

US EPA ARCHIVE DOCUMENT



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May 7, 2013

Mr. Michael J. Mikulka
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Land & Chemicals Division
US Environmental Protection Agency
77 West Jackson Blvd
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RE: Responses to EPA Comments on "EPA Comments on Tyco Response to Comments and Revised Dredged Material Treatability Study Results"

Dear Mr. Mikulka:

On behalf of Tyco Fire Products LP (Tyco), CH2M HILL has prepared this correspondence to respond to the Environmental Protection Agency (EPA) comments received on April 26, 2013 "EPA Comments on Tyco Response to Comments and Revised Dredged Material Treatability Study Results" as received on March 29, 2013. The attached technical memorandum has been revised to include the requested EPA changes as identified in the comments document and represents the final version of the treatability study results.

For ease of review, the EPA comment is presented in plain text followed by the Tyco response in italics:

GENERAL COMMENTS:

1. **Quality Assurance Project Plan:** Tyco included the onsite laboratory information in the QAPP Addendum 4 submitted on April 8, 2013. EPA review of the QAPP Addendum 4 is ongoing.

No response required.

2. **Reagents Selected for Study:** Tyco added additional text to the Revised Treatability Study Report discussing the alternative reagents considered in 2012 for the mix design. Tyco proposes using dry ferric sulfate for stabilizing arsenic in the dredged material. Because there is a limited supply of dry ferric sulfate worldwide, Tyco should include contingencies in the Hazardous Waste Variance Modification Request (Variance) for stabilizing the arsenic if dry ferric sulfate is not available.

As presented on pages 8-9 of the Revised Hazardous Waste Variance Modification Request, dated April 23, 2013, liquid ferric sulfate may be used to replace dry ferric sulfate for the soft sediments as needed. In addition, as presented on page 5 of the Hazardous Waste Variance Modification Request, limited "out of phase sequence" dredging may be necessary in order to avoid delays in dredging and processing.

3. **Use of Wood Chips or other Additives:** While Tyco does not anticipate using wood chips in treatment and sediment management, the use of wood chips should be discussed in the Variance as a contingency to dewatering the dredge material.

A discussion of the potential use of wood chips is presented on page 9 of the Revised Hazardous Waste Variance Modification Request, dated April 23, 2013.

4. **Sediment Mixing:** Tyco states that the intent of the Treatability Study Report was to state the procedures that CH2M HILL used during the study. Tyco added additional text to clarify details concerning the mixing of the samples. The SOP in Attachment 1 of the Treatability Study Report should clearly state the procedures used during the study and that the SOP applies to laboratory sampling and not the field work. The field mixing and sampling SOPs were included in the QAPP Addendum 4 or should be added to the Variance for the 2013 season. Dust control during mixing should also be discussed in the Variance.

Attachment 1 of the Treatability study has been revised as requested. The title now reads: TYCO TREATABILITY STUDY – MIX DESIGN SOP.

5. **Use of Portland Cement:** The Tyco response states that additional dry ferric sulfate will be used to meet the paint filter test requirements and any workability issues. No mention was made of using additional Portland cement. Contingencies for retreatment of material or use of additional dry ferric sulfate or Portland cement to pass the paint filter test/workability requirements should be included in the Variance for the 2013 dredging season. As discussed during the March 22, 2013 meeting, the DNR is seeking a contingency plan outlining how the treated dredge material will be handled and disposed if the TCLP arsenic level of <5 ug/L cannot be achieved after two rounds of treatment. Per condition number 17 of the July 2012 Hazardous Waste Remediation Variance, any treated dredge material that contains a characteristic hazardous waste will need to be disposed of as a hazardous waste. The disposal of the hazardous waste should occur immediately.

The Hazardous Waste Remediation Variance Conditional Approval allows for re-treatment of material that fails to meet the TCLP requirement for landfill disposal. As presented on page 11 of the Revised Hazardous Waste Variance Modification Request, dated April 23, 2013, treated sediment that fails to meet disposal criteria for disposal at the Waste Management Menominee Landfill will be re-treated using the prescribed dosage for untreated material. If the re-treated material fails to meet the landfill disposal criteria, it will be transported from the site in licensed trucks for disposal as hazardous waste.

6. **Results Pending:** Tyco updated Tables B-1 through B-4 with pending results and added an overall legend. However, the tables no longer have table headings. For example, it is unclear which table is B-1. Table headings need to be added. Tyco did not mention whether the text was updated or the overall conclusions were impacted by the pending results. The recommendations section has been changed slightly in the Revised

Treatability Study Report. For soft dredge material, the wet reagent is not indicated in any of the tables as the recommended wet mix. Update either text or tables so that they match. In the tables, two dry mixes are chosen for the semi-consolidated material but the text only mentions one mix. The text does specify that up to 7.5 wt% Ferix-3 and up to 5 percent Portland cement is the preferred dry mix which accounts for both the preferred mixes in the tables.

The table headings have been restored and included in the revised document.

The wet mixes for soft DM B6 and SCM11LOW have been identified in the tables.

The mix design recommendations were not impacted by the pending results except for ongoing solidification testing of SCM11LOW and SCM10 during early February 2013. The treatability study narrative for the SCM source materials has been updated to reflect the pending results.

EPA is correct on their restatement on a dry mix recommendation of up to 7.5% Ferix-3 and up to 5% PC for the SCM. Mixes were identified and recommended for each SCM source material used in the project. Each dry mix is discussed in the SCM11LOW and SCM10 section, the recommendation section assimilates the two dry mix design recommendations into a single statement. However, the proposed field operations have currently specified the wet mix recommendation.

7. **Tables B-1 through B-4:** The tables should be revised to indicate all mixes that fail the paint filter test or that are not tested due to visual confirmation of free liquid. These mixes should not be included for consideration, which would increase the readability of the table by making it easier to determine which mixes should not be considered. Currently, the TCLP-As results are displayed green for passing the TCLP even if they failed the paint filter. The reader may conclude that the mix is still viable because it passed the TCLP test. Only mixes that pass both the paint filter test and the TCLP-As test should be displayed in green.

The green coloring has been removed in the reagent cost column (e.g. far right column of Tables B-1 to B-4) for samples that either failed the paint filter test or were not tested (NT).

8. **Onsite Laboratory:** Tyco added text clarifying that the rapid TCLP and XRF were only for prescreening. The QAPP Addendum 4 (under review) includes all SOPs for the onsite laboratory.

No response required.

10. **Holding Times in the Treatment Bins:** Holding times for treated material in the treatment bins should be addressed in the Variance.

Holding times for treated material is not specifically discussed in the Hazardous Waste Variance Modification Request. The chemical treatment process to stabilize the arsenic is nearly instantaneous upon application, with additional curing (3-5 days) required to allow for the Portland cement to sufficiently "dry" the sediments to meet paint filter criteria for landfill disposal. Laboratory testing of the treated material is being conducted to expedite analytical testing results for landfill disposal. Once analytical testing results demonstrate the material

meets landfill disposal criteria, the material will be transported to the landfill for disposal. As such, treated material is not expected to remain on-site for more than approximately 10 days (assuming re-treatment is not needed). Bins space limitation, transportation limitations, and project schedule necessitate removal of treated material from the site in an expeditious manner.

11. through 13. **XRF and Mini TCLP:** Tyco confirmed that XRF and Mini-TCLP are being used as prescreening tools only. The QAPP Addendum 4 (under review) includes SOPs for XRF and Mini-TCLP including calibration and verification procedures.

No response required.

14. **Post-Treatment Samples.** The provided response assumes the analytical parameters specified in condition number 14 of the July 2012 Hazardous Waste Remediation Variance have been modified. To date, the DNR has made no determinations regarding whether or not to modify the parameters listed in this condition.

No response required.

SPECIFIC COMMENTS

1. **Mix Design Methods, Page 4:** The Tyco response to the comment stated four possible sampling intervals within the first 3 days of testing are 1-hour, 1-day, 2-day, and 3-day. Although the text was updated to clarify the issue, it is still unclear to the reader. Recommend that the statement in the response to comments should be added to the text to clarify.

The Mix Design Methods Section, first sentence of paragraph 3 was revised to read:

For this study, there were four possible sampling intervals within the first 3 days of testing: 1-hour (1HR), 1-day (1D), 2-day (2D) and 3-day (3D). The mini-TCLP procedure was used on the first three sampling intervals, see Attachment 3.

3. **SCM11LOW Source Material, Page 5-6:** Tyco added an overall table legend that clarified the term "Work". If only the term "Pass" is used, does that mean that the material passed the paint filter test but was not workable? This still needs clarification.

