GRU
More than Energy
GAINESVILLE REGIONAL UTILITIES
Water/Wastewater Division

July 29, 2011

Mr. Scott Miller
Remedial Project Manager
United States Environmental Protection Agency
Region IV, Superfund North Florida Section
61 Forsyth Street, SW
Atlanta, GA 30303

RE: Comments to *Former Process Area In-Situ Geochemical Stabilization Remediation Demonstration Project Workplan for Hawthorn Group Deposits, Former Koppers, Inc. Site, Gainesville, Florida,* Tetra Tech (May 24, 2011)

Dear Mr. Miller:
Attached are GRU's comments to the *Former Process Area In-Situ Geochemical Stabilization Remediation Demonstration Project Workplan for Hawthorn Group Deposits, Former Koppers, Inc. Site, Gainesville, Florida* submitted to EPA on May 24, 2011 by Tetra Tech.

Thank you for your on-going effort in addressing the Cabot/Koppers Superfund site. If you need additional information, please contact me at 352-393-1218.

Sincerely,

Richard H. Hutton

Rick Hutton, P.E.
Supervising Utility Engineer

xc: John Mousa (ACEPD)
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GRU Comments to ISGS Demonstration Work Plan – Former Process Area

July 29, 2011

This document provides GRU's comments to the "Former Process Area In-Situ Geochemical Stabilization Remediation Demonstration Project Workplan for Hawthorn Group Deposits, Former Koppers, Inc. Site, Gainesville, Florida" submitted to EPA on May 24, 2011 by Tetra Tech. As we understand it, this Work Plan is intended to comply with the EPA 2011 ROD for the Koppers site. That ROD includes the use of ISGS to treat the South Lagoon and former Process Area, subject to site-specific testing to determine specific parameters and remedial effectiveness, as well as an ongoing demonstration of effectiveness over time. The ROD states that the ISGS treatment is "subject to acceptable performance demonstration during pilot test or treatability studies". The ROD is explicit in that if the pilot test does not demonstrate "acceptable performance" for the first 65 ft of soil beneath the Koppers site, then this zone will be treated by In-Situ Solidification and Stabilization. Performance goals described in the ROD include:

1. Consistent and controlled delivery and distribution of ISGS injectate throughout the treatment area— i.e., 'good sweep' – with subsequent reduction in permeability and encapsulation of DNAPL;
2. Pronounced reduction in groundwater contaminant concentrations associated with the creosote DNAPL and reduction in mass flux both laterally and vertically; and
3. Demonstrated longevity and stability of stabilized matrix, with no rebound in dissolved contamination.

It is critical to us that all of these performance goals be demonstrated as part of the ISGS pre-demonstration pilot test (i.e. the Phase II Pre-Demonstration ISGS Injection Testing), and the demonstration study to assure GRU and the community that the ISGS treatment will be successful in the short-term and the long-term without interruption as part of the solution to protect the Murphree Well Field.

It should be Beazer's responsibility to demonstrate the effectiveness of all remedial actions at the site. This is particularly true for ISGS since it is an unproven technology. GRU's primary concern with the Work Plan is that it does not include sufficient testing to demonstrate the initial viability of ISGS for the UHG. Furthermore, it does not include adequate short-term and long-term performance of the demonstration. The Work Plan should include a schedule that specifies milestones for evaluating performance of the ISGS remedial alternative. Milestones should be decision points that determine whether the ISGS injection is achieving specified performance goals. If ISGS fails to meet performance goals at any milestone then corrective action will be required, which may include adjustment of the ISGS approach or switching to IS/SS. The major stakeholders should participate in evaluation of the data and determination of the path forward after each milestone. Milestones should be set at the following points in time at a minimum:

1. Source Area Characterization (prior to treatment) – to characterize the DNAPL architecture, i.e., the spatial distribution of the creosote, treatment zone hydrogeology and establish baseline mass flux values;
2. After Pre-Demonstration Pilot Test – to assess ISGS delivery and permeability reduction at the pilot-test scale;
3. Immediately Post-treatment (i.e., after full-scale “demonstration”) – to assess ISGS delivery and permeability reduction at the full-scale;
4. Short-term (12-18 months post-injection) – to demonstrate reduction in DNAPL recovery, dissolved flux and permeability reduction;
5. Mid-term (36 months post-injection) – continue demonstration of reduction in DNAPL recovery, dissolved flux and permeability reduction; and
6. Long-term – on-going monitoring to assess mass flux reduction & long term stability of encapsulation and permeability reduction (periodically thereafter – minimally at the required 5-year review).

Table 1 presents our preliminary recommendations on performance parameters and milestones (this is a modification of the table FDEP presented in its February 1, 2011 recommendations on ISGS performance criteria). We recommend that a table similar to this be developed that identifies:

- Milestones (with specific times),
- Actions to characterize ISGS effectiveness,
- Specific success criteria
- Specific failure indicators and criteria, and
- Actions to be performed if criteria are not achieved.

Our comments to the Work Plan are as follows:

1. **We would like EPA to clarify where the remediation activity proposed in this Work Plan falls in the CERCLA process.** For example, is this Work Plan part of the Remedial Design phase? The full-scale implementation of the ISGS process described in general terms in section 3.2.3 of the Work Plan, which is defined in 3.3 as “a field-scale demonstration project”, appears to constitute a full-scale CERCLA Superfund remedial action implementation within the Former Process Area, while the ROD indicates that a pilot test or treatability study is

required before such full-scale implementation. Please clarify the CERCLA phase of work that this “field-scale demonstration project” will be conducted under and what document this Work Plan represents in this CERCLA process. If this activity constitutes full-scale remediation, then it should be implemented in full accordance with the Superfund process, which requires development and review of a detailed Remedial Design, signed and sealed by a registered Professional Engineer, followed by a formal Remedial Action Implementation Plan.

Comments related to characterization and ISGS Treatment

2. **As we understand it EPA’s decision to include the use of ISGS in the South Lagoon and Process Area is based on the presumption that contamination is less extensive in those areas as compared to the other source areas. If based on characterization it is determined that this is not the case, EPA should reconsider whether ISGS is an appropriate alternative in these areas.**

3. **The 2008 Surficial Aquifer ISGS test showed poor sweep.** The Work Plan should explain how sweep of the UHG will be improved compared to the poor sweep that the GRU DNAPL Team believes was obtained in the 2008 pilot test in the Surficial Aquifer.

