

- Compiled comments on the work plan are in black text
- Response to comments are provided in red text

From Alachua County Environmental Protection Department (John Mousa email on 6/6/13)

1.1 Program Purpose and Objectives and

1.2 Site and Technology Background

It is not clear in the text whether it is the purpose of the ISCO Treatment to treat the COPCs in the GW only or is it intended to treat the adsorbed residual COPCs and the GW in the UHG? Also the report comment "The purpose of ISCO, if effective, would be to remediate the source area." is confusing. The source area consists of the more tarry DNAPL contaminated surficial contamination and the contamination GW and soils in the UHG.

Assuming that the bench testing indicates that ISCO can effectively treat contaminants of concern (COCs), the intended remedial approach is to use ISCO to oxidize COC mass present in groundwater, soil or as free product in the source area in the UHG formation. In this context, the term "source area" refers to an area(s) within the UHG where COCs are present as NAPL or elevated groundwater concentrations reflective of NAPL. We are not considering ISCO for potential source area treatment in the surficial aquifer.

1.2 Site and Technology Background

The report statement is made ... "However, pine tar is natural material that is readily oxidized under normal environmental conditions (e.g decaying of pine trees , bark and needles), so it is expected that ISCO can be used to effectively degrade this material at the Site". There is no backup or support given for this conclusion.

The statement is simply meant to imply that pine trees and pine tree derived materials degrade under natural oxidizing conditions and have for millennia; hence it is expected that pine tar constituents would be amenable to degradation using ISCO.

Pine tar is known to have remained in the Springstead Creek deposits for many decades and has not naturally decayed or degraded. So it is doubtful that ISCO can effectively degrade or treat all the pine tar present in the soils.

To clarify, our objective for UHG source treatment is to destroy enough mass of the COCs that are relatively mobile in groundwater to reduce the mass discharge of COCs from the source area(s) into the downgradient groundwater plume. We realize that complete destruction of all hydrocarbons associated with pine tar is not achievable, but similar to the pine tar found in Springstead Creek, the goal is to destroy the mobile COCs from the tar, and hence improve groundwater quality.

2.3 Background Soil and Groundwater Samples

The locations specified in the workplan where the two kilograms of soil and five liters of groundwater will be collected from the Hawthorn Group need to be reviewed to make consistent with the recent map and email communications from Gradient and Weston. For example, boring location 13 specified in the workplan does not appear in the latest map and looks like has been changes to boring location 12. This paragraph should be reviewed.

Compositing for the bench test will be performed using the samples of UHG soil, surficial soil (containing residual NAPL), and UHG groundwater that are listed in the three tables below. The soil and groundwater sample locations are shown on the attached updated map.

While NAPL was not observed in UHG soils during the recent investigation, we suspect the presence of residual NAPL in the UHG formation based on the concentration profile in UHG groundwater in the former lagoon area. As shown in the attached revised schematic and explained in further detail below in response to comment 4 from Neil Thompson, the bench test reactors will contain composites of UHG soil and NAPL-impacted surficial soil in a ratio of 1:1 by mass.

Upper Hawthorne Group Soil for Compositing

Location ID	Depth Interval	Mass of Soil
	(ft bgs)	kg
SB-5	40-45	2.2
SB-5	50-55	1.9
SB-6	60-65	2.0
SB-7	55-60	2.6
SB-11	55-60	2.8

Surficial Aquifer Soil (containing residual NAPL) for Compositing

Location ID	Depth Interval	Mass of Soil
	(ft bgs)	Kg
SB-10A	25-26	3.1

UHG Groundwater for Composting

Location ID	Volume of Groundwater
	Liters
HG-29S	18
HG-28S	18

3.2 Background Non-Target Oxidant Demand Tests

Shouldn't a time "zero" sample of the test mixture be analyzed for each oxidant to determine the actual starting concentration of oxidant in the background soil mixture?

This is not needed, because we know the concentration of oxidant at time zero (C_0), given that we are adding a known mass of oxidant to each reactor. Also, it is not feasible to add oxidant to the reactors then collect samples fast enough to ensure no oxidant depletion occurs in the interim.

3.4 Test Setup- Soil and Groundwater Slurry COPC Treatment Tests

What is the definition of "nominal" headspace?

Nominal headspace is the minimum headspace required to collect off-gas without having water/foam flow from the reactor as the gas vents. Initial reactivity testing will be performed prior to initiating the comparative screening test; this testing is designed to better understand gas production volume and rate and required nominal headspace.