That is correct. The additional qualifier that only applies to mix designs analyzed after the date shown in the legend for "B" tables. Additional clarification added to legend for Tables B-1 to B-4.

4. **Recommendations, Page 6:** Tyco describes the use of a clamshell bucket to reduce the water content in the dredged material. Information in Tyco's response to comments should be included in the Variance for 2013 dredge season.

This specific information is not provided in the Revised Hazardous Waste Variance Modification Request submitted on April 23, 2013. Water content in the dredged material impacts the treatment process of the sediments. Much of the water content issue is related to the debris encountered in the sediments that prevents full recovery of sediment using environmental clamshell buckets. Information related to the difficulties in recovery and the rationale for using the standard clamshell bucket are provided on page 5 of the Revised Hazardous Waste Variance Modification Request document. If additional detail is necessary beyond the information provided herein and in the revised document, an addendum to the revised document will be submitted under separate cover.

6. **Tables in Appendix B:** See comment for General Comment 6.

Refer to the response to General Comment 6 above.

7. **Tables in Appendix B:** Tyco states that deionized (DI) water was added to the B6 Suite D to determine if the reagent dose is adequate to absorb the additional water present during Fall 2012 dredging, and that all subsequent testing with B6 material was done at an elevated moisture content of 200 percent. The table for B6 calls out for DI water for only Suite D. The treatability study report should be revised to specify whether DI water was used for all subsequent tests for B6 and to describe how the elevated moisture content was achieved.

The last sentence in the 3rd paragraph of the B6 section has been revised to read:

All subsequent testing with B6 material was performed at an elevated moisture content of 200 percent, with DI added on a mass basis to achieve the desired water content.

8. **Attachment C:** The EPA comment referred to the first and fourth bullets on page 5 of Attachment C. The Tyco response stated that the text would be revised to say one sample will be collected per 100 cubic yards of material in the scow and that all material will require some treatment. These revisions were not found in the document. Please specify the location of the changes if revisions were made to the text.

The first bullet of the summary section Rapid TCLP Testing Summary in the 2013 Tyco Dredge Material Rapid TCLP Study Report refers to a recommended testing frequency of 10 samples per barge, which roughly corresponds to every 100 cubic yards.

We trust the information provided is responsive to your comments submittal. Should you have any questions regarding this correspondence, please contact Larry Wilson at 561-226-3481.

Sincerely,
CH2M HILL, Inc.



Jeffrey Danko
Project Manager

cc: Larry Wilson - Tyco, Simplex Grinnell
Joe Janeczek - Tyco International
Kristin DuFresne - WDNR
David Panofsky - WDNR
Cheryl Bougie - WDNR
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Attachments

Dredged Material Treatability Study Results, Tyco Fire Products LP Menominee River Sediment Removal Project, Marinette, Wisconsin

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DATE: May 7, 2013

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During December 2012 and January 2013 (winter treatability study), CH2M HILL performed additional mix designs on arsenic-containing sediment at the Tyco Fire Products LP (Tyco) facility in Marinette, Wisconsin. This technical memorandum reports on the results of this recently completed treatability study. The scope of work included two main elements:

- Conducting a supplemental round of new mix designs and long-term curing studies to evaluate alternate reagents to more efficiently (and cost-effectively) treat the arsenic-containing soft dredged material (DM) and semi-consolidated material (SCM). Alternatives were sought for the current dosing rate of up to 25 percent (by weight [wt%]) of a 60 percent ferric sulfate solution plus 10 percent portland cement added to the soft DM.
- Evaluating the potential for deploying a rapid, real-time assessment approach/tool for determining the total arsenic, toxicity characteristic leaching procedure (TCLP) arsenic, and moisture content of the DM and SCM in the scows before unloading. Having these data would enable the possibility to optimize (lower) reagent dosing.

Both scope items were performed at the CH2M HILL Applied Services Laboratory (ASL) in Corvallis, Oregon.

The first scope item sought to increase the overall treatment efficacy by identifying alternative reagent pairings (for the same DM conditions) that are more efficient to apply and have lower overall unit cost without loss in treatment effectiveness. The results of this testing program are the subject of this technical memorandum. The mix design standard operating procedure (SOP) and the mix design summary sheets are included as Attachments 1 and 2, respectively.

CH2M HILL conducted many internal and external discussions with reagent suppliers, technologists, and subject matter experts in an effort to identify suitable reagent alternatives to the sodium hypochlorite (oxidant), 60 percent ferric sulfate solution (arsenic immobilizing agent) and bed boiler ash/fly ash (solidifying agent) used in earlier project phases. CH2M HILL retained an external subject matter expert (Dr. Larry Twidwell) with knowledge of highly arsenic-impacted systems who assisted in the final selection of reagents and the specific geochemical and reagent deployment issues for sediment at the Tyco facility.

The second element of the scope of work involved testing two rapid assessment analytical techniques. The first study successfully evaluated the development of a rapid total arsenic content assessment technique based on using a handheld (portable) X-ray fluorescence (XRF) device (CH2M HILL 2013a). The second study successfully developed a rapid TCLP assessment technique to conservatively assess the TCLP-arsenic leaching behavior of the DM within a 4-hour timeframe (CH2M HILL 2013b). This technique is referred to as "mini-TCLP" throughout the document; a full description of the method is described in Attachment 3. The mini-TCLP approach (reduced

volume, reduced extraction period) was shown to be more conservative of the full TCLP results. The results of both studies are provided as independent white papers in Attachment 3.

The rapid XRF and mini-TCLP methods are *screening* techniques that were researched and developed to help assess the total and leachable arsenic concentration of the incoming barges. These screening methods will be used only to assist in establishing appropriate reagent dosing levels (not eliminate dosing); these screening techniques will not be used for compliance testing of treated DM.

Background

Technical Summary

The DM at the Tyco facility presents multiple stabilization/solidification (S/S) challenges and traditional S/S reagents have not been effective—they actually cause the DM to leach more arsenic than its in-situ condition.

The arsenic-containing compounds in the DM and SCM contain arsenic (V), which must be first cleaved (oxidized) from their organic functional groups (e.g., moieties) for immobilization. Optimal conditions for arsenic (V) immobilization occur at mid-range pH values (3 to 8.5 standard units) and under oxidized conditions (high oxidation-reduction potential [ORP] or Eh). This is a narrow range of environmental conditions (e.g., specified pH, ORP range, or “coordinate”) to target, and not many combinations of reagents can achieve this coordinate, irreversibly immobilize high levels of arsenic, and solidify the resulting mixture under said conditions.

Ferric iron is one of the most efficient means to immobilize arsenic, both through sorption and precipitation. It was determined in the fall 2012 treatability study that ferric iron consistently and successfully treated the highly arsenic-impacted DM, while the combined use of wood chips (or small portland cement dose) simultaneously reduced the DM moisture content to pass the paint filter test and improved its workability at the landfill.

Moreover, using liquid ferric sulfate demonstrated the arsenic immobilization reaction was almost instantaneous (based on 1-hour cure times).

Fall 2012 Activities

Beginning in mid-August 2012, significant problems were encountered with the S/S processing operations at the project site, which deployed 5 wt% sodium hypochlorite (as 12.5 percent aqueous solution) and 18 wt% reactive fly ash (RFA) to treat the incoming wet DM. In some cases, depending on whether re-treatment was required, the reagent doses approached 10 wt% sodium hypochlorite and 36 wt% RFA. The re-treatment doses also were found to be unsuccessful because of high arsenic levels (up to 7,000 milligrams per kilogram [mg/kg]) and high water contents of the DM (greater than 200 percent), which the 18 to 36 wt% RFA was not always able to solidify.

Liquid ferric sulfate (60 wt%) solution had been discontinued because of its interactions with the sodium hypochlorite; chlorine gas generation was a concern since the two aqueous reagents were not being applied in a two-stage process as performed in the ASL treatability studies. Since both ferric sulfate reagent and its delivery system was still located onsite, requests were made to determine if the ferric sulfate solution could be used for bin material reprocessing, and processing of fresh DM in the absence of sodium hypochlorite.

During the treatability study performed at Waste Stream Technology (WST, a wholly owned subsidiary of Severson) in the fall 2012, it was determined that continued use of sodium hypochlorite did not appear worthwhile since it did not reduce the ferric sulfate demand. In addition, sodium hypochlorite added water to an already very wet DM, which made solidification and passing the paint filter test more problematic. Lastly, sodium hypochlorite cannot be used alone - it did not necessarily contribute either to arsenic immobilization, ferric iron by itself was effective on both bin material re-treatments and fresh DM.