4. **The Phase II Pre-Demonstration ISGS Injection testing which precedes the “field-scale demonstration project” is the most critical milestone in the Work Plan. Delivery and distribution of the ISGS reagent must be demonstrated at this stage for ISGS to be viable for full-scale demonstration.** We recommend that performance assessment of these pilot tests occurs three months after their completion. Evaluation of the pilot test performance will be the only opportunity that Beazer, the agencies, and the stakeholders will have to evaluate performance of the ISGS system before moving to the “field-scale demonstration project”. “Field-scale demonstration”, which is not a pilot test in our opinion but a CERCLA Remedial Action for the Process Area operable unit, will commit a large amount of resources (time and money) and it will be very difficult to change course once full-scale implementation has begun. We propose several methods to evaluate performance in Table 1. We believe this is the most critical milestone in the Work Plan and that it is given too far little attention. Therefore, it is critical that the Work Plan be revised to reflect the importance of the Phase II pilot tests that need to demonstrate much better in-situ performance than the 2008 ISGS test.

Technical staff from Beazer, EPA, FDEP, the City of Gainesville and Alachua County should review results of this testing to determine whether (a) these are sufficiently promising for full-scale demonstration to proceed and what modifications of the Work Plan are warranted, or (b) results do not indicate sufficient achievement of goals and a different remedial technology is called for.

5. **For the Pre-Demonstration ISGS Injection, testing only two test locations per injection method may not be sufficient to test the capability of ISGS in all the appropriate settings.** The number of injection points required will depend on the nature of the DNAPL distribution. We consider this to be a pilot test to determine the preferred injection method, and to determine whether or not full-scale application is potentially viable. Therefore is must demonstrate good sweep and acceptable DNAPL encapsulation. For example in one area, it may be possible that DNAPL is found in a single thick accumulation of clearly mobile DNAPL, while in other areas DNAPL is distributed in numerous widely-spaced thin zones of potentially mobile DNAPL and residual DNAPL. The injection methods must be shown to be effective in all such settings. Cores collected around the ISGS injection test sites must demonstrate that the ISGS reagent contacted all the DNAPL zones present in the cores.

6. **All DNAPL impacted zones should be treated. From the Work Plan it is unclear whether Tetra Tech intends to treat all DNAPL contaminated zones, or just those containing "free-phase DNAPL". Furthermore, the meaning of the term "free-phase DNAPL" is not clear, although we infer that this refers to zones in which DNAPL readily flows from the matrix. As we have discussed previously, we believe that DNAPL in the source zones at the site should be considered potentially mobile, principal threat wastes and should be treated.** Tetra Tech needs to define the meaning of the term "free-phase DNAPL" –as used in this Work Plan - so that we are sure that we are all referring to the same idea of mobile DNAPL. Similarly on page 10, we need to eliminate apparent confusion over concepts of "free-phase DNAPL", by which GRU infers a meaning of mobile DNAPL, and residual phase DNAPL (e.g., ganglia). We need to make sure we are using the same terminology to avoid confusion.

7. **The need for additional borings outside the mapped "source areas" should be acknowledged in order to map the full extent of DNAPL migration in the UHG.** The Work Plan does not appear to provide for additional borings outside

the preliminary grid to "chase the DNAPL" if DNAPL is found at the margins of the grid. This should be specified.

8. **We believe that the field categorization of cores (per page 10 of the Work Plan) will provide useful data. However, the DNAPL categorization in the Work Plan will not be able to provide an accurate differentiation between DNAPL present below residual saturation and DNAPL above residual saturation.** Observation of whether DNAPL flows freely from a core (category 4) vs. forming droplets when sprayed with water (category 3) may provide some relative indicator of mobility. However, it will not be possible to tell whether the DNAPL is above or below residual saturation under in-situ conditions based on this test. As we have stated before, just because this viscous DNAPL does not flow freely does not mean it is immobile. It is not possible to make a definitive visual determination of its state of saturation quantitatively. This is partly because the core will be heated by the mini-rotasonic drilling thereby reducing the viscosity of the DNAPL and causing it to be more mobile than at ambient temperature. This effect might cause Beazer to install DNAPL recovery wells in areas at which DNAPL is not actually mobile at ambient conditions. Quantitative data should be collected regarding DNAPL mass in the cores to help determine the mobile/residual nature of the DNAPL.

9. **Testing of cores (section 3.1.3): We believe that all individual samples – the ten in Step 1 and the three columns described in Appendix D – should be comprehensively characterized for creosote COCs so that the source material with which the permanganate solution is to react is well characterized.** We are unclear from what is stated here and in Appendix D as to which samples TetraTech plans to composite for analysis. It will be necessary to analyze each core individually in order to evaluate quantitatively each column test. Tests of composited samples should not be performed. Also, please discuss how these lab pNOD data are to be scaled up to be representative of in situ conditions. Specifically, explain how a volume to solids ratio of 0.67 g/mL (50 g in 75 mL of solution) is representative of the UHG, and how a 48 hr or 7 days exposure period reflects the intended treatment reaction timeframe for this ISGS demonstration.

10. **All permeable zones near observed DNAPL should be treated. In addition permeable zones above deeper DNAPL-impacted zones must be treated.**

We believe that Beazer needs to treat all permeable zones in the HG near locations where impacts are observed – because DNAPL migration in three dimensions is very complex and unpredictable. DNAPL could be observed in one boring and not be observed in another only a couple of feet away.

Sandy/gravelly zones that (1) do not exhibit creosote impacts and (2) are located above zones that do exhibit creosote impacts should be treated with ISGS reagents. DNAPL would have migrated through and impacted a portion of any shallower, higher permeable zone (whether observed or not) in order to reach the deeper zone where impacts are observed.

11. **Pressure increase during injection can be predicted and should be avoided.**
Has Beazer considered pumping groundwater from wells/piezometers during ISBS injection to steepen the groundwater gradients, reduce pressure in the interior of the treatment area, and encourage flow of ISGS solution from injection points? This could reduce the pressure required to inject fluids and improve the sweep efficiency/radius of influence. (This issue is also discussed in the first paragraph of Section 3.1.3.)

