking water (Table 1 summarizes these results). Any increases in metals concentrations resulting from field application of oxidant are expected to be localized and temporary. Moreover, as the bench-scale test results suggest, dissolved metals concentrations in groundwater are not expected to exceed their respective MCLs. The concentrations of dissolved metals would decrease after exhaustion of the permanganate (Moore 2008; Siegrist et al.).

TABLE 1

SUMMARY OF BENCH-SCALE TEST METALS MOBILITY RESULTS

Parameter	Units	Control	Test 1	Test 2	Test 3	MCL [1]
Permanganate dose	g/Kg	0	0.4	0.8	0.8	NA
Test Duration	days	3	3	3	7	NA
Chromium	µg/L	< 0.5	23	17	34	100
Selenium	µg/L	1.9	10	6.8	13	50
Zinc	µg/L	21	57	34	34	5,000

µg/L Micrograms per liter
g/Kg Grams per kilogram
MCL Maximum contaminant level
NA Not applicable
[1] The MCL for zinc is a secondary standard

In the unlikely event that dissolved metals are detected at concentrations above their MCLs in the downgradient temporary monitoring well, the groundwater could be treated with reducing agents to quench the oxidant. Once the oxidant has been quenched, the concentrations of dissolved metals will decrease. Sodium thiosulfate and sodium bisulfite are examples of reducing agents that may be used to quench the oxidant. However, other products may be used if found to be more cost effective, subject to approval by NDEP. It should be noted that quenching the oxidant would be detrimental to the goal of corrective action because such treatment would also stop the destruction of PCE in groundwater.

4.4 Precipitation of Mineral Phases that Occlude Porosity and Permeability of the Soil

Manganese dioxide is an end product of permanganate oxidation-reduction reactions that occur at pH between 3.5 and 12 (Interstate Technology & Regulatory Council [ITRC] 2005). One mole of potassium permanganate will produce one mole of manganese dioxide. Therefore, 205 pounds of permanganate will produce 0.36 cubic feet of manganese dioxide (see Appendix A for calculations). Oxidant applied to 1,280 square feet of soil is expected to extend 2 feet into native material below the water table and 2 feet into coarse granular fill above the water table. The estimated effective pore volume of the oxidative zone is 1,408 cubic feet. Thus, precipitated manganese dioxide is expected to occupy an estimated 0.026 percent of the treated pore volume, rendering reduction in porosity and permeability insignificant. No contingency measures are necessary.

4.5 Explosive Exothermic Reaction

Explosive reactions can occur when permanganate in either solid form or in concentrated solutions mixes with incompatible chemicals, including strong reducing agents. When used for remediation, permanganate is typically applied at a concentration of less than 10 percent, and explosive reactions are not a concern. For this corrective action, permanganate will be applied at a 3 percent concentration, at which explosion or significantly exothermic reactions are not likely even if the permanganate solution contacts PCE nonaqueous-phase liquid. Furthermore, the bench-scale test did not show any increase in temperature even with a higher dose of permanganate (Attachment 1).

4.6 Unexpected Breakthrough of Injectate

This refers to surfacing of the injected permanganate solution through the borehole annulus. Because boreholes will not be used to inject permanganate into the targeted treatment area, unexpected breakthrough is not possible. No contingency measures are necessary.

4.7 Damage to Utilities and Buried Infrastructure

This is not a concern because the permanganate will be applied to the bottom of an open excavation approximately 20 feet below ground surface. There are no buried utilities anywhere near the targeted treatment zone, and shallower utilities in the vadose zone are not at risk. No contingency measures are necessary.

5.0 REFERENCES

Interstate Technology & Regulatory Council (ITRC). 2005. Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater. Second Edition. January.

Moore, Kelly. 2008. Geochemical Impacts From Permanganate Oxidation Based on Field Scale Assessments. Master's Thesis. East Tennessee State University. December.

Nevada Division of Environmental Protection (NDEP). 2010. Letter regarding the Draft Soil Corrective Action Plan, Maryland Square Shopping Center. From Tim Swickard, NDEP. To Irwin Kishner. October 27.

NDEP. 2011. Email regarding the Contingency Plan. From Mary Siders, NDEP. To Lisa Medve, Tetra Tech. March 30.