Summary of Bin Reprocessing Treatments at WST

Samples of once- and twice-treated bin materials were shipped from the project site to WST to explore re-treating these materials to pass the TCLP-arsenic criterion of 5 milligrams per liter (mg/L). A secondary goal was to identify alternate treatment reagents to pass the TCLP-arsenic criterion using cost-effective, widely available reagents.

Re-treatment treatability testing (Bin 5 material; highest total arsenic concentration of approximately 3,800 mg/kg) involved sodium hypochlorite and peroxide as liquid oxidants; liquid ferric sulfate, liquid ferric

chloride, and basic oxygen furnace iron dust as iron sources; and cement kiln dust, lime, granular activated carbon, calcium chloride, and kiln-dried pine bedding and wood chips (trade name: Sani-chips) as potential sorbents, and precipitating/solidifying agents. Permanganate-based reagents were excluded from consideration based on their toxicity and health and safety considerations. Bin 5 material was strategically selected for the main round of treatability study work to establish an upper limit on reagent dosing for bin material re-treatments.

After completing approximately 90 S/S mix designs on the Bin 5 materials, it was identified that the most successful coupling of reagents was liquid ferric sulfate with cellulosic material (pine bedding), primarily because this produced near neutral pH and oxidized conditions (high ORP), which corresponded to arsenic(V) immobilization by iron. Specifically, a 20 wt% ferric sulfate dose with 4 wt% pine bedding material was recommended for re-treatment of Bin 5 material. Other bin material re-treatments followed similar dosing recommendations with ferric sulfate and wood chips being added as needed, primarily because of its ability to uptake moisture and improve workability at the landfill. Bin re-treatments in the field were subsequently successful with respect to TCLP-arsenic and paint filter testing.

Summary of Fresh DM Mix Designs at WST

Given the high levels of arsenic that were encountered in numerous scows, a resampling round was undertaken to obtain the highest arsenic-impacted DM possible. The technical approach was to use the most contaminated DM possible to establish an upper cap on reagent dosing to avoid future failures. Then, once this upper cap was established, the objective was to attempt to optimize reagent dosing to make the process more economical. Because of the multiple constraints and high variability in the arsenic concentrations of the DM, the main challenge during the fall 2012 season was few treatment options were available other than to deploy a conservative dose of the 60 wt% ferric sulfate solution.

Two soft DM sources were used to attempt to bracket expected dosing levels based on arsenic contamination (greater detail next section). *Soft DM B4 source material* was characterized as having total arsenic concentrations of 3,524 mg/kg and TCLP-arsenic of 20 mg/L based on several homogenized buckets. Mix designs were launched on September 7, 2012. Individual doses of 2 to 8 wt% sodium hypochlorite (5 wt% used previously) and 2 to 8 wt% hydrogen peroxide both with wood chips (10 wt%) were unable to lower the TCLP-arsenic below 5 mg/L. Conversely, 10 to 12.5 wt% of the ferric sulfate solution and Ferix-3 (dry ferric sulfate) with wood chips (8 to 12 wt%) were both found to be effective. This stressed the role of ferric iron in arsenic immobilization, and led to the elimination of oxidants from further use.

The *soft DM B6 source material* was used as the surrogate material for soft DM to establish an upper cap on reagents dosing (total arsenic of 6,166 mg/kg; TCLP-arsenic of 39.5 mg/L). Building on the soft DM B4 results, it was determined that a 25 wt% ferric sulfate solution with 12 wt% wood chips was successful, as was a 25 wt% ferric sulfate solution with 10 wt% portland cement. In the latter case, the 10 wt% portland cement dose was sufficiently low so as to achieve solidification without producing the elevated pH conditions that were associated with the prior bin material failures. More importantly, using portland cement was a more sustainable and logistically attractive option than using wood chips (extremely bulky). Also tested was 20 wt% Ferix-3 coupled with 10 wt% PC, which produced TCLP-arsenic less than 1 mg/L.

Soft DM treated in the field with approximately 25 wt% of the ferric sulfate (60 percent) solution with 8 to 12 wt% wood media or 10 wt% portland cement both provided the best technical solution to fresh DM processing (of those mix designs tested) given the multiple constraints associated with site processing needs in fall 2012.

Winter Treatability Study

Dredged Material Sources and Reagents

For project continuity purposes, the strategy, approach, and data sets generated by this treatability study performed at ASL are consistent with the approach used at WST (as discussed above). As part of the ASL scope of work, two soft DM and two SCM source materials (from different areas within the project site) were tested to develop recommended dosing strategies for the soft DM and SCM, which underlies the soft DM and is more sandy/silty in nature. The soft DM and SCM source materials tested include:

- Soft DM B6 source material (6,295 mg/kg total arsenic; 35 mg/L TCLP-arsenic). Because of its high arsenic content and leaching, this DM source material was used to establish an upper limit on reagent dosing for soft DM.
- Soft DM B4 source material (4,198 mg/kg total arsenic; 13 mg/L TCLP-arsenic). B4 represents more moderately arsenic-impacted soft DM.
- SCM11LOW source material (1,066 mg/kg total arsenic; 32 mg/L TCLP-arsenic). Because of its relatively high arsenic content and leaching (for SCM), this DM source material was used to establish an upper limit on reagent dosing for SCM.
- SCM10 (884 mg/kg total arsenic; 2 mg/L TCLP-arsenic). This DM source material was taken to be representative of SCM not requiring arsenic immobilization, only needing sufficient solidification or drying to pass U.S. Environmental Protection Agency (USEPA) 9095B (paint filter test). That is, the goal was to determine whether the additional use of ferric sulfate compounds in some portions of SCM is unnecessary.

The soft DM was the main focus of the fall 2012 DM treatability studies. It was established during the 2012 site operations that a 25 wt% dose of liquid ferric sulfate (60 percent solution) with 10 percent portland cement was effective for treating highly arsenic-impacted soft DM. For moderately arsenic-impacted soft DM (e.g., B4), only 10 to 12.5 wt% of the ferric sulfate solution successfully immobilized arsenic. However, solidification remained a challenge, with significant material handling issues and landfill workability problems even following 3 days of curing. Accordingly, switching to dry reagents is preferable. The initial effort of this study was to confirm the prior results from fall 2012 and demonstrate continuity between the two treatability studies. Thereafter, the focus was on the feasibility of using alternate reagents to increase efficiency and lower treatment costs without loss in arsenic immobilization, solidification, or workability at the landfill.

For SCM, only brief characterization work was completed in fall 2012, so emphasis was placed on the SCM11LOW media to set an upper threshold for reagent dosing should it be required in the field where SCM with elevated concentrations of leachable arsenic is encountered.

Table 1 summarizes the reagents that were used in this study along with the acronyms that are used in the Mix Design Summary Tables included in Attachment 2. The need for an independent oxidant was revisited as part of this scope of work and was eliminated based on prior treatability work conducted in fall 2012. In addition, the use of bulky, cellulosic drying agents (woods chips/shavings) was ruled out because of their logistical and regulatory acceptance issues.

A 38 wt% ferric chloride solution was selected because it is used in conventional wastewater treatment and was determined to have a lower unit cost than the ferric sulfate solution. Bentonite, calcium bentonite, and the ZT fines were selected as near neutral pH drying agents to avoid the potential for arsenic leaching at an elevated pH. A series of ferric sulfate and sulfur-containing reagents (Enviroblend series, FF100FS, Ferix-3, and Terrabond) were evaluated based on the success of preliminary trials that showed dry ferric sulfate compounds were successful in immobilizing elevated concentrations of arsenic in the soft DM. The fall 2012 study found that Ferix-3 was successful in limited curing studies. A ferric hydroxide sludge also was used (as recommended by Dr. Twidwell) because it contained high quantities of ferric iron, which plays a central role in arsenic immobilization. Portland cement (low doses) also was used based on prior success at the site and in prior treatability studies.