12. **Beazer should avoid inducing fractures and liquefaction during injection (see previous comment).**
It is not clear from the Work Plan whether TetraTech intends to induce fractures. The wording of task 10 in Figure 11 suggests that this might be an objective. We believe that fracturing the fine-grained portions of the Upper Hawthorn should be avoided if at all possible because the DNAPL is presumably in thin relatively coarse-grained zones and not in the fine-grained section. We understand from personal communication with Jim Erickson, that it is not the intent to induce fractures during ISGS injection. The Work Plan should therefore clarify this point. For example, on p.21 it is unclear how “unacceptably high (injection) pressures” is defined. We recommend that Tetra Tech develop guidelines based upon vertical stress vs. horizontal hydraulic conductivity relationships that would indicate preferred injection rates to avoid liquefaction and fracturing (if that is indeed their intent) so that improved sweep of the ISGS fluid is obtained.

13. **The injection of ISGS at the outer perimeter first, and then working inward may result in the need for increased injection pressures.**
TetraTech proposes to conduct the first injections at the Former Process Area at the outer perimeter of the treatment area and to progress with injection moving gradually toward the center of the treatment area (page 20 of plan). The intent is

to minimize the potential to mobilize DNAPL away from the treatment area. However, if the ISGS solution is successful at reducing permeability, then higher and higher injection pressures would presumably be needed to force ISGS solution into the permeable zones as the process progresses.

14. **The injection of ISGS reagent will displace groundwater. This will likely result in a temporary decrease in groundwater contaminant concentrations in and around the source areas due to flushing.**
    a. What is the fate of the contaminated groundwater that will be displaced from the Former Process Area?
    b. Beazer should use a conservative tracer within the injected ISGS fluid to identify the quantity of recovered injected ISGS fluids in each sample. That should make it possible to correct the creosote COC concentrations for dilution by the injected ISGS fluid.

Performance Evaluation Comments

GRU's primary concern with Phase III of the Work Plan is that, after the ISGS field-scale demonstration is completed, neither Beazer, the regulators, nor the stakeholders will have sufficient data to determine the degree to which the demonstration project has decreased contaminant mass flux from the treated area. At a minimum, the Work Plan should include the following:

- UHG DNAPL Producing Wells
- UHG Dissolved Flux wells
- LHG Dissolved Flux Wells
- Floridan Aquifer monitoring well (depending on extent of LHG contamination)
- Post Treatment Cores
- Specific performance criteria by which success will be evaluated

All of the performance evaluation wells should be installed before injection of the ISGS solution begins so limited but extremely important baseline information can be collected. As shown in Table 1, and described previously the Plan should contain milestones with specific performance criteria. Failure to meet these criteria at any point should trigger re-evaluation.

15. **UHG wells need to be installed in the source area and monitored for dissolved flux prior to treatment, post-treatment and long-term.** The Work Plan includes construction of UHG wells with flowing DNAPL as a means to

measure reduction in DNAPL mobility. However, it will be necessary to install additional wells (without flowing DNAPL) to assess pre- and post-treatment horizontal mass flux.

A number of wells should be located throughout the treatment area with some near the upgradient edge (the upgradient wells will be the first to be influenced by unimpacted ground water following treatment). Our initial thought is to include:

- 3-5 downgradient dissolved flux monitoring wells
- 1-2 dissolved flux wells near the upgradient edge
- ~3 dissolved flux wells in the interior of the source area
- ~3-4 DNAPL producing wells in the interior of the source area

The exact number and locations will need to be determined after the initial characterization (phase 1 of Work Plan). The attached figure illustrates the concept.

The monitoring wells should be screened only at the depth of treatment so that the effect of ISGS treatment is captured rather than the sample being collected from untreated zones of the UHG. Several groundwater samples should be collected once a month (in a sequential pattern with pumping of the well for an hour or so) from each of these new wells for 3-4 months to establish a baseline to evaluate the effectiveness of treatment. Following treatment, these wells should be sampled using the same protocol after allowing for an adequate time for natural flow conditions to be re-established. To evaluate this, the samples must be chemically analyzed to determine the fraction of injected treatment fluid in the sample and the fraction that is 'native' groundwater. This will require identifying and monitoring a conservative analyte within the ISGS injectate. Without such testing, the performance assessment program is quite meaningless and the ROD is not honored.

16. **The UHG wells which are to be monitored for reduction in recoverable DNAPL need to be producing sufficient recoverable DNAPL prior to treatment in order to provide useful data.** We suspect that some of the wells constructed for this purpose may not produce sufficient DNAPL (pre-treatment) to evaluate the reduction in DNAPL mobility, which may necessitate installing additional wells to ensure that at least 3 wells do produce sufficient DNAPL. Depending on their locations, wells that don't produce DNAPL may still be useful to measure pre- and post-treatment contaminant mass flux and hydraulic

conductivity, presence of reagents, groundwater elevations and groundwater chemistry.

17. **LHG monitoring wells should be installed to better characterize the extent of contamination in the LHG, and to provide a long-term indication of the success of the ISGS treatment.** At present there are no LHG wells in the Process Area and the extent of DNAPL contamination in the LHG is not known. One criterion for success specified in the ROD is reduction of mass flux both laterally and vertically. At present there are no LHG monitoring wells that can be used to measure concentrations and hydraulic conductivity (or Darcy velocity) to determine the vertical flux of contaminants from the UHG to the LHG. We recognize that it will likely be a number of years before a direct response is seen in the LHG. However, a primary objective of the ISGS is to reduce the vertical flux of both DNAPL and dissolved phased material.

18. **Depending on the results from the LHG characterization, a Floridan well should be installed at or immediately downgradient of the process area to verify that contamination has not reached the Floridan at this location and to provide on-going long-term assurance that the remedy is meeting the bottom line goal of protecting the Floridan.** The well should be constructed as a typical "B-Zone" multilevel Westbay completion. The location of the well should be determined after additional LHG data are obtained and evaluated. The Upper FAS Westbay well need not be installed before or during ISGS injection because we expect that impacts to the Upper FAS will not occur for a minimum of several years after injection. Timing of installation of this well will be driven by other data needs.