General Comment: Has Cabot consulted with Tetra Tech and Beazer to compare their experience with chemical oxidation treatment of contaminants in the soils at the former Koppers site in regards to the issue of potentially high natural oxidant demand of the soils at the Koppers site?

Our understanding is that Tetra Tech and Beazer have performed bench and field pilot testing of an in situ biogeochemical technology using modified permanganate solution for DNAPL stabilization. While permanganate is a proven oxidant for in situ treatment of many common contaminants in groundwater, this oxidant does not degrade all of the COCs present in UHG groundwater at the Cabot portion of the Site. Further, the literature has shown that permanganate can reduce the mobility of certain NAPLs by forming a manganese dioxide rind around the NAPL mass. Our bench testing program is intended to identify oxidants that can effectively destroy COCs in the UHG as opposed to reducing the mobility of NAPL in the formation.

From GRU (email dated 6/6/13)

1. We question the proposed sequence for adding materials assembling sample reactors. The stated sequence starts by placing soil in the vessel, then adding concentrated oxidant from a stock solution, and then adding site groundwater. We wonder about the reaction of the concentrated oxidant with the soil before dilution by the groundwater. See Section 3.2 Background Non-Target Oxidant Demand Tests – for example.

We agree – the new proposed sequence is provided below:

For the comparative screening study, liquid oxidant reactors will be constructed by first adding 40 g (measured gravimetrically) of homogenized UHG soil and 40 g of homogenized NAPL-impacted surficial aquifer soil to sterile 250 mL (nominal volume) screw cap Boston round clear glass bottles (Systems Plus, New Hamburg, ON), or equivalent vessels. Approximately 100 mL of Site groundwater will then be added to create a soil and groundwater slurry, and liquid oxidants (persulfate or hydrogen peroxide) will be added to the reactors using concentrated stocks. Activators (concentrated stocks) and an additional 100 mL of Site groundwater will be added to reactors leaving a zero headspace. As discussed below (see response to N. Thomson's comment #4), the mass ratio of UHG soil to NAPL-impacted surficial soil has been adjusted to 1:1.

A similar sequence of reactor construction is proposed for the background NOD testing, but soil used for this test will not be impacted with COCs.

2. We expect the delivery of oxidants to the COCs in situ in the Hawthorn Group at this site to be a challenge – and ozone especially so.

We agree. The bench test is focused on evaluating the reaction chemistry of these selected oxidants in the presence of both background and contaminated Site soil and groundwater. We recognize that delivery of any in-situ remediation amendment will be challenging in the UHG formation; however should the bench test lead to the selection of one or more selected oxidants or oxidant/activator combinations, the feasibility of delivering these remediation amendments will be evaluated during later field pilot testing.

From Neil Thomson (email dated 6/20/2013)

Comments on Geosyntec ISCO Bench Test Work Plan, Dated May 2013

By N.R. Thomson

Comments are provided in order of occurrence and referenced by page and paragraph number. (Note that some are repeats from a previous set of comments provided).

1. P 2. Parg 1. Innocuous degradation products is a blanket statement. There is no attempt to collect data to confirm/refute. Given the complex mixture, what are the end products?

This statement is intended to provide a general description of the ISCO process rather than the specific chemistry at the site. Carbon dioxide and water are given as examples of common degradation products resulting from ISCO. We have added reporting of tentatively identified compounds (TICs) to both VOC (EPA Method 8260) and SVOC (EPA Method 8270) methods for the bench test. Some intermediate breakdown products may be identified by the TICs analysis, but we do not intend to attempt a carbon mass balance for this testing. Our primary performance metric for this testing is the destruction of Site COCs that are mobile in groundwater.

2. P 2. Parg 1. There is still no attempt made to justify the use of the selected oxidants: ozone, ozone with hydrogen peroxide, catalyzed hydrogen peroxide (CHP) and peroxide-activated persulfate (PAP). No case made for delivery and target treatment zone (TTZ) is not defined. Is a gas oxidant appropriate? Success will only result if good sweep is possible. All these systems lead to highly reactive species, but very short half-lives in situ. Lack of persistence means careful delivery to TTZ is required to ensure contact. This is a key element of this effort that should be addressed now otherwise much of this effort is useless! Also CHP typically stands for catalyzed H_2O_2 propagations.