Siegrist, Robert L., Michael A. Urynowicz, Olivia R. West, Michelle .L. Crimi, and Kathryn S. Lowe. Principles and Practices of In Situ Chemical Oxidation Using Permanganate. 2001. Chapter 2. Literature Review of the Impact of Permanganate Oxidation on Metals in the Subsurface. Battelle Press.

Tetra Tech. 2010. Corrective Action Plan for Source Area Soil. Maryland Square Shopping Center. 3661 South Maryland Parkway, Las Vegas, Nevada. December 14.

Tetra Tech. 2011. Draft Corrective Action Plan for Groundwater. Maryland Square PCE Site. 3661 South Maryland Parkway, Las Vegas, Nevada. June 14.

APPENDIX A

Calculations

Appendix A - Calculations
Maryland Square PCE Site
Corrective Action for Source Area Soil
Chemical Oxidation Contingency Plan

General Parameters

Plan view area of treatment zone	1,280	sf	*Proposed*
Thickness of treatment zone	4	ft	*Proposed*
Soil dry bulk density	100	pcf	*Estimated from pre-design geotechnical investigation (GES 2011)*
Effective porosity	0.35		*Estimated from Section 2.3 of GW CAP (Tetra Tech 2011)*
Moisture content	10%		*Estimated from Section 2.3 of GW CAP (Tetra Tech 2011)*
Soil wet bulk density	110	pcf	
Mass of permanganate added	205	lbs	*Proposed*
Volume of water added	820	gal	*Proposed*

Permanganate Solution Concentration

Mass of potassium permanganate	205	lbs
Volume of water	820	gal
	110	cf
Unit weight of water	62.4	pcf
Mass of water	6,841	lbs
Concentration of permanganate in solution	3.00%	

Solution Volume

Mass of potassium permanganate	205	lbs
Mass of water	6,841	lbs
Mass of water + permanganate	7,046	lbs
Unit weight of 3% solution	1.02	g/mL
	63.65	pcf
Volume of solution	110.7	cf
	828.0	gal

Appendix A - Calculations
Maryland Square PCE Site
Corrective Action for Source Area Soil
Chemical Oxidation Contingency Plan

Permanganate Dose per Unit Mass of Soil

Volume of treatment zone	5,120	cf
Mass of soil in treatment zone	563,200	lbs
	256,000	Kg
Mass of permanganate added	205	lbs
	93,182	g
Permanganate dose	0.364	g/Kg

Displacement of Contaminated Groundwater

Plan view area of treatment zone	1,280	sf	
Total volume of solution	828	gal	
	111	cf	
	1.04	in	
Volume of permanganate solution applied to groundwater	414	gal	
	55	cf	
	0.52	in	
Field capacity of coarse sand fill material	0.5	in water/ft soil	Conservative value
Unit volume of permanganate solution stored in fill	399	gal/ft soil	
Thickness of fill layer dosed with oxidant	2	ft	
Total volume of permanganate solution stored in fill	798	gal	
Volume of permanganate solution percolating	0	gal	
	0	cf	
Total aquifer thickness inside treatment area	10	ft	*Assumed*
Effective porosity of aquifer	0.35		
Total pore volume of aquifer	4,480	cf	
Aquifer pore volume displaced	1.24%		

Appendix A - Calculations
Maryland Square PCE Site
Corrective Action for Source Area Soil
Chemical Oxidation Contingency Plan

Increase in Moisture Content

Volume of soil in treatment zone	5,120	cf
Dry unit weight of soil	100	pcf
Mass of soil in treatment zone	512,000	lbs
Volume of water added	820	gal
	110	cf
Unit weight of water	62.4	pcf
Mass of water added	6,841	lbs
Increase in moisture content	1.3%	

Porosity Occlusion

$$4KMnO_4 + 3C_2Cl_4 + 4H_2O \rightarrow 6CO_2 + 4MnO_2(s) + 4K^+ + 12Cl^- + 8H^+$$

$$\frac{[KMnO_4]}{[MnO_2]} = \frac{4}{4} = 1$$

1 mole $KMnO_4$ = 158.03 g

1 mole MnO_2 = 86.9 g

1 g	$KMnO_4$	--->	0.55 g	MnO_2
205 lb	$KMnO_4$	--->	113 lb	MnO_2

Particle Density of MnO_2 = 5.03 g/cc
313.9 pcf

Volume of 113 lb MnO_2 = 0.36 cf

Appendix A - Calculations
Maryland Square PCE Site
Corrective Action for Source Area Soil
Chemical Oxidation Contingency Plan