19. **Baseline Pre-treatment groundwater data must be collected in order for performance to be evaluated.** The long-term performance evaluation must be planned and instrumentation installed prior to commencing the demonstration. With no background measurements of any sort, long-term monitoring would be meaningless. GRU proposes that Beazer measure the pre-treatment mass flux after the monitoring wells have been installed (during the time when Beazer will be documenting DNAPL recovery).

20. **Post-treatment cores should be collected from areas that were impacted and from areas that were not impacted to evaluate performance.** Cores should be collected post-treatment to evaluate the degree of success of the ISGS treatment. Some core locations should be randomly selected within those areas where DNAPL was observed pre-treatment. Other core locations should

be randomly selected where DNAPL was not present to evaluate the potential for redistributing DNAPL during injection.

21. **Performance evaluation criteria should include geochemical parameters (at a minimum including dissolved manganese, pH, EC, DO and ORP).** We believe that an increase in dissolved manganese could indicate failure of the ISGS treatment because that would indicate dissolution of the precipitate that is intended to plug pore space and reduce mass flux *(See Appendix A for more detail).* Adventus should an estimate of the equilibrium concentration of Mn^{+2} they anticipate in the UHG during successful permanganate remediation.

22. **Initial post-treatment COC concentrations or flux values must be used with caution.** We expect that an immediate decrease in creosote COC concentrations after injection will occur. We caution against making any conclusions as to the degree of success of the ISGS injection based on uncorrected sample concentrations because we believe that any concentration decrease may be as much a result of dilution by ISGS fluid as being due to destruction of dissolved COCs and encrustation of the DNAPL, i.e., the treatment. The ISGS solution is approximately 4.5 weight % RemOx in clean water. A sustained decline in dilution-corrected COC concentrations and mass flux will be evidence of remedial success. The Work Plan should specify measuring the mass of contaminant (SVOC and VOC) contained within the recovered water and the concentration of a conservative tracer from the ISGS injectate to determine the amount of dilution. This correction should be agreed upon before the Work Plan is approved.

23. **The UHG dissolved flux measurements performed as part of the performance evaluation will be complicated by the fact that the slurry wall will disrupt the natural groundwater flow pattern.**

24. **The ROD requires that, absent a successful demonstration of ISGS in the Surficial Aquifer at the Process Area and the South Lagoon, ISS/S will be implemented there.** An additional demonstration in the Surficial Aquifer is required by the ROD (Declaration, page 2) copied below:

In-situ geochemical stabilization (ISGS) (also referred to as in-situ biogeochemical stabilization (ISBS) of DNAPL from ground surface to the bottom of the upper Hawthorn Group zone (0 to 65 feet bls) at two of the four principal contaminant source areas (former Process area and the former South Lagoon). The ISGS component of this remedy component will be implemented through injection of oxidizing and stabilizing chemicals into the ground surface. This ISGS treatment is subject to acceptable performance demonstration during pilot tests or treatability studies. Pilot tests/treatability studies are tests conducted with contaminated Site materials and stabilizers to determine if cleanup goals will be met. If pilot tests/treatability studies do not demonstrate to EPA acceptable performance of the ISGS treatment for the Surficial Aquifer zone, the Surficial Aquifer zone at the former Process area and at the former South Lagoon will be treated with In-situ solidification (ISS/S).

Surficial Aquifer

25. **Any ISGS pilot test in the Surficial Aquifer must overcome limitations of previous efforts.** While GRU understands Beazer's desire to take advantage of the opportunity to treat the Surficial Aquifer while the equipment is onsite, we believe pilot testing of injection similar to that proposed for the Upper Hawthorn is required. The 2008 North Lagoon ISBS pilot test in the Surficial Aquifer was, in our opinion, clearly not successful, and we were not persuaded that the Denver pilot test was successful. Problems with the 2008 Surficial Aquifer pilot test included poor sweep of the injectate. That issue needs to be resolved by an additional demonstration in the Surficial Aquifer (see GRU & ACEPD Proposed Performance Metrics for ISGS, May 10, 2010, p.2, item 2).

Appendix A

Comments Related to Geochemistry: Former Process Area In-Situ Geochemical Stabilization Remediation Demonstration Project Workplan for Hawthorn Group Deposits, Former Koppers Inc. Site, Gainesville, Florida

The Work Plan makes several claims regarding the mechanisms through which the injection of RemOx EC will oxidize, contain, and isolate subsurface DNAPL. These include the following:

a. A manganese dioxide (MnO_2) precipitate with associated silicate minerals and other ISGS reagents is quickly deposited around DNAPL ganglia and droplets following reagent injection.
b. The deposition of the MnO_2 mineral shell reduces the overall formation permeability in the treated area, thereby reducing the volumetric flux of upgradient groundwater into and through the impacted area.

A number of published papers and reports indicate that manganese dioxide minerals formed from permanganate are unstable under reducing geochemical conditions, like those present at the Koppers site. These studies have found that MnO_2 particles that form through permanganate reactions can dissolve and form dissolved manganese plumes. These papers include both laboratory and field test results. For example:

- Hrapovic et al. (2005) conducted laboratory column tests on the use of permanganate oxidation for treating TCE. Following the application of permanganate, the formation of MnO_2 minerals was visibly apparent in the columns. Reducing conditions were then established in the columns to stimulate in-situ anaerobic biodegradation of the remaining TCE. After reducing conditions were established, dissolved levels of manganese of up to 1,600 mg/L were measured in the column effluent. Because Mn was not being added to the influent, the only source of Mn was the precipitated MnO_2 solids.

- Sahl, et al. (2007) conducted similar studies in a laboratory to evaluate the effects of permanganate on microbial populations. After applying permanganate to test columns containing sand and TCE, formation of manganese dioxide minerals was visibly apparent in the columns. Sand from the columns was analyzed to confirm the presence of these manganese precipitates. Reducing conditions were established to evaluate post-ISCO impacts to microorganisms. Over the remaining course of the test, the MnO_2 minerals began to dissolve and were determined to be almost completely dissolved by the end of the test.

- Westersund et al. (2006) implemented full-scale permanganate treatment to remediate chlorinated solvents at a contaminated site. Subsequently, due to evidence of reducing conditions and reductive dechlorination of the remaining solvents, full-scale anaerobic reductive biological treatment was implemented to treat remaining contamination. After the onset of reducing conditions, dissolved manganese levels reached as high as 173 mg/L, indicating that the manganese dioxide that had been precipitated by permanganate was dissolving.