TABLE 1
Mix Design Reagent Summary

Reagent Acronym	Product	Supplier
Aqueous		
60 percent $\text{Fe}_2(\text{SO}_4)_3$	60 percent ferric sulfate solution	General Chemical
38 percent FeCl_3	38 percent ferric chloride solution	Hydrite Chemical
Dry		
Bentonite	Sodium bentonite (Premium Gel)	CETCO
Ca-bentonite	Calcium bentonite (thickener)	S&B Industrial
Env 25/75	Enviroblend 25/75 [$\text{MgO}/\text{Fe}_2(\text{SO}_4)_3$ ratio]	Premier Magnesia LLC
Env 50/50	Enviroblend 50/50 [$\text{MgO}/\text{Fe}_2(\text{SO}_4)_3$ ratio]	Premier Magnesia LLC
Env 80/20	Enviroblend 80/20 [$\text{MgO}/\text{Fe}_2(\text{SO}_4)_3$ ratio]	Premier Magnesia LLC
$\text{Fe}(\text{OH})_3$	Ferric hydroxide sludge	Hedin Environmental
Ferix-3	Ferric sulfate containing blend	Kemira
FF100 FS	Ferric Sulfate containing blend	Free Flow Technologies
Portland cement	Type I Portland Cement	Lafarge (Alpena plant)
Terrabond WP	Proprietary sulfur containing blend	Terra Materials, LLC
ZT Fines	Superabsorbent polymer Zapsorb fines	Zappa-TEC

Mix Design Methods

The SOP for the mix design process is included as Attachment 1. In some cases, water from the site (or deionized water) was added to the DM to simulate the high water content DM that was encountered in the fall 2012 DM processing season (as noted in Attachment 2 tables, when necessary). Each DM source material and its overburden water present in the same sealed container was homogenized using an electric paint mixer until an even consistency was visually present throughout the entire solid phase. The homogenized DM subsequently was characterized in terms of moisture content, pH, ORP, TCLP-arsenic, and total arsenic. The inventory numbers of the individual sample containers were tracked, and sample nomenclature was established to monitor the curing process at multiple intervals (typically 1HR; 1D, 2D, 3D, 7D, 28D; where HR denotes hour and D denotes day).

Reagents were added on a total weight percent (percent) basis to the wet DM. Hence for dry reagents, the total weight was the dry weight. Each mix design was batched and blended for approximately 1 minute using wood spatulas in 1-liter Tri-pour containers until they were visually homogenized. The mixes were then covered with aluminum foil until subsamples were collected for each specified curing interval. For each curing interval, the treated DM was tested for paint filter, pre- and post-extraction pH and ORP, and TCLP-arsenic with a reporting of the fluid determinations to assist in understanding the environmental conditions (pH and ORP) associated with the TCLP-arsenic result for the reasons discussed in the background section above. For each testing interval, the ability to pass the paint filter test (USEPA 9095B) was first assessed either visually (and not tested), or it was subjected to testing no later than the third day.

For this study, there were four possible sampling intervals within the first 3 days of testing: 1-hour (1HR), 1-day (1D), 2-day (2D) and 3-day (3D). The mini-TCLP procedure was used on the first three sampling intervals, see Attachment 3). Full TCLP testing according to USEPA Method 1311 was performed on the 3-, 7- and 28-day samples. On rare occasions because of scheduling constraints, a 2-day sample may have been submitted in lieu of the 3-day sample for full TCLP testing. Since the ferric-based reaction chemistry was shown to be rapid (typically within 1 hour to 1 day), some mixes were terminated early because of TCLP-arsenic failures.

Mix Design Testing Results

Attachment 2 contains the mix design summary results for DM source material. The top of each summary table contains the DM source material characterization results and the tracking numbers of the samples. In some cases (e.g., B6), the number of mix designs performed were so high that the initial batching source materials were exhausted and a change was made to the next most highly arsenic-leachable soft DM from the sample collection location. When this occurred, such characterization information is noted between suites (e.g., immediately above Suite E).

The far left columns have the individual mix design identification numbers followed by relevant batching and moisture content information for the DM source materials. At the beginning of the mix design study (December 10), the first several mix design suites (orange highlights) included up to 15 mixes per day. Some mixes contained up to three reagents (yellow highlights) with percent dosing reported as percent dry reagent to wet weight of DM.

Up to five blocks of curing interval data (1 hour, 1 day, 2 days, 3 days, 7 days, and/or 28 days) are shown per mix design in the center and right sections of each mix design summary page, where the first two curing periods are varying combinations of 1HR, 1D, and 2D data depending on scheduling constraints. The typical data sets per curing interval are paint filter, pre- and post-extraction pH and ORP, TCLP extracting fluid, and the TCLP-arsenic, the last of which is highlighted in green/brown for passing and failing results, respectively. Lastly, up to two mixes may be identified with blue or yellow borders (see bottom note on Tables B-1 to B-4), which denote the recommended dry and wet mixes, respectively.

B6 Source Material (Soft Dredged Material)

In Table B-1, Suite A contains the same aqueous ferric sulfate dosing completed during the fall 2012 treatability study with Severson. The CH2M HILL ASL confirmed the 25 to 30 wt% doses of the 60 percent ferric sulfate solution with 10 percent portland cement were successful based on all tested curing intervals. These blends passed the paint filter on the third day, but they were still moist and presented the same workability challenges that were encountered in the fall 2012 DM processing season. Suite B contained a parallel series of doses but using a 38 wt% ferric chloride solution that was generally more effective in terms of arsenic immobilization (see Suites A and B starting with 2-day data except 15 percent FeCl_3 plus 10 percent portland cement).

However, while arsenic was successfully immobilized by many ferric chloride containing mixes (see also Suites C and E), it was virtually impossible to create a workable consistency beyond passing the paint filter because of its tacky consistency despite adding in other drying agents and reducing the ferric chloride dose. Ferric chloride-bentonite drying trials also were performed with additional supplements such as food-grade starch and oatmeal in an attempt to dry out the mixes further (data not shown). However, more than 30 percent of the fine dry cellulosic reagents had to be added to get a workable material (still dough-like); this was deemed impractical. In addition, the ferric chloride-rich mixes also off-gassed carbon dioxide.

Suite D began mix design testing on dry ferric-containing compounds (FF100 FS; Env 25/75, and Ferix-3). Because of the low initial moisture content of the DM, Suite D testing yielded dry samples within 1 hour of mixing. Accordingly, deionized water was added to the B6 Suite D after 1 day of reaction to determine whether the original reagent dose could adequately absorb the additional water that would have been present during the fall 2012 DM processing season where the moisture content approached 200 percent. All subsequent testing with B6 material was performed at an elevated moisture content of 200 percent, with DI added on a mass basis to achieve the desired water content.

For Suite D, the FF100 FS was terminated early because of possible hydrogen sulfide production, as the treated mixes emitted a rotten egg odor indicative of reduced sulfur gases. The FF100 FS data set also illustrates the significance of elevated pH (approximately 11) on the corresponding TCLP-arsenic results (more than doubled to greater than 70 mg/L in three of five tests), and why the straight application of traditional stabilizing reagents was not successful.

Similarly, it became clear that the Env 25/75, while dominated by ferric sulfate, did not have the necessary buffering capacity to offset the portland cement that was required for solidification. Hence the pH increased, and TCLP-arsenic failures resulted. Ferix-3 at greater than 15 wt% doses was compliant on the TCLP-arsenic criterion of 5 mg/L (15 percent was borderline until 28 days), but the lowest Ferix-3 combination with portland cement to produce a workable solid was the 20 wt% Ferix-3 plus 10 percent portland cement.

Suites E to G sought alternatively successful mix designs that could match the arsenic immobilization, lower the unit cost, and match or exceed the workability of the treated DM. While every mix after the 20 wt% Ferix-3 plus 10 percent portland cement successfully immobilized the arsenic (except discontinued FF100 FS series), no mix combination was able to produce a moist/dry friable solid that would be workable in a landfill. The closest were the 15 and 20 wt% Env 25/75 with 20 wt% calcium-bentonite, but the efficiency of blending these mixes in the field was considered impractical.

In summary, the most efficient (and cost-effective) mix that passed the TCLP-arsenic by a comfortable margin and produced a workable mix design was 20 wt% Ferix-3 plus 10 percent portland cement. The key was not arsenic immobilization (many ferric-containing mixes were successful), it was the ability to simultaneously solidify the mix into a workable condition. In this regard, Ferix-3 and portland cement are well paired for the doses used.

B4 Source Material (Soft Dredged Material)

Arsenic shown in Table B-2, only Ferix-3 and portland cement were tested on the soft DM B4 source material. Liquid reagents were not tested as the dosing strategy for moderately arsenic-impacted DM was established in the fall 2012 DM processing season, and ferric chloride produced a media that could not be solidified. No other dry reagent combinations were tested because B4 has the same consistency as B6, and therefore, constituted the same solidification challenge.

In summary, the most efficient (and cost-effective) mix that passed the TCLP-arsenic by a comfortable margin and produced a workable mix design was 20 wt% Ferix-3 plus 10 percent portland cement. However, the use of the rapid assessment tools (XRF and mini-TCLP) to characterize the DM in the incoming scows may allow for successful lowering of the Ferix-3 dose. More specifically, the data shown in Table B2 suggest that for less arsenic-impacted soft DM, a dose of 15 wt% Ferix-3 with 10 percent portland cement would pass by a wider TCLP-arsenic margin and still be workable.