	Treatment Zone				
	Area	Thickness	Volume	Porosity	Pore Vol
	sf	*ft*	*cf*	*cf*	*cf*
Native soil	1,280	2	2,560	0.35	896
Sandy gravel fill	1,280	2	2,560	0.2	512
Total					**1,408**

Total pore volume of treatment zone 1,408 cf

0.36 cf MnO_2 in 1,408 cf pore volume

Therefore, porosity occlusion = 0.026%

RemOx® S and L ISCO Reagents Estimation Spreadsheet

Input data into box with blue font

Site Name: Input site name here
Date: Input date here

	Estimates	Units
Treatment Area Volume		
Length	40	ft
Width	32	ft
Area	1280	sq ft
Thickness	4	ft
Total Volume	190	cu yd
Soil Characteristics/Analysis		
Porosity	35	%
Total Plume Pore Volume	13405	gal
Avg Contaminant Conc	10	ppm
Mass of Contaminant	1.12	lb
PNOD	0.4	g/kg
Effective PNOD	60	%
Effective PNOD Calculated	0.24	
PNOD Oxidant Demand	135.168	lb
Avg Stoichiometric Demand	1.3	lb/lb
Contaminant Oxidant Demand	1.45	lb
Theoretical Oxidant Demand	136.62	lb
Confidence Factor	1.5	
Calculated Oxidant Demand	204.9335	
Injection Volumes for RemOx S		
RemOx S Injection Concentration	3.0%	%
Total Volume of Injection Fluid	819	gal
Pore Volume Replaced	0.06	%
Amount of RemOx S ISCO Reagent Estimated		**205 pounds**
Injection Volumes for RemOx L		
RemOx L Injection Concentration	10.0%	%
Calculated Specific Gravity	1.091623	g/ml
Total Volume of Injection Fluid	202	gal
Pore Volume Replaced	0.02	%
Amount of RemOx L ISCO Reagent Estimated		**460 pounds**
		40 gallons

ATTACHMENT 1

Bench-Scale Test Report

Carus Remediation Technologies
Bench Scale Testing

9 June 2011

Customer: Tetra Tech
518 17th Street, Suite 900
Denver, Colorado 80202

Cc: K. Frasco

Attention: C. Christian

From: L. Mueller

TECH # 11-077

Subject: Soil Oxidant Demand and Screening for Impact of RemOx® S ISCO Reagent on Metals Following Contact with Soil

Summary
Treatment of the soil/caliche composite with 0.4 g/kg or 0.8 g/kg RemOx® S ISCO reagent resulted in minimal potassium permanganate ($KMnO_4$) demand and negligible impact on the temperature under the parameters tested. Dissolved manganese, chromium, selenium, and zinc were observed to be increased after 3 days and 7 days.

Background
Two tubes of soil and one tube of caliche were received from the Maryland Square Shopping Center MSSC Project from Tetra Tech on May 11, 2011. The soil tubes were labeled B 13-B 19' to 19.5' and B 13-B 19.5' to 20'. The caliche tube was labeled B 13-B 3.0' to 5.0'. The client requested that a composite be prepared by mixing 9 parts of soil with 1 part caliche by volume. The composite sample was analyzed for permanganate natural oxidant demand (PNOD) following ASTM D7262-07 Test Method A and total oxidant demand (TOD) following Carus Analytical methods. The sample were then dosed with levels of RemOx S indicated by the natural oxidant demand testing in order to screen for the impact of *in situ* chemical oxidation (ISCO) on the mobility of arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver and zinc.

Experimental
One soil/caliche composite was prepared. The contents of the soil tubes B 13-B 19' to 19.5 and B 13B 19.5' to 20'and caliche tube B 13-B 3.0' to 5.0' were mixed at a ratio of 9 parts by volume soil to one part by volume caliche. The samples were blended using hand tools at the Carus laboratory.