It is important to remember that the state of Florida groundwater standard (GCTL) for manganese is 0.05 mg/L. Thus the dissolved manganese plumes resulting from the use of permanganate in the examples above were up to 32,000 times higher than the state of Florida groundwater standard. Based on the experiences cited, the use of RemOx EC, which includes 4.5% permanganate, clearly has the potential to result in an exceedance of the state of Florida GCTL for manganese in groundwater.

The instability of manganese dioxide increases at sites with low Eh (redox potential) and lower pH, such as Gainesville Koppers site groundwater. The Surficial Aquifer at the Koppers site has been found to have Eh and pH characteristic of the range in which reduced manganese (Mn^{+2}) is a stable form and under which conditions the dissolution of MnO_2 will be favored. Evidence of reducing conditions in Koppers site groundwater includes:

- Elevated dissolved iron is present within the Surficial Aquifer and Upper Hawthorne aquifer. Iron reduction occurs only under anaerobic conditions and occurs at a lower redox potential than manganese reduction.
- The ORP of the groundwater has been reported in many monitoring reports for the site to be in the reducing range. In some cases highly negative values were reported.
- Sulfide odors, indicating sulfate-reducing conditions, have been noted during purging of monitoring wells at the site. The presence of hydrogen sulfide is a strong, reliable indicator of reducing conditions in groundwater. Sulfide reduction occurs well below the redox potential required for manganese reduction.
- Groundwater samples collected during the ISBS pilot test indicate that pH of the shallow aquifer in many wells ranges from 4.6 to 6. A groundwater pH in this range favors enhanced dissolution of MnO_2 solids.
- The presence of large quantities of organic materials in an aquifer, such as the creosote DNAPL at the Koppers site, is known to result in reducing geochemical conditions. Given that the great majority of the organic contamination will remain in the ground with the proposed RemOx EC treatment, reducing groundwater conditions at the site are likely to become re-established after the permanganate has been injected and fully reacted.

We are unaware of any peer-reviewed published technical literature that corroborates Beazer's claims about the stability of the manganese dioxide precipitates formed through the use of RemOx EC, which is purportedly enhanced through the use of proprietary silicate additives. Minerals formed during this ISGS process must remain completely stable for many decades, possibly centuries, to maintain the protectiveness of the remedy. We believe the lack of verifiable long-term stability of these minerals is a significant data gap.

A key cause of MnO_2 dissolution under reducing groundwater conditions is biologically-mediated manganese reduction, which occurs when manganese is used as an electron acceptor by bacteria. It is important to note that biodegradation of naphthalene, a primary COC at the Koppers site, has been shown to occur under manganese-reducing conditions (Langenhoff, et al, 1996). Thus a key process that may cause manganese dissolution at the Koppers site after application of RemOx EC is biological-mediated manganese reduction.

In addition, other chemicals present in creosote and in Koppers groundwater, such as toluene and phenol, have been shown to be substrates that can be used by metal-reducing bacteria to promote dissimilatory manganese reduction (Stone, 1987; Langenhoff, 1997). Large reservoirs of naphthalene and these other chemicals will remain onsite within the creosote DNAPL after the RemOx EC has been injected. Much of the naphthalene and other organics from the creosote will be in close physical contact with MnO_2 solids that precipitate on the DNAPL surface. The proximity of these electron donors (naphthalene and other organics) to the electron acceptor (MnO_2) will increase the likelihood of biologically-mediated manganese reduction occurring.

We request that the following information be provided, if available, for the manganese dioxide minerals that are expected to be formed through the ISGS process:

- Balanced stoichiometric reactions showing the specific minerals formed through the ISGS process;

- Applicable Gibbs free energy or other calculations showing that the formation of these minerals is geochemically and thermodynamically favored under the conditions expected and concentrations of reagents to be applied at the Koppers site;

- An Eh-pH diagram for the anticipated minerals (RemOx, EC precipitates);

- Field data that show the variability in the types of manganese dioxide minerals formed through injection of RemOx EC using injection methods similar to those proposed for the Koppers site. In particular, data that show the relative quantity of silica-modified manganese dioxide solids versus non-silica modified manganese dioxide solids would be helpful;

- A discussion of factors that may interfere with formation of the desired minerals and which of these factors are expected to interfere with desired mineral formation at the Koppers site. These factors may include variations in Eh, ORP, pH, TDS, aquifer minerals or geochemistry, competing reactions, changes in oxidant or silicate concentration as a function of distance from the injection point, or other factors. Any information about the bioavailability of the manganese in the minerals formed or testing done to assess its ability to act as an electron acceptor in the presence of naphthalene or other organic substrates.

The ISGS process is an experimental treatment approach with a minimal track record. Because long term stability has not been proven, it is reasonable to expect that ideal chemical reactions may not occur throughout the injection zone and that some percentage of the manganese dioxide minerals formed will have the same degree of geochemical instability as manganese dioxide created at other permanganate sites (even if good sweep is achieved).

The geochemical conditions of the target aquifers should be well established prior to any injection activities. This should be done through thorough analysis of groundwater samples from monitoring wells within the treatment zones and underlying Upper Floridan aquifer for the full suite of geochemical parameters prior to any RemOx EC injections. The analyte list should include field parameters (dissolved oxygen, oxidation reduction potential [ORP], pH, specific conductance, temperature, turbidity), total and dissolved metals (Fe and Mn in particular), nitrate/nitrite, sulfate, sulfide, TOC, carbon dioxide, and alkalinity. It is particularly important to establish the natural background concentration of manganese in all aquifer zones prior to initiating RemOx EC injections. The full list of organic COCs and arsenic should also be analyzed.

Additionally, long term monitoring of dissolved manganese in all aquifer zones, including the Upper Floridan aquifer, is essential for assessing long term impacts of the RemOx EC injections. Increases in dissolved manganese in groundwater in any of the aquifer areas within or downgradient (vertically or horizontally) of the RemOx EC-treated zones will be an early indicator of ISGS remedy failure, since it will indicate that the manganese dioxide crusts that may have formed around DNAPL are dissolving.