SCM11LOW Source Material

Homogenization of the SCM11LOW material did not fully entrain its overburden water (contained in same bucket) like other the DM source materials; it behaved more like sand, which quickly settles out. Because of the concern that successful decanting in barges would not occur in the field for a variety of reasons, it was sampled through the water column, and nevertheless was saturated with water (24 wt%). This approach was believed to be the most representative of site conditions (i.e., limited dewatering in barges).

Given the results for the soft DM B6 and B4 source materials, the initial approach was to use several pairings of Ferix-3 and portland cement to treat SCM. Given the silty/sandy nature of this SCM sample, the strategy was to identify a much lower overall dosing, while counter-balancing the acidity of the Ferix-3 with the alkalinity of the portland cement.

A dose of 5 wt% Ferix-3 on its own produced a dry friable material within 2 days of curing; no portland cement was required, as shown in Table B-3. Enviroblend 25/75 produced a similar result. The Ferix-3 dose could not be lowered to 2.5 wt% because of workability issues after 3 days. Low doses of only portland cement produced several TCLP-arsenic failures (Suite E).

In terms of an aqueous ferric reagent, a 5 wt% dose of the 60 percent ferric sulfate solution plus 5 percent portland cement was found to be an adequate dose combination that would satisfy the TCLP-arsenic criteria and provide sufficient workability (like moist sand) on the third day of curing. In Table B-3, the term “work” in the paint filter column for the wet reagent addition suites denotes that the sample both passed the TCLP and was deemed workable (see Suite F, replicates C,D).

SCM10 Source Material

The SCM10 source material was greater than 50 percent wetter than the SCM11LOW sample. While the SCM10 material is slightly coarser than the SCM11LOW material (CH2M HILL 2013a), it contains four times the organic matter, which is why it exhibits a greater propensity to retain moisture. The SCM10 source material was already TCLP-arsenic compliant (less than 5 mg/L), but the addition of a small quantity of portland cement (up to 5 percent) for pure drying purposes produced borderline TCLP-arsenic results or TCLP-arsenic failures because of the relationship between elevated pH and arsenic leaching (Suite B).

The SCM material embodies the technical challenge involved in stabilizing the sediments from the project site. Since a pure drying approach with portland cement jeopardized TCLP-arsenic compliance, Ferix-3 had to be added to counter-balance the alkalinity of the portland cement. Thus, while SCM10 was much less arsenic impacted than SCM11LOW, it actually required up to 7.5 wt% Ferix-3 plus 5 percent portland cement to be workable and remain TCLP-arsenic compliant. That is, more Ferix-3 was required for SCM10 despite its being initially TCLP-arsenic compliant.

In terms of an aqueous ferric reagent, a 5 wt% dose of the 60 percent ferric sulfate solution plus 7.5 percent portland cement was found to be the minimum dose combination that would satisfy the TCLP-arsenic criteria and provide sufficient workability (like moist sand) on the third day of curing. The 5 wt% dose of the 60 percent ferric sulfate liquid solution with 5 percent portland cement just passed the paint filter test, but was not considered workable.

Recommendations

These recommendations are collectively based on this treatability study (winter) and the work performed in conjunction with Severson (fall 2012). Between the two studies, more than 200 mix designs were evaluated. Dry mixes are preferred to wet regardless of cost because of workability, avoiding re-treatment, and maintaining throughput. Reasonable efforts should be made to lower the water content of the incoming DM during the dredging process.

Soft Dredged Material

- Dry reagent: 20 wt% Ferix-3 plus 10 percent portland cement
 - Rationale: Best consistent performer on soft DM with low TCLP-arsenic (less than 1 mg/L) results and best overall workability at lowest cost for soft DM with moisture contents on the order of 170 to 200 percent. A wide variety of reagents have been tested to dry out the DM without raising pH or lowering ORP (keys for arsenic immobilization). The combination of 20 wt% Ferix-3 plus 10 percent portland cement has been shown by both Severson and CH2M HILL to be effective in terms of arsenic immobilization, passing paint filter tests, and having sufficient workability with a repeatability that will keep site operations moving.
- Wet reagent: 25 wt% of 60 percent $\text{Fe}_2(\text{SO}_4)_3$ solution plus 10 percent portland cement
 - Rationale: Previously demonstrated success onsite; some issues with workability.

Semi-Consolidated Material

- Dry reagent: Up to 7.5 wt% Ferix-3 with up to 5 percent portland cement, as needed
 - Rationale: In terms of TCLP-arsenic, Ferix-3 is the most consistent performer on SCM, with as little as 5 wt% Ferix-3 lowering the TCLP-arsenic result by approximately two orders of magnitude from an initial concentration of 32 mg/L (SCM11LOW). Based on site characterization testing, it is not likely that SCM containing higher concentrations of arsenic than the samples tested herein will be routinely encountered. However, the water content (approximately 25 to 80 percent) of SCM has a significant impact on the ability of Ferix-3 to solidify SCM, and up to 5 percent portland cement may be required for wetter SCM. However, increased portland cement dosing results in a loss of arsenic immobilization potential in the more arsenic-impacted horizons (see SCM 11LOW, Suite C, Mix A).

Accordingly, using portland cement is recommended on an “only as-needed basis.” This is because the loss of arsenic immobilizing potential (approximately 10 times difference based on SCM11LOW) is associated with a greater risk of TCLP-arsenic failures, especially given the variable SCM conditions at the site.

- Wet reagent: 5 wt% dose of 60 percent $\text{Fe}_2(\text{SO}_4)_3$ solution with 5 to 7.5 percent portland cement, as needed
 - Rationale: 5 wt% of the 60 percent $\text{Fe}_2(\text{SO}_4)_3$ solution with 5 percent portland cement was workable for SCM11LOW, but SCM10 required an additional 2.5 percent portland cement, which appears to be related to its organic matter content.

References

CH2M HILL. 2012. “Technical memorandum: Summary of Severson Mix Designs Fall 2012,” by D. G. Grubb, CH2M HILL Engineers, 9191 S. Jamaica Street, Englewood, CO 80112, November 13, pp. 10.

CH2M HILL. 2013a. “Technical memorandum: Rapid Assessment of Total Arsenic in Tyco Fire Products LP (Marinette, WI Project) Dredged Material Using Portable XRF Device,” by B. Thompson, CH2M HILL Engineers, 9191 S. Jamaica Street, Englewood, CO 80112, January 19, pp. 8.

CH2M HILL. 2013b. “Technical memorandum: 2013 Tyco DM Rapid TCLP Study Report,” by D.G. Grubb and D.R. Berggren, CH2M HILL Engineers, 9191 S. Jamaica Street, Englewood, CO 80112, January 25, pp. 19.

Attachment 1
Mix Design Standard Operating Procedure

TYCO Treatability Study Mix Design SOP

Homogenize source material in sealed buckets by available methods. Measure MC, pH, ORP, total As and TCLP-As.

Batch sufficient sediment sample to perform 5 Full TCLPs; TCLP fluid determination, 3 ORP and 3 pH (outside of TCLP); 1 Paint Filter (PF) test with wastage (e.g. 500 g).

Use sample nomenclature of year-month-day without hyphens followed respectively by the DM source, letter sample number and curing period (1HR; 1D, 2D, 3D, 7D, 28D), e.g. 20121201-B6-A-1H.

Batch material (500 g) in single Tri-pour container for individual mixes. Label container with sample prefix (Date-DM source-sample number; 2101201-B6-A)

Weigh out and add Reagent 1 to DM in Tri-pour. Thoroughly homogenize. Cover with Al foil. HOLD for specified reaction time, if any.

Weigh out and add Reagent 2 to DM in Tri-pour. Thoroughly homogenize. Cover with Al foil. HOLD minimum of 1 hour prior to additional testing.

Measure pH and ORP of Mix Design

Submit for TCLP testing at designated interval (1-hour, 1-, and/or 2- days; as indicated by schedule)

- Assess ability to pass PF (likely/unlikely) and/or run on first opportunity for success (test performed only once, so make it count). When PF test is performed, use this same subsample material to perform ORP, pH and mini-TCLP.
- Measure and report pre-extraction pH and ORP
- Use mini TCLP quantities (500 ml container; 400 ml solution; 20 g solid)
- Label TCLP container with sample ID and curing interval (e.g. 20121201-B6-A-1H)
- Measure and report TCLP extraction fluid; TCLP-pH, TCLP-ORP, TCLP-As

Submit for TCLP testing at designated interval (3-, 7-, 28-days)

- Perform paint filter test on 3rd day if not already completed
- Measure and report pre-extraction pH and ORP
- Use full TCLP quantities (2 L solution; 100 g solid)
- Label TCLP container with sample ID and curing interval (e.g. 20121201-B6-A-28D)
- Measure and report TCLP extraction fluid; TCLP-pH, TCLP-ORP, TCLP-As.