To determine the PNOD following ASTM D7262-07 Test Method A, a portion of the composite sample was weighed, then baked at 105°C for 24 hours, and then allowed to cool to room temperature. The sample was again weighed and the moisture calculated. The baked composite sample was then blended and passed through a U.S. 10 sieve (2 mm). Some rocks were retained on the sieve. For each sample, reactors were loaded with 50 grams of soil and 100 mL of 20.0 g/L potassium permanganate ($KMnO_4$) for an initial dose of 40.0 g/kg $KMnO_4$ on a dry soil

weight basis at a 1:2 soil to aqueous reagent ratio. Each soil dose was performed in triplicate. The reaction vessels were inverted once to mix the reagents. Residual permanganate (MnO_4^-) was determined at 48 hours. The demands were calculated on a dry weight basis.

To estimate the total oxidant demand (TOD), the moisture content for each soil sample was calculated from the composite above. One reactor was loaded with 50 grams soil as received (not baked or sieved) and 100 mL of 2% $KMnO_4$. Due to a limited soil volume one replicate was performed for this test. The reaction vessel was inverted once to mix the reagents. Residual permanganate (MnO_4^-) was determined within the first hour and at 48 hours. The demands were calculated on a dry weight basis.

To test the effect of *in situ* chemical oxidation (ISCO) treatment on the metals, portions of approximately 181 g of each unbaked composite soil were prepared. The samples were kept refrigerated until about 16 hours prior to testing. When it was time to start the test, the sample and the temperature of the dosing solution were measured.

The sample for Test 3 was dosed with 300 mL of a 0.4 g/L solution that had been prepared from RemOx® S ISCO reagent lot 001-5-1029 for an initial dose of 0.8 g/kg on a dry weight basis. The sample was inverted several times to mix the soil and solution. The temperature was then measured at 3 minutes, 5 minutes, 10 minutes, 20 minutes, 24 hours, 48 hours, 72 hours, 96 hours, 120 hours, 144 hours, and 168 hours.

The samples for the Control, Test 1 and Test 2 were dosed with 300 mL of deionized water, 0.2 g/L or 0.4 g/L $KMnO_4$ solution described above for initial doses of 0 g/kg, 0.4 g/kg, or 0.8 g/kg on a dry weight basis. The samples were inverted several times to mix. Temperature was measured at 3 minutes, 5 minutes 10 minutes, 20 minutes, 24 hours, 48 hours, and 72 hours.

The samples were then checked for residual $KMnO_4$ at the end of the reaction period (72 hours for Test 1 and Test 2 and 168 hours for Test 3). The samples were then quenched with sodium thiosulfate and the liquid portion passed through a 0.45 micron filter collected in nalgene bottles, acidified with nitric acid and placed in a refrigerator. The samples were packed in a cooler with ice and shipped overnight to a contract laboratory (Advanced Technology Laboratories, 3151 W. Post Road, Las Vegas, Nevada) specified by the client. Information from the client that analysis for arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver and zinc by EPA 6020/200.8 would be requested was included with the samples.

Results and Discussion

The permanganate demand is the amount of permanganate consumed in a given amount of time. It should be noted that in a soil or groundwater sample, the oxidation of any compound by permanganate is dependent on the initial dose of permanganate and the reaction time available. As the permanganate dose is increased, the reaction rate and oxidant consumption may also increase. Some compounds that are not typically oxidized by permanganate under low doses can become reactive with permanganate at higher concentrations.

The 48-hour PNOD results can be seen in Table 1 (on a dry soil basis). From the initial dose of 40.0 g/kg $KMnO_4$ the average 48-hour demand was 0.4 g/kg.

The TOD is performed on a sample that is not baked or sieved. The result of the TOD is often similar to the NOD, but may vary if the soil contains rocks retained on the sieve, a high concentration of organic materials that are volatilized or changed during baking. The amount of moisture present in the soil is included in the calculation with the assumption that all of the moisture from the soil will be available to mix with the dosing solution. For some soils not all of

the soil moisture mixes with the solution, or it mixes slowly compared to the time frame of the test.