In the event that a dissolved manganese plume is observed outside the slurry wall in the Surficial Aquifer or Upper Hawthorn, or anywhere in the Lower Hawthorn or Floridan, a contingency plan should be in place to provide for capture and treatment of all groundwater impacted by dissolved manganese that exceeds the state of Florida GCTL of 0.05 mg/L or site background concentrations. Dissolved manganese should not be allowed to migrate beyond the Koppers site boundary in any aquifer at concentrations above the state of Florida GCTL or site background concentrations.

References

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TABLE 1

Koppers- Proposed ISGS Milestones and Performance Criteria

Milestone	Performance Goal	Demonstration Method	Success indicators	Failure indicators	Notes/Comments
Source Area Characterization (***before Pre-Demonstration Pilot test)***	**Baseline** - Determine aquifer baseline pre-treatment conditions in Surficial, Upper Hawthorn, and Lower Hawthorn aquifer units	1) SA, UHG & LHG cores; 2) UHG & LHG dissolved groundwater analytical data; 3) UHG DNAPL Flow into wells; 4) Slug/ pumping tests	NA	NA	Baseline data to which post-treatment data will be compared. Requires UHG & LHG cores, and installation of DNAPL producing wells in UHG (&LHG if applicable), & dissolved phase wells in UHG & LHG. See notes[1, 2, 3].
	DNAPL Distribution - Determine DNAPL distribution and architecture vertically and horizontally in Surficial, Upper Hawthorn, and Lower Hawthorn units.	Same	NA	NA	Same
	FLA Well - Collect additional baseline FLA data if LHG is impacted.	Multilevel/Westbay completion consistent with other onsite FLA wells.	NA	NA	Well will be installed in FLA if the LHG is impacted at the Former Process Area. Location of FLA well to be determined after evaluation of LHG data.
Pre Demonstration Pilot Test (***Success must be demonstrated before initiating full-scale demonstration test)***	**ISGS Delivery** - Consistent, controlled delivery and distribution of ISGS injectate throughout designated treatment area; i.e. good "sweep" of ISGS injectate.	1) Field observations demonstrating control 2) Cores show ISGS injectate contacted all the DNAPL zones with good sweep and no significant by-passing of DNAPL zones. 3) Conservative tracer in ISGS injectate 4) GW monitoring (see Notes[1,2,3])	1) No liquefaction, no daylighting, maintain control of injection pressures 2) Injectate contacts all DNAPL zones identified in cores. Cores show 80% coverage of precipitate encrustation in the DNAPL zones 3) Conservative tracer and purple ISGS show good sweep/ROI in MWs/recovery trenches 4) Compliance with UIC ZOD laterally and vertically	1) Liquefaction of soil or daylighting of injectate; loss of injection pressure control or insufficient injection rate, 2) Injectate failed to contact all DNAPL zones identified in cores and/or less than 80% encrustation of DNAPL. By-passing by injectate. 3) Uneven distribution of tracer 4) UIC exceedances, 5) Groundwater analytical data indicating ISGS failure	Use previously installed monitoring wells to assess distribution and treatment success. Inspection of cores supported by thin section analysis/ documentation. GRU believes this is the most critical of all performance metrics for the pilot tests because 1) without adequate DNAPL/injectate contact the remedial alternative can not succeed and 2) decision to proceed to full-scale demonstration of ISGS or switching to ISS/S - will be determined at this milestone.

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Milestone	Performance Goal	Demonstration Method	Success indicators	Failure indicators	Notes/Comments
	Permeability Reduction - Reduction in permeability and encapsulation of DNAPL to minimize DNAPL mobility	Pre and post treatment slug test/pump test in treatment zone	Reduction in hydraulic conductivity	No change in hydraulic conductivity	Slug /pump test to confirm significant reductions in both horizontal and vertical hydraulic conductivity and specific yield sufficient to curtail contaminant flux
		Pre and post pilot test water level measurements in MWs/piezometers in source and perimeter area	Significant change in hydraulic gradients throughout the UHG, velocity due to reduced permeability in source area	No change in hydraulic gradients or velocity	MWs/piezometers to be installed in both surficial, UHG and LHG (see note 2)
Immediate Post-Demonstration ISGS Reagent Injections ***(3 months after final demonstration project injection)***	**ISGS Delivery** - Consistent, controlled delivery and distribution of ISGS injectate throughout designated treatment area; i.e. good "sweep" of ISGS injectate.	1) Field observations demonstrating control 2) Cores: Minimum of 30 cores through entire treated interval 3 months after injection. 3) Conservative tracer in ISGS injectate 4) GW monitoring	1) No liquefaction, no daylighting, 2) Cores show homogenous distribution of precipitate encrustations, 3) Contact of MnO_2 injectate with 80% or more of DNAPL in Immediate Post-Treatment cores. 4) Compliance with UIC ZOD laterally and vertically 5) Bromide and purple ISGS show good sweep/ROI in MWs and recovery trenches	1) Daylighting, 2) uneven distribution of injectate in cores, 3) Insufficient contact between injectate and contaminants (contact of MnO_2 injectate with less than 80% of DNAPL in Immediate Post-Treatment cores) 4) UIC exceedances, 5) Uneven distribution of tracer	This is a critical decision point that will be largely based on how well the injectate was delivered to the DNAPL. If delivered well - the evaluation can move forward. If not, this remedial alternative can not succeed in meeting remedial objectives. Installation of appropriate monitoring points is required to assess distribution and treatment success (see notes[1,2]). Inspection of cores supported by thin section analysis/ documentation.
	Permeability Reduction - Reduction in permeability and encapsulation of DNAPL to minimize DNAPL mobility	Pre and post treatment slug test/pump test in treatment zone	Reduction in hydraulic conductivity	No change in hydraulic conductivity	Slug /pump test to confirm significant reductions in both horizontal and vertical hydraulic conductivity and specific yield sufficient to curtail contaminant flux
		Pre and post pilot test water level measurements in MWs/piezometers in	Significant change in hydraulic gradients throughout the UHG, velocity due to reduced	No change in hydraulic gradients or velocity	MWs/piezometers to be installed in both surficial, UHG and LHG (see note 2)
	DNAPL Recovery - Decline in rate of DNAPL recovery	Continue method of DNAPL monitoring used during pre-test characterization.	Early and significant decline in rate of DNAPL flow to wells.	Increase in flow of DNAPL to wells or little change in DNAPL flow rate.	Early and significant decline in rate of DNAPL flow to wells is expected.