NOTES:

Sample can be likely terminated for additional testing if TCLP-As exceeds 10 mg/L (reaction happens pretty quick, but not always. It is important to watch progress daily. If it's not below 10 mg/L at 1-D or 2-D, it's not likely to drop into compliance at later time.

Attachment 2
Mix Design Summary Sheets

Master Legend for Tables B-1 through B-4

Raw Dredged Material Characteristics

MC - Moisture content, dry soil mass

Total As - Total arsenic content, dry soil mass

TCLP-As - Certified TCLP-arsenic concentration

Initial ORP - Oxidation reduction potential, 1:5 dredge material to water mixture

Initial pH - pH of a 1:5 dredge material to water mixture

Mix Identification and Material Characteristics

Treatment/ Sample ID – Identification for individual mix designs

Launch Day – Date mix was prepared

Sample wt – Wet mass of the dredge material used in the mix

Target MC – Target moisture content for the raw dredged material

Actual MC – Actual moisture content for the raw dredged material

Mix Designs

Suite ID – Set of mix designs

Reagent 1-3 – Reagents used in the mix design; Reagents added in order presented

60% $\text{Fe}_2(\text{SO}_4)_3$ – 60% Ferric sulfate solution

PC – Type 1 Portland Cement

38% FeCl_3 – 38% Ferric chloride solution

ZT Fines – ZappaTec's ZapZorb (super absorbant polymer), fine grade

Env 50/50 – Enviroblend "50/50" mix

Env 25/75 – Enviroblend "25/75" mix

FF100 FS – Free Flow 100 FS

Terrabond WP- Terrbond WP

Ca-Bent – Calcium Bentonite

Na-Bent – Sodium Bentonite

$\text{Fe}(\text{OH})_3$ – Ferric hydroxide solids

Leaching Measurements

Interval – Time after mix when sample was collected for TCLP (1HR, 1D, or 2D). 400 ml designation in header denotes mini-TCLP analysis technique. All others by Method 1311.

Paint Filter – Results of the paint filter test

NT – Sample not tested for paint filter due to visual free fluid

PASS – Sample passed paint filter test, see also WORK definition below for additional qualification.

WORK – A modified “Pass” designation initiated 1/23/13 to indicate SCM samples (only) that both passed the paint filter test and were deemed workable. Some SCM treatments that passed the paint filter were not necessarily workable (not friable enough).

ORP – oxidation reduction potential of the mix design prior to TCLP testing

pH – pH of the mix design prior to TCLP testing

Fluid – TCLP fluid used (1 or 2) for TCLP extraction per USEPA Method 1311

TCLP-ORP – ORP of the TCLP extraction fluid following the extraction

TCLP-pH - pH of the TCLP extraction fluid following the extraction

TCLP-As – Arsenic concentration in the TCLP extraction fluid

Results Interpretation

Reagent Cost – Cost of mix design per treated ton of dredged material



TCLP-As < 5 mg/L and/or reagent cost of passing mix design



TCLP-As > 5 mg/L; failing mix design



Recommended dry mix



Recommended wet mix

Table B-1
Stabilization/Solidation Mix Design Results for B6 Source Materials
Tyco Fire Products, Marinette, WI