The 48 hour total oxidant demand (TOD) results in Table 2 showed an apparent negative demand when calculated using moisture contribution with the assumption that all of the soil moisture mixed with the $KMnO_4$ dosing solution. An estimation of the TOD by calculating the difference between the solution concentration at less than 1 hour and 48 hours gave an apparent change of 2.0 g/kg. This alternate calculation assumes that the amount of moisture that mixed with the solution at 1 hour was the only moisture available. It is anticipated that this is not a true demand.

Table 1: 48-Hour PNOD *

Soil Sample Identification	Average and Standard Deviation (g/kg)	Replicate 1 (g/kg)	Replicate 2 (g/kg)	Replicate 3 (g/kg)
Composite	0.4 ± 0.2	0.4	0.4	0.3

*Demands were calculated on a weight $KMnO_4$/dry soil weight basis from an initial dose of 40.0 g/kg $KMnO_4$ at a 1:2 soil to aqueous solution ratio.

Table 2: 48-Hour TOD *estimate

Soil Sample Identification	Initial Dose Solution (g/L)	Reaction Time (hours)	$KMnO_4$ residual in aqueous portion (g/L)	% Moisture	Total Oxidant Demand (g/kg)	Apparent Change in Oxidant Demand from 1 hour to 48 hours (g/kg)
Composite	20.0	<1	19.6	17.2%	Apparent negative value	
Composite	20.0	48	18.6	17.2%	Apparent negative value <0.1	2.0

*Demands were calculated on a weight $KMnO_4$/dry soil weight basis from an initial dose of 48.4 g/kg $KMnO_4$ at a 1:2 soil as received to aqueous solution added ratio.

The Test Doses for the metals mobility study were chosen by the client after reviewing the NOD. Table 3a and b show that the temperatures of the soils and solutions were similar to the blank which was kept with them. Table 4 shows the results of the residual permanganate analysis at the end of the reaction period. Very little permanganate was consumed by the soil in this test.

The samples from Test 1, Test 2, and Test 3 were quenched with sodium thiosulfate just prior to filtration. The control was not quenched. No pink or brown coloration was observed in the quenched samples after filtration. The absence of coloration was not confirmed with a spectrophotometer due to the low amount of sample volume. The soil in the Control and in Test 2 were the better settled at the end of the reaction time prior to quenching compared to Test 1 and Test 3.

Table 3a: Temperature Observations for Composite Control, Test 1 and Test 2

Parameter/time	Composite Control	Composite Test1 (°C)	Composite Test 2 (°C)	Blank (°C)
Concentration of Test solution g/L	0	0.2	0.4	
Oxidant Dose to soil, g/kg as $KMnO_4$	0	0.4	0.8	
Soil Temperature before addition, °C	22.5	22.5	22.6	
Solution Temperature before addition, °C	22.5	22.6	22.6	22.6°
Temperature at 3 minutes, °C	22.5	22.7	22.6	
Temperature at 5 minutes, °C	22.5	22.5	22.5	
Temperature at 10 minutes, °C	22.5	22.6	22.5	
Temperature at 20 minutes, °C	22.5	22.7	22.5	
Temperature at 24 hours, °C	22.9°	22.9°	22.9°	22.9°
Temperature at 48 hours, °C	23.4°	23.4°	23.5°	23.4°
Temperature at 72 hours, °C	22.3°	22.3°	22.3°	22.4°

Table 3b: Temperature Observations for Test 3

Parameter/time	Composite Test 3 (°C)	Temperature Blank (°C)
Concentration of Test solution g/L	0.4	
Oxidant Dose to soil, g/kg as $KMnO_4$	0.8	
Soil Temperature before addition, °C	22.4°	
Solution Temperature before addition, °C	22.6°	22.6°
Temperature at 3 minutes, °C	22.8°	
Temperature at 5 minutes, °C	22.7°	
Temperature at 10 minutes, °C	22.7°	
Temperature at 20 minutes, °C	22.7°	
Temperature at 24 hours, °C	23.2°	23.5°
Temperature at 48 hours, °C	23.1°	23.1°
Temperature at 72 hours, °C	22.6°	22.6°
Temperature at 96 hours, °C	22.5°	22.5°
Temperature at 120 hours, °C	22.9°	22.9°
Temperature at 144 hours, °C	23.4°	23.4°
Temperature at 168 hours, °C	22.3°	22.4°