We have proposed the use of strong oxidants and oxidant/activator systems that have the highest likelihood of fully oxidizing all of the COCs present at the Site. The bench test is focused on evaluating the reaction chemistry of these selected oxidants in the presence of both background and contaminated Site soil and groundwater. While a weaker oxidant like permanganate has the potential to react over a longer period of time (and potentially travel farther downgradient from the point of injection with migrating groundwater), permanganate will not treat all target COCs at this Site. We recognize that delivery of any in-situ remediation amendment will be challenging in the UHG formation; however should the bench test lead to the selection of one or more oxidants or oxidant/activator combinations, the feasibility of delivering these remediation amendments will be evaluated during later field pilot testing.

3. P3. Parg 1. Non-target oxidant demand or NOD is a rather mis-used term and assumes that all oxidants have a finite demand. While not all site materials behave the same, permanganate has a NOD, whereas peroxide and persulfate both show enhanced decomposition (and no finite non-target oxidant demand NOD).

We agree that the term NOD is often mis-used. We intend to conduct a separate test for each oxidant to assess differences in behavior among oxidants in the presence of Site soil and groundwater

containing low levels of COC contamination. This test will include measurement of oxidant concentrations at 2, 5, and 10 days at a minimum (twice daily for ozone tests), providing information on the rate of oxidant decomposition in the presence of Site materials. In our experience, there is value in observing oxidant consumption in contaminated and uncontaminated media at the bench-scale.

4. P4. Parg 3. Note that homogenization of contaminated soils, particularly if NAPLs are present, is non-trivial. How will this be done? What is the basis for the 4:1 mass ratio?

We agree that homogenization of contaminated soils may be difficult, particularly if NAPLs are present. To address this, we plan to homogenize the UHG and surficial (e.g., NAPL-impacted) soils separately before combining them in individual reactors. Soil samples from the UHG will be combined and mixed by hand to create a composite sample. Similarly, surficial soil containing residual NAPL will be taken from a single soil core, and the sample will be mixed to improve homogeneity. A list of selected samples is provided above in our response to comment #2.3 from Alachua County EPD. Samples from each composite (UHG and surficial) will then be submitted for baseline analysis of VOCs, SVOCs and TOC prior to testing. After reviewing the results of the baseline analysis, aliquots of each soil composite will be added to individual reactors using the sequence described above in our response to GRU comment #1. Once the reactors have been prepared with homogenized UHG and surficial soils, time zero samples will be collected from each set of reactors to quantify the initial COC concentrations (C_0).

The 4:1 mass ratio of UHG soil to surficial soil was initially selected to provide a standard dose of NAPL-impacted soil to each reactor, while using UHG soil as the primary soil matrix. Since providing the ISCO Bench Test Work Plan to the US EPA on May 28, 2013, we received the laboratory analytical results for the NAPL-impacted surficial soil sample collected at location SB-10A from 25 to 26 ft below ground surface. These results led us to modify the mass ratio of UHG soil to NAPL-impacted surficial soil from 4:1 to 1:1, to increase the likelihood that residual NAPL would remain in the bench test reactors after the NAPL-impacted surficial soil was combined with UHG soil and groundwater. While NAPL was not observed in UHG soils during the recent investigation, we suspect the presence of residual NAPL in the UHG formation based on COC concentrations in UHG groundwater in the former lagoon area. As a result, we have adjusted our sample preparation procedure to include more residual NAPL-impacted surficial soil in the reactors. A schematic of the sample preparation procedure is attached.

5. P4. Parg 5. Again the non-target oxidant demand terminology.

Noted (see response to comment #3 above).

6. P5. Parg 3. To treat the presence of solids as simply having a competing oxidant demand is rather simplistic. There is a lot more happening.

We recognize that the presence of solids introduces a number of physical and chemical factors that may influence the oxidation of COCs. Many of these factors would also be expected to influence the reactions occurring under in-situ conditions, where both soil and groundwater will be present; however, the laboratory procedure for this bench test is not intended to simulate in-situ conditions. Competing oxidant demand is cited as a factor that is expected to influence oxidation of COCs in both lab and field settings.

7. P6. Parg 1. Are the ozone tests comparable with respect to dosing as the liquid oxidant tests? Will mixing be the same? I guess I'd like to know if there is a bias. The gas flow rate interval seems rather wide, how will you know what to use?

Direct comparison of the oxidant doses is problematic due to differences in reaction chemistry.

The primary performance metric will be COC treatment with oxidant dose and the magnitude of oxidant consumption considered as secondary metrics. Oxidant costs range widely and therefore comparison between oxidants on a chemical basis (mass per mass or electron equivalents per mass) may be misleading if costs of the oxidant are compared. For example, hydrogen peroxide costs less than \$1/pound versus over \$4/pound for persulfate. Additional cost and performance considerations will likely need to be assessed after bench-scale testing to identify the most viable oxidant type(s) to ultimately assemble an ISCO alternative, if any prove to be viable.