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Milestone	Performance Goal	Demonstration Method	Success indicators	Failure indicators	Notes/Comments
	LHG water quality	Sampling LHG monitoring wells.	NA	Significant negative change in water quality, ISGS solution, or ISGS tracers in LHG wells.	No change of water quality in LHG is expected at this early stage of remedial actions.
Short-term perf criteria *(1st 12-18 months after final demonstration project injection)*	**Permeability Reduction** - Reduction in permeability and encapsulation of DNAPL to minimize DNAPL mobility	Pre and post demostration test water level measurements in MWs/piezometers in source and perimeter area	Change in potentiometric surface, velocity due to reduced permeability in source area	No change in potentiometric surface or velocity	MWs/piezometers to be installed in both surficial, UHG and LHG
	DNAPL Recovery - Decline in rate of DNAPL recovery	Continue monitoring DNAPL recovery in UHG wells & compare with pre-test data.	Continued decline in rate of DNAPL flow to wells.	1) No material reduction in DNAPL recovery , 2) Appearance of DNAPL in previously unaffected MWs	Continued decline in DNAPL flow is expected.
	Dissolved COC Flux - Significant reduction in contaminant flux both vertically and laterally	Pre-test and Quarterly post-treatment groundwater sampling with trend analysis	Pronounced and lasting reduction in dissolved GW contam concentrations and mass flux indicating isolation of source, laterally and vertically	1) No significant reduction in GW contam conc and mass flux, laterally and vertically, 2) Vertical contaminant migration w/ increased GW concentrations in deeper MWs, 3) GW contamination observed in nearby Floridan Aquifer MWs	Attainment of goal demonstrated by sampling of MWs and use of PFM (flux meters).
	Compliance with UIC	Pre-test and post treatment groundwater monitoring	1) No unpermitted migration of ISGS components beyond ZOD laterally or vertically, 2) No ISGS solution observed beyond ZOD, laterally or vertically.		Work plan must include contingency plan to address uncontrolled migration of ISGS injectate or contaminant plume migration
Mid-term perf criteria *(begins after short term performance criteria are met and extends for 3 years)*	**Permeability Reduction** - Continued reduced permeability/encapsulation of DNAPL	Measurement of groundwater water levels and hydraulic conductivity	1) continued potentiometric responses that reflect reduced hydraulic conductivity, 2) Continued reduced GW flow into trenches and perimeter wells	Groundwater flux into trenches/wells returns to pre-treatment levels	

TABLE 1

Koppers- Proposed ISGS Milestones and Performance Criteria

Milestone	Performance Goal	Demonstration Method	Success indicators	Failure indicators	Notes/Comments
	DNAPL Recovery - Cessation of lateral/vertical DNAPL migration	Monitoring of DNAPL recovery in surficial, UHG, LHG	Deeper MWs continue to show decline in contaminant concentrations	1) Increased contaminant concentrations downgradient, 2) Newly observed contamination in deeper MWs or Floridan aquifer MWs	
	Dissolved COC Flux -Continued reduction in mass flux, both laterally and vertically.	Quarterly GW monitoring including recovery trenches/wells	1) GW monitoring shows continued reduction in COC concentrations, 2) No inferred DNAPL concentrations , 3) No observed contamination in nearby Floridan aquifer wells.	1) Rebound of contaminants in GW, 2) Reappearance of inferred or observed DNAPL, 3) GW contamination observed in nearby Floridan Aquifer MWs.	
	Compliance with UIC	Post treatment groundwater monitoring	1) No unpermitted migration of ISGS components beyond ZOD laterally or vertically, 2) No ISGS solution observed beyond ZOD, laterally or vertically.		Contingency plans are implemented to address uncontrolled ISGS or contaminant plume migration.
Long-term perf criteria *(begins after short term performance criteria are met and extends for duration of pilot and O&M of final remedy if ISGS is selected)*	**Permeability Reduction** - Reduced permeability/encapsulation of DNAPL is maintained	Measurement of groundwater water levels and hydraulic conductivity	1) Continued potentiometric responses that reflect reduced hydraulic conductivity, 2) Continued reduced GW flow into trenches and perimeter wells	Groundwater flux into trenches/wells returns to pre-treatment levels	
	DNAPL Recovery - Cessation of lateral/vertical DNAPL migration is maintained	Monitoring of DNAPL recovery in surficial, UHG, LHG	Deeper MWs showing decline in contaminant concentrations is maintained. COC concentrations that indicate no nearby DNAPL in monitoring wells inside slurry wall are maintained.	1) Dissolved concentrations indicating DNAPL inside slurry wall where not previously observed, 2) Increasing concentrations outside slurry wall or beneath treated zone indicating nearby DNAPL.	