Table 4: Oxidant Doses and Demands* on Samples Prepared for the Metals Impact Screening

Test Identification	Initial Soil Dose $KMnO_4$ (g/kg)	Initial Dose Solution (g/L)	Reaction Time (hours)	$KMnO_4$ residual in aqueous portion (g/L)	Soil Oxidant Demand (g/kg)	% Moisture
Composite Test 1	0.4	0.201	72	0.167	0.02	17.2
Composite Test 2	0.8	0.403	72	0.357	0.02	17.2
Composite Test 3	0.8	0.403	168	0.332	0.06	17.2

*Oxidant doses and demands were calculated on a weight $KMnO_4$/dry soil basis.

Table 5 shows the results of the dissolved metals analyses manganese, chromium, selenium and zinc were elevated for the permanganate treated samples. The increase in manganese is anticipated to be due to the treatment with permanganate and quenching.

The assay for the lot of RemOx®S ISCO reagent used in this study indicated 1.857 mg/kg chromium, 0.002 mg/kg selenium, and 0.016 mg/kg zinc. The calculated contribution due to the RemOx S was about 0.38 µg/L chromium, <0.01 µg/L selenium, and <0.01 µg/L zinc for Test 1 and 0.75 µg/L chromium, <0.01 µg/L selenium, and 0.01 µg/L zinc for Test 2 and Test 3.

As described by Siegrist et. al. (2001), metals including chromium and selenium which can exist in a non-detectable reduced state naturally, become more soluble and thus mobile in their oxidized state. Once the oxidation conditions disappear soils can have the capacity to naturally attenuate the metal species as described in Clayton et. al. (2000) and in Hou and Chou (2001). The natural attenuation processes can include sorption and reduction back to an immobile valence.

Table 5: Concentration of Dissolved Metals in Solution Following Contact with Composite Soil

Parameter	Composite Control	Composite Test1	Composite Test 2	Composite Test 3
Arsenic (µg/L)	3.2	0.16	0.12	0.15
Cadmium (µg/L)	<0.5	<0.5	<0.5	<0.5
Chromium (µg/L)	<0.5	23	17	34
Copper (µg/L)	1.9	1.0	<1.0	<1.0
Iron (µg/L)	<10	<10	<10	<10
Lead (µg/L)	<1	<1	<1	<1
Manganese (µg/L)	2.0	1000	260	840
Nickel (µg/L)	<1	<1	<1	<1
Selenium (µg/L)	1.9	10	6.8	13
Silver (µg/L)	<0.5	<0.5	<0.5	<0.5
Zinc (µg/L)	21	57	34	34
Mercury (µg/L)	<0.2	<0.2	<0.2	<0.2

Conclusions

Minimal oxidant demand from the soil was observed. Treatment of the soil/caliche composite with 0.4 g/kg or 0.8 g/kg as $KMnO_4$ resulted in negligible observed change in temperature and minimal oxidant demand. Dissolved manganese, chromium, selenium, and zinc increased. The effects of increased manganese, chromium, and selenium have been observed during oxidant treatment and are temporal.

Literature Cited

Siegrist, R. L.; Urynowicz, M. A.; West, O. R.; Crimi, M. L.; Lowe, K. S. (2001) Principles and Practices of In Situ Chemical Oxidation Using Permanganate; Battelle Press: Columbus, OH,.

Clayton, W.S.; Marvin, B.K.; Pac, T.; Mott-Smith, E. (2000) A multisite field performance evaluation of in situ chemical oxidation using permanganate. In: G.B. Wickramanayke, A. R. Gavaskat, A.S.C. Chem (ed.). (2001) Chemical Oxidation and Reactive Barriers: Remediation of Chorinated and Recalcitrant Compounds, Battelle Press, Columbus, OH pp. 101-108.

Hu, G., Chou, R. (2001). "*In Situ* Application of Potassium Permanganate Solution for VOCs-Impacted Groundwater Cleanup – The Regulatory Perspective." International Containment & Remediation Conference Proceedings, Orlando, FL. June 10-13.

RemOx® ISCO reagent is a registered trademark of Carus Corporation