The objective of the bench test is to evaluate chemical reactivity and the viability of each oxidant system for treatment of COCs at loading rates typical of field deployments by the industry. Selection of the most viable ISCO alternative may require pilot scale testing to evaluate the feasibility of and costs (driven by the number of injection locations and number of treatments) for a full scale ISCO alternative.

- Mixing will not be the same for ozone as for the liquid oxidants because ozone will be applied by continuous sparging into the slurries; whereas liquid oxidants will be applied in a single dose at the start of the test and mixed periodically.
- The gas flow rate for the ozone reactors will be chosen to provide adequate mixing of the slurry within the reactor while limiting the potential for soil and groundwater losses to the effluent line. The duration of the ozone test may be adjusted based on the gas flow rate selected.

8. P6. Parg 2. Aside from convenience what is the basis for the 10-day reaction period?

The 10-day reaction period was selected for the background test (as opposed to the 5-day reaction period used for the comparative screening studies) to allow sufficient time for oxidant depletion. Based on past experience with similar studies, the proposed doses for liquid oxidants are likely to be depleted in less than 10 days. The test duration may be modified depending on the results of samples taken at $t = 5$ days. Further, if oxidant concentrations are observed to persist past $t = 5$ days in the background test, the duration of the comparative screening study may be extended beyond five days (see response to comment #11 below).

9. P6. Parg 5. Why do you need to destructively sample aqueous reactors?

Sample volumes required to be removed from the aqueous reactors to evaluate COC treatment would result in significant mass loss from the reactor without destructive sampling. If removed, it would either create headspace in the reactors or require the replacement of material removed with additional site groundwater. Given these potential complications, destructive sampling was chosen as a conservative sampling approach.

10. P7. Parg 3. Again, what is the purpose for this blending of sediments? Why add oxidants before groundwater?

See response to comment #4 regarding the blending of soils.

The proposed sequence for adding materials to the reactors has been modified to allow for the addition of some Site groundwater before adding oxidants (see response to comment #1 from GRU).

11. P7. Parg 5. What is the basis for the 5-day reaction period? Seems rather short. Provide additional details on the use of ascorbic acid to “quench”.

Based on past experience with similar studies, the proposed doses for liquid oxidants are likely to be depleted within five days. If oxidant concentrations are observed to persist past $t = 5$ days in the background test, the duration of the comparative screening study may be extended beyond five days (see response to comment #8 above).

For additional information on ascorbic acid quenching, please see:

- Huling, S.G., Ko, S., and Pivetz, B. 2011a. Groundwater sampling at ISCO sites – Binary mixtures of volatile organic compounds and persulfate. Ground Water Monit. Remed. 31(2), Spring 72-79.
- EPA/600/R-12/049, August 2012.

12. P8. Parg 2. This experimental design will not provide in situ oxidant dosing values.

While we do not expect the results from the bench test to provide final oxidant doses for full-scale in situ source treatment, the bench scale results can be used to select the starting oxidant doses for pilot scale testing.

13. P9. Parg 1. Bullet 2. See comment 12.

See response to comment #12.

14. P9. Parg 4. Why use “75 g of homogenized Site soil with residual NAPL” here and not in the comparative studies where some blending was used.

The “75 g of homogenized Site soil” referred to here was to consist of 60 g of homogenized UHG soil and 15 g of homogenized residual NAPL-impacted surficial soil as in the comparative studies. However, as noted in our response to comment #4 above, the mass ratio of UHG soil to NAPL-impacted surficial soil has been adjusted to 1:1. Thus, 40 g of composited UHG soil and 40 g of composited NAPL-impacted surficial soil each would be added to each reactor, in addition to the specified aqueous components (e.g., groundwater, liquid oxidant).

15. P10. Parg 1. Again, why run 2 sets of identical tests given the expected high variability in initial conditions and hence results. Design the system so that COC and oxidants samples/data can be

collected together. If needed you can use oxidant data to inform if COC analyses should proceed. These don't appear to be sacrificial reactors hence will need to open them to sub-sample solids – mass lost?

The oxidant consumption testing is a low-cost test compared to the COC treatment test, due to the analyses required in the latter (e.g., VOCs and SVOCs) to adequately evaluate COC treatment. We intend to use this low cost oxidant consumption test to select the oxidant doses/activator concentrations for the COC treatment test. The objective of this phased approach is to leverage the results from lower cost testing to maximize the potential return on the more expensive COC treatment test.