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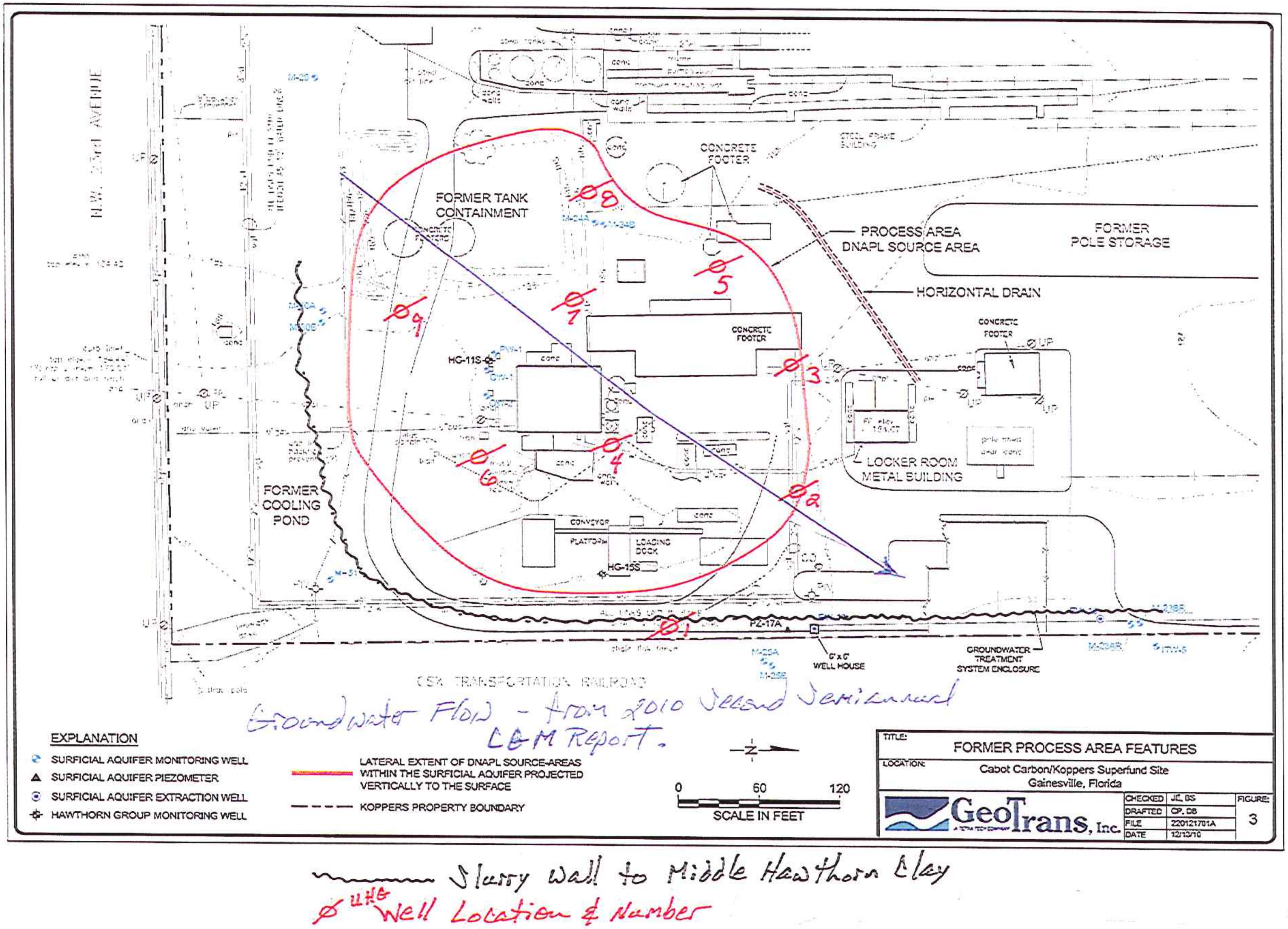
Koppers- Proposed ISGS Milestones and Performance Criteria

Milestone	Performance Goal	Demonstration Method	Success indicators	Failure indicators	Notes/Comments
	Dissolved COC Flux - Maintained reduction in mass flux, both laterally and vertically.	GW monitoring including recovery trenches/wells	1) GW monitoring shows reduction in COC concentrations is maintained, 2) No inferred DNAPL concentrations , 3) No observed contamination in nearby Floridan aquifer wells.	1) Rebound of contaminants in GW, 2) Increased contaminant concentrations downgradient or outside the slurry wall, 3) Newly observed contamination in deeper MWs or Floridan aquifer MWs .	
	Compliance with UIC	Post treatment groundwater monitoring	1) No unpermitted migration of ISGS components beyond ZOD laterally or vertically, 2) No ISGS solution observed beyond ZOD, laterally or vertically.		Contingency plans are implemented to address uncontrolled ISGS or contaminant plume migration

[1] Adequate characterization of DNAPL and groundwater contaminant levels in surficial, UHG, LHG and FL aquifer including installation of new monitoring wells in both Process Area and South Lagoon will be conducted prior to pre-demonstration pilot test and will be included in pre-pilot baseline sampling.

[2] Purpose of the MWs is to support design of pre-demonstration pilot test, evaluation of effectiveness of ISGS and demonstrate compliance with UIC. Monitoring wells will be installed within source areas, ISGS pre-demonstration pilot treatment area, and at perimeter of source areas.

[3]Groundwater Monitoring - Parameters monitored to evaluate ISGS performance should include the following: field parameters (dissolved oxygen, oxidation reduction potential [ORP], pH, specific conductance, temperature, turbidity), total and dissolved metals (Fe and Mn in particular), nitrate/nitrite, sulfate, sulfide, TOC, carbon dioxide, and alkalinity. It is particularly important to establish the natural background concentration of manganese in all aquifer zones prior to initiating RemOx EC injections. The full list of organic COCs and arsenic should also be analyzed.


N.W. 23rd AVENUE
FORMER TANK CONTAINMENT
CONCRETE FOOTER
PROCESS AREA DNAPL SOURCE AREA
FORMER POLE STORAGE
HORIZONTAL DRAIN
CONCRETE FOOTER
LOCKER ROOM METAL BUILDING
FORMER COOLING POND
CONVEYOR
PLATFORM
LOADING DOCK
HG-11S
HG-15S
PZ-17A
6'x6' WELL HOUSE
GROUNDWATER TREATMENT SYSTEM ENCLOSURE
CSX TRANSPORTATION RAILROAD
Groundwater Flow - from 2010 Second Semiannual LEM Report.
EXPLANATION
SURFICIAL AQUIFER MONITORING WELL
SURFICIAL AQUIFER PIEZOMETER
SURFICIAL AQUIFER EXTRACTION WELL
HAWTHORN GROUP MONITORING WELL
LATERAL EXTENT OF DNAPL SOURCE-AREAS WITHIN THE SURFICIAL AQUIFER PROJECTED VERTICALLY TO THE SURFACE
KOPPERS PROPERTY BOUNDARY
N
0
60
120
SCALE IN FEET
TITLE: FORMER PROCESS AREA FEATURES
LOCATION: Cabot Carbon/Koppers Superfund Site
Gainesville, Florida
GeoTrans, Inc.
A TETRA TECH COMPANY
CHECKED JC, BS
DRAFTED CP, DB
FILE 220121701A
DATE 12/13/10
FIGURE: 3
Slurry Wall to Middle Hawthorn Clay
UHG Well Location & Number