B6 MC=			169%		Total As		6295 mg/kg 34.6 mg/L		Initial ORP		-309.1 7.92		12097/12099 (75%) plus 12100 (25%)																																
Sample		Target		Actual		Suite		Reagent 1		Reagent 2		Reagent 3		1st Cure Period (400 ml)						2nd Cure Period (400 ml)						3-Day						7-Day						28-Day						Reagent Cost	
Treatment	Sample	Launch	wt	MC	MC	Suite	Reagent 1	Reagent 2	Reagent 3	Interval	Paint	ORP	pH	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Interval	Paint	ORP	pH	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Paint	ORP	pH	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	TCLP-ORP	TCLP-pH	Fluid	TCLP-As	TCLP-ORP	TCLP-pH	Fluid	TCLP-As	Reagent Cost				
ID	ID	DAY	(g)	(%)	(%)	ID	(g)	(g)	(g)	(HR/DAY)	Filter	(mV)	(SU)	(-)	(mV)	(SU)	(mg/L)	(HR/DAY)	Filter	(mV)	(SU)	(-)	(mV)	(SU)	(mg/L)	Filter	(mV)	(SU)	(-)	(mV)	(SU)	(mg/L)	(mV)	(SU)	(-)	(mg/L)	(mV)	(SU)	(-)	(mg/L)	(\$/ton)				
20121210-B6	A	Monday 12/10/12	500	250	169	Suite A	60% Fe2(SO4)3	PC		1 HR	NT	439.2	2.39	1	0.4	4.43	1.92	2-DAY	NT	411.9	2.63	1	144.8	4.47	1.66	NT	442.1	2.50	1	58.8	4.48	1.81	384.8	2.85	1	5.51	-30.2	4.86	1	1.69	\$52.90				
20121210-B6	B		500	250	169		100 g (20 wt%)			1 HR	NT	445.4	2.35	1	22.7	4.34	1.73	2-DAY	NT	420.6	2.57	1	165.4	4.38	1.48	NT	452.8	2.39	1	63.1	4.38	1.81	351.3	2.96	1	14.0	73.3	4.70	1	2.25	\$66.12				
20121210-B6	C		500	250	169		150 g (30 wt%)			1 HR	NT	450.8	2.28	1	42.8	4.18	1.52	2-DAY	NT	425.3	2.57	1	183.5	4.17	1.23	NT	459.1	2.33	1	68.7	4.31	1.42	387.4	2.84	1	16.9	82.1	4.65	1	3.86	\$79.35				
20121210-B6	D		500	250	169		100 g (20 wt%)	50 g (10 wt%)		1 HR	NT	18.2	9.03	1	-154.4	6.43	1.43	2-DAY	NT	-302.1	10.06	2	54.5	5.16	3.15	NT	117.6	9.35	2	-52.5	5.58	4.51	52.9	9.11	2	8.13	53.1	5.32	2	5.78	\$65.60				
20121210-B6	E		500	250	169		125 g (25 wt%)	50 g (10 wt%)		1 HR	NT	48.5	7.96	1	-71.8	5.45	0.67	2-DAY	PASS	-226.1	8.20	2	76.3	4.90	0.64	PASS	199.3	6.23	2	-29.4	5.26	0.53	120.8	9.07	2	0.77	-10.4	5.71	1	2.21	\$78.82				
20121210-B6	F		500	250	169		150 g (30 wt%)	50 g (10 wt%)		1 HR	NT	107.9	4.62	1	102.4	5.28	0.61	2-DAY	PASS	-106.5	4.87	1	53.2	5.71	0.54	PASS	210.8	5.25	2	-14.6	4.92	0.45	125.4	8.13	1	0.74	45.7	4.76	2	0.797	\$92.05				
20121210-B6	G		Tuesday 12/11/12	500	250	169	Suite B	38% FeCl3	PC		1 HR	NT	478.2	2.38	1	90.4	4.46	14.5	2-DAY	NT	-78.3	4.03	1	84.7	4.69	0.78	NT	107.5	3.93	1	7.4	4.74	0.68	112.2	4.88	1	0.897	-38.9	4.78	1	1.26	\$37.14			
20121210-B6	H			500	250	169		100 g (20 wt%)			1 HR	NT	491.7	2.25	1	85.9	4.26	21.7	2-DAY	NT	207.3	2.90	1	100.1	4.52	0.59	NT	114.1	3.40	1	24.1	4.62	0.584	115.2	3.89	1	0.714	-24.1	4.53	1	0.914	\$49.52			
20121210-B6	I			500	250	169		125 g (25 wt%)			1 HR	NT	501.1	2.13	1	91.7	3.97	30.4	2-DAY	NT	287.5	2.24	1	129.2	4.29	0.90	NT	459.1	2.20	1	56.7	4.40	0.661	422.0	2.44	1	0.689	93.5	4.32	1	0.707	\$61.90			
20121210-B6	J/K1			500	250	169	mini	TCLP	150 g (30 wt%)			1 HR	NT	507.9	2.06	1	81.0	3.88	32.1	2-DAY	NT	470.0	2.07	1	175.1	4.03	1.32	NT	500.7	1.99	1	154.4	4.22	0.852	481.9	2.06	1	0.794	107.0	3.86	1	1.24	\$74.28		
20121210-B6	J/K2			500	250	169	FULL	TCLP	150 g (30 wt%)			1 HR	NT	507.9	2.06	1	73.9	3.72	29.9	2-DAY	NT	470.0	2.07	1	186.9	4.05	1.36	NT	500.7	1.99	1	163.0	4.15	1.02	484.3	2.08	1	0.822	134.3	3.95	1	1.16	\$74.28		
20121210-B6	L			500	250	169		75 g (15 wt%)	50 g (10 wt%)		1 HR	NT	-237.2	10.43	2	-177.4	5.52	2.40	2-DAY	NT	-309.1	10.42	2	17.3	5.40	7.17	PASS	12.7	10.45	2	-52.8	6.69	13.70	60.8	10.07	2	37.9	-70.1	5.31	2	3.26	\$49.84			
20121210-B6	M			500	250	169		100 g (20 wt%)	50 g (10 wt%)		1 HR	NT	-205.3	8.28	1	-171.9	6.13	1.03	2-DAY	NT	-289.8	9.64	2	33.4	4.98	1.37	NT	12.9	9.82	2	8.6	5.08	1.47	88.3	9.45	2	3.24	-70.7	5.24	2	2.75	\$62.22			
20121210-B6	N			500	250	169		125 g (25 wt%)	50 g (10 wt%)		1 HR	NT	-152.1	5.83	1	-180.3	5.30	0.48	2-DAY	NT	-217.4	8.01	2	55.9	4.68	0.58	NT	79.1	7.83	2	18.0	4.87	0.59	145.4	8.66	1	1.20	-89.1	5.69	1	2.19	\$74.60			
20121210-B6	O			500	250	169		150 g (30 wt%)	50 g (10 wt%)		1 HR	NT	-124.6	4.81	1	-114.2	4.80	0.39	2-DAY	NT	-315.4	6.31	1	24.9	5.19	0.52	NT	93.7	7.16	2	12.7	4.71	0.47	121.5	7.94	1	0.66	-77.7	5.45	1	1.13	\$86.98			
20121211-B6	A	Friday 12/14/12		500	250	169	Suite C	38% FeCl3	PC	ZT Fines	1 HR	NT	-170.2	5.26	1	-257.8	5.77	1.24	2-DAY	NT	19.5	9.29	2	-23.0	5.02	3.08	PASS	-263.3	9.45	2	-249.7	5.23	2.23	-253.6	8.91	2	4.32	48.0	4.89	2	2.81	\$46.66			
20121211-B6	B			500	250	169		75 g (15 wt%)	37.5 g (7.5 wt%)	5g (1 wt%)	1 HR	NT	-316.6	9.52	2	-162.1	4.88	1.28	2-DAY	NT	-227.8	9.53	2	-36.5	5.07	4.29	PASS	-287.3	9.40	2	-251.5	5.23	2.8	-215.8	9.31	2	4.08	64.0	4.70	2	2.85	\$59.66			
20121211-B6	C			500	250	169		75 g (15 wt%)	37.5 g (7.5 wt%)	10 g (2 wt%)	1 HR	NT	-416.8	8.28	1	-195.0	5.80	1.77	2-DAY	NT	19.8	9.24	2	-32.4	5.07	4.99	PASS	-274.4	9.46	2	-252.7	5.27	3.58	-198.3	9.31	2	5.1	67.7	4.71	2	3.13	\$72.66			
20121211-B6	D			500	250	169		100 g (20 wt%)	37.5 g (7.5 wt%)		1 HR	NT	-189.3	4.80	1	-173.3	5.38	0.54	2-DAY	NT	36.1	8.52	2	-12.1	4.76	0.88	NT	-279.9	7.96	2	-236.4	4.87	0.563	-172.6	8.73	2	0.805	28.5	5.45	1	2.05	\$59.04			
20121211-B6	E			500	250	169		100 g (20 wt%)	37.5 g (7.5 wt%)	5g (1 wt%)	1 HR	NT	-299.8	5.43	1	-163.6	5.48	0.70	2-DAY	NT	148.1	7.24	2	-20.3	4.81	0.88	NT	-269.0	8.47	2	-238.4	4.88	0.66	-200.1	8.40	1	1.19	31.4	5.43	1	2.11	\$72.04			
20121211-B6	F			500	250	169		100 g (20 wt%)	37.5 g (7.5 wt%)	10 g (2 wt%)	1 HR	NT	-253.2	5.25	1	-151.1	5.38	0.67	2-DAY	NT	-147.2	8.19	1	-48.2	5.34	0.90	NT	-267.5	8.19	1	-256.1	5.13	0.92	-160.2	8.07	1	1.13	14.5	5.46	1	1.88	\$85.04			
20121211-B6	G		500	250	169		75 g (15 wt%)	37.5 g (7.5 wt%)	25g (5 wt%)	1 HR	NT	-412.2	8.56	1	-273.9	9.19	33.2	2-DAY	PASS	-226.0	9.51	2	-70.5	5.84	3.12	PASS	-242.2	9.51	2	-271.9	6.64	5.99	-182.4	10.11	2	8.26	40.2	5.14	2	2.11	\$76.41				
20121211-B6	H		500	250	169		75 g (15 wt%)	50 g (10 wt%)	25g (5 wt%)	1 HR	NT	-317.0	10.23	2	-161.6	5.68	1.09	2-DAY	PASS	-232.6	10.01	2	-93.5	6.46	7.59	PASS	-248.2	10.13	2	-280.7	8.17	29.0	-1												

Table B-1
Stabilization/Solidation Mix Design Results for B6 Source Materials
Tyco Fire Products, Marinette, WI

TYCO Mix Designs
CH2M HILL

B6
MC=

169%

Total As
TCLP-As

6295 mg/kg
34.6 mg/L

Initial ORP
Initial pH

-309.1
7.92

12097/12099 (75%) plus 12100 (25%)

Treatment	Sample	Launch	Sample	Target	Actual	Suite				1st Cure Period (400 ml)							2nd Cure Period (400 ml)							3-Day							7-Day				28-Day				Reagent Cost (\$/ton)																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																										
			wt	MC	MC		Reagent 1	Reagent 2	Reagent 3	Interval (HR/DAY)	Paint Filter	ORP (mV)	pH (SU)	Fluid (-)	TCLP-ORP (mV)	TCLP-pH (SU)	TCLP-As (mg/L)	Interval (HR/DAY)	Paint Filter	ORP (mV)	pH (SU)	Fluid (-)	TCLP-ORP (mV)	TCLP-pH (SU)	TCLP-As (mg/L)	Paint Filter	ORP (mV)	pH (SU)	Fluid (-)	TCLP-ORP (mV)	TCLP-pH (SU)	TCLP-As (mg/L)	TCLP-ORP (mV)	TCLP-pH (SU)	Fluid (-)	TCLP-As (mg/L)	TCLP-ORP (mV)	TCLP-pH (SU)		Fluid (-)	TCLP-As (mg/L)																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																								
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Master legend precedes Tables B-1 through B-4

Table B-2
Stabilization/Solidification Mix Design Results for B4 Source Materials
Tyco Fire Products, Marinette, WI

TYCO Mix Designs B4 Total As 4198 mg/kg Initial ORP -283.8
CH2M HILL MC= 206% TCLP-As 13.5 mg/L Initial pH 7.45 12087-03 (50%) + 12087-04 (50%)