16. P10-11. Section 4.2.2. Why back to the blended sediments again? Again, why not inject this solution into a packed column to simulate the more appropriate soil to solution volume ratio?

As you pointed out in your first round of comments, laboratory tests are highly ideal and cannot be expected to be representative of in-situ conditions. The primary focus of the bench test program is to evaluate reactivity of oxidants with Site COCs. We acknowledge that the proposed slurry-phase reactor design will not fully capture the variability and uncertainty associated with in-situ application. The well-mixed slurry phase batch reactors were selected for use in the detailed tests because they provide a relatively low cost (as compared to columns) means of evaluating oxidant reactivity in the presence of site materials. The work plan has been modified to include batch reactors instead of columns for all ozone testing to provide a more consistent basis for comparison of results among oxidants.

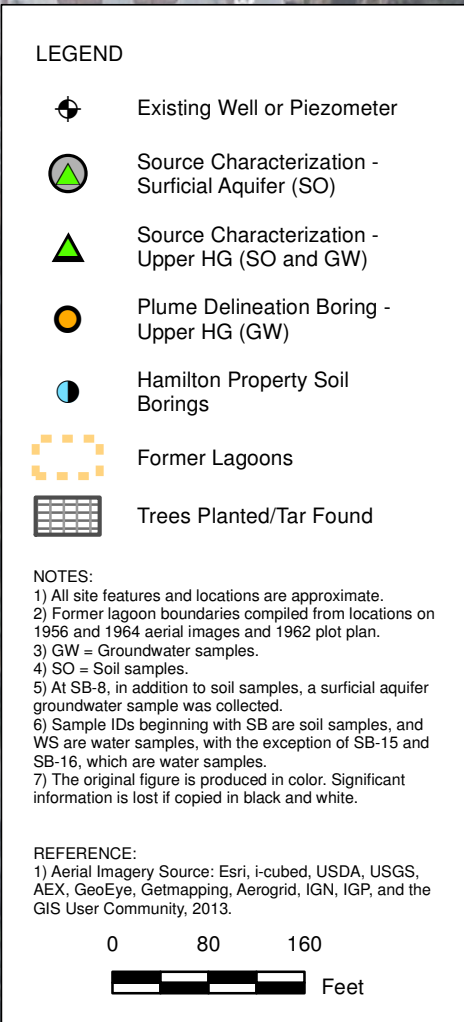
Once the potential for COC treatment with a given oxidant has been established, questions regarding the scalability of treatment, delivery of oxidant to the target treatment zone, and the behavior of the oxidant under in-situ conditions will be considered during later field pilot testing.

17. P15. Not sure if you have asked all the design questions yet, some data can be used, but the scale-up from well-mixed batch reactors etc is weak. Also the number of replicates you are planning to run is very low and will not capture sufficient variability. Use of these data to design a field-scale pilot-test is will be problematic.

Bench testing with duplicate reactors and samples goes beyond the industry standard for commercial remediation applications. The treatability laboratories conducting this bench test have performed many successful studies without the use of duplicate reactors. In these studies, sampling of reactors at multiple time points is used to evaluate contaminant destruction, and trends in contaminant concentration as a function of time are used to assess the effectiveness of a given oxidant. The use of multiple time points to evaluate trends provides robustness against sample variability while limiting the need for duplicate reactors. In cases where significant variability is anticipated, duplicate analytical samples may be taken from individual reactors; however, based on our experience, the industry standard for ISCO treatability studies with respect to duplicates is 10% of the primary samples. Duplicate analysis of all samples is relatively rigorous for samples run at certified laboratories. Triplicate analysis is more common at laboratories that are not certified such as specialty treatability laboratories or academic institutions. Triplicate analysis is typically cost prohibitive when certified laboratory analyses are utilized.

The proposed procedure for the detailed study phase of this bench test is conservative in its use of duplicate reactors as well as multiple time points to address the potential for variability among samples. Further, the evaluation of data from these tests will include consideration of potential variability and margin of error in laboratory analysis in identifying performance standards for oxidant selection. We have performed slurry-phase bench tests using duplicate reactors/analyses for many sites, including sites where NAPL treatment was required. We have used the results of these bench tests to inform the design of many successful pilot and full-scale remediation projects.

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ISCO Bench Test Sample Preparation

40 g UHG Soil + 40 g Surficial Soil (impacted w/ residual NAPL)
+ 100 mL UHG GW + Liquid Oxidants (as applicable) + 100 mL UHG GW → Reactors