Treatment	Sample	Launch	Sample			Suite	Target	Actual	1st Cure Period (400 ml)									2nd Cure Period (400 ml)									3-Day						7-Day				28-Day				Reagent Cost (\$/ton)				
			wt	MC	MC				Reagent 1	Reagent 2	Reagent 3	Interval	Paint	ORP	pH	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Interval	Paint	ORP	pH	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Paint	ORP	pH	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP		TCLP-pH	TCLP-As		
ID	ID	DAY	(g)	(%)	(%)	ID			(g)						(HR/DAV)	Filter	(mV)	(SU)	(-)	(mV)	(SU)	(mg/L)	(HR/DAV)	Filter	(mV)	(SU)	(-)	(mV)	(SU)	(mg/L)	Filter	(mV)	(SU)	(-)	(mV)	(SU)	(mg/L)	(-)	(mV)	(SU)	(mg/L)	(-)	(mV)	(SU)	(mg/L)
20121226-B4	A	Wednesday 12/26/12	500	200	206	Suite A	Ferix-3	PC		1-DAY	PASS	16.4	10.35	2	-250.2	7.98	17.3	2-DAY	PASS	-245.7	10.52	2	-351.4	8.32	19.8	PASS	-272.3	10.00	2	-141.3	5.13	2.07	2	10.6	5.02	1.21	2	-89.5	5.39	0.952	\$68.43				
20121226-B4	B		500	200	206		50 g (10 wt%)	50 g (10 wt%)		1-DAY	PASS	9.4	9.40	2	-162.9	6.51	1.38	2-DAY	PASS	-185.5	9.58	2	-203.1	6.42	1.49	PASS	-251.6	8.95	2	Broken			2	25.5	4.76	0.615	2	-64.8	5.10	0.169	\$96.29				
20121226-B4	C		500	200	206		100 g (20 wt%)	50 g (10 wt%)		1-DAY	PASS	86.9	6.97	1	-100.4	5.62	0.341	2-DAY	PASS	-99.0	7.93	1	-146.6	5.64	0.435	PASS	-236.8	8.07	1	-146.9	5.57	0.266	1	-15.2	5.61	0.241	1	-57.5	5.66	0.127	\$124.15				
20121226-B4	D		500	200	206		125 g (25 wt%)	50 g (10 wt%)		1-DAY	PASS	85.6	6.09	1	-122.7	5.47	0.244	2-DAY	PASS	-102.2	7.61	1	-151.5	5.44	0.338	PASS	-241.5	7.83	1	-150.3	5.44	0.271	1	-5.7	5.43	0.242	1	-69.4	5.50	0.181	\$152.02				
20121226-B4	E		500	200	206		150 g (25 wt%)	50 g (10 wt%)		1-DAY	PASS	108.2	5.49	1	-117.2	5.09	0.211	2-DAY	PASS	-164.6	5.85	1	-136.9	5.17	0.203	PASS	-213.7	7.19	1	-142.7	5.19	0.247	1	39.4	5.12	0.191	1	-97.7	5.33	0.092	\$179.88				

Master legend precedes Tables B-1 through B-4

Table B-3
Stabilization/Solidification Mix Design Results for SCM 11LOW Source Materials
Tyco Fire Products, Marinette, WI

TYCO Mix Designs
CH2M HILL

SCM 11-LOW
MC= 24%

Total As 1066 mg/kg
TCLP-As 32 mg/L

Initial ORP -251.4
Initial pH 8.68

12115-02 DM water saturated, sampled thru standing column of site water.

		Sample		Target	Actual	1st Cure Period (400 ml)							2nd Cure Period (400 ml)							3-Day							7-Day				28-Day				Reagent						
Treatment	Sample	Launch	wt	MC	MC	Suite	Reagent 1	Reagent 2	Reagent 3	Interval	Paint	ORP	pH	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Interval	Paint	ORP	pH	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Paint	ORP	pH	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Cost
ID	ID	DAY	(g)	(%)	(%)	ID	(g)	(g)	(g)	(HR/DAY)	Filter	(mV)	(SU)	(-)	(mV)	(SU)	(mg/L)	(HR/DAY)	Filter	(mV)	(SU)	(-)	(mV)	(SU)	(mg/L)	Filter	(mV)	(SU)	(-)	(mV)	(SU)	(mg/L)	(-)	(mV)	(SU)	(mg/L)	(-)	(mV)	(SU)	(mg/L)	(\$/ton)
		Wednesday 12/19/12	Suite A Ferix-3 PC							2-DAY Samples Certified Suite A only																															
20121219-S11	A		500	SAT	24		25g (5 wt%)	25g (5 wt%)		1-HR	PASS	-308.6	10.47	2	-222.9	6.51	3.75	1-DAY	PASS	-185.1	10.64	2	-247.4	6.39	2.65	PASS	-213.6	10.72	2	-104.6	6.60	3.11	2	76.7	6.38	2.54	2	96.7	5.28	1.32	\$34.21
20121219-S11	B		500	SAT	24		50 g (10 wt%)	25g (5 wt%)		1-HR	PASS	-186.9	4.99	1	-245.9	5.91	0.359	1-DAY	PASS	-120.5	8.84	1	-241.6	6.20	0.446	PASS	-201.0	8.61	1	-85.7	6.54	0.543	2	97.4	5.90	0.377	2	106.2	5.15	0.316	\$62.08
20121219-S11	C		500	SAT	24		75 g (15 wt%)	25g (5 wt%)		1-HR	PASS	437.1	2.81	1	-236.1	5.38	0.144	1-DAY	PASS	109.7	5.30	1	-226.6	5.46	0.097	PASS	-161.3	7.20	1	-148.9	5.89	0.154	1	92.5	6.00	0.233	1	77.8	5.66	<0.250	\$89.94
20121219-S11	D		500	SAT	24		100 g (20 wt%)	25g (5 wt%)		1-HR	PASS	477.1	2.61	1	-168.2	5.05	0.512	1-DAY	PASS	398.7	3.03	1	-225.7	5.41	0.087	PASS	-106.4	4.55	1	-43.5	5.40	0.117	1	111.5	5.58	0.166	1	103.1	5.45	<0.250	\$117.80
20121219-S11	E		500	SAT	24		125 g (25 wt%)	25g (5 wt%)		1-HR	PASS	486.9	2.51	1	-198.8	4.57	0.12	1-DAY	PASS	460.8	2.55	1	-217.6	4.92	0.097	PASS	-58.6	4.06	1	-10.7	5.56	0.070	1	95.4	5.45	0.166	1	97.6	5.29	<0.250	\$145.67
20121219-S11	F		500	SAT	24		50 g (10 wt%)	50 g (10 wt%)		1-HR	PASS	-224.1	9.87	2	-242.1	6.54	0.811	1-DAY	PASS	-177.6	9.43	2	-157.7	6.74	1.37	PASS	-199.5	9.86	2	-96.9	6.89	1.47	2	55.5	6.70	1.88	2	61.4	6.09	0.991	\$68.43
20121219-S11	G		500	SAT	24		75 g (15 wt%)	50 g (10 wt%)		1-HR	PASS	-28.7	5.96	1	199.4	6.36	0.359	1-DAY	PASS	-157.1	9.32	2	-231.1	7.17	2.27	PASS	-186.7	6.29	1	-137.7	6.94	0.592	2	83.2	6.16	0.347	2	55.1	5.74	0.318	\$96.29
20121219-S11	H		500	SAT	24		100 g (20 wt%)	50 g (10 wt%)		1-HR	PASS	70.6	4.34	1	-207.1	5.57	0.109	1-DAY	PASS	165.2	7.08	1	-236.5	5.82	0.101	PASS	-297.1	6.16	1	-85.4	6.27	0.123	1	72.3	6.48	0.308	1	75.4	5.84	<0.250	\$124.15
20121219-S11	I		500	SAT	24		125 g (25 wt%)	50 g (10 wt%)		1-HR	PASS	473.8	2.53	1	-221.6	5.12	0.088	1-DAY	PASS	190.6	4.84	1	-237.9	5.39	0.075	PASS	-174.6	5.20	1	-73.3	6.05	0.084	1	83.5	5.89	0.166	1	79.8	5.70	<0.250	\$152.02
20121219-S11	J	500	SAT	24		150 g (30 wt%)	50 g (10 wt%)		1-HR	PASS	489.6	2.47	1	-218.8	5.02	0.085	1-DAY	PASS	386.4	3.11	1	-37.7	5.17	0.068	PASS	-143.6	4.42	1	-140.2	5.88	0.068	1	105.4	5.65	0.127	1	82.5	5.55	<0.250	\$179.88	
		Wednesday 12/26/12	Suite B Ferix-3 PC Na-Bent																																						
20121226-S11	A		500	SAT	24		25g (5 wt%)			1-DAY	PASS	98.3	5.83	1	-127.5	5.61	0.335	2-DAY	PASS	-89.1	6.30	1	-144.6	5.71	0.381	PASS	-93.4	7.32	1	-172.1	5.79	0.304	1	-21.5	5.84	0.406	2	-46.0	5.11	0.484	\$27.86
20121226-S11	B		500	SAT	24		50 g (10 wt%)			1-DAY	NT	407.7	2.82	1	-109.5	5.04	0.271	2-DAY	PASS	145.0	3.60	1	-133.6	5.15	0.228	PASS	-72.9	5.51	1	-159.6	5.28	0.232	1	-1.2	5.62	0.242	1	-122.5	5.76	0.325	\$55.73
20121226-S11	C		500	SAT	24		75 g (15 wt%)			1-DAY	NT	460.5	2.65	1	-97.1	4.79	0.225	2-DAY	PASS	428.7	2.76	1	-123.8	5.00	0.234	PASS	402.5	3.01	1	-123.0	5.04	0.306	1	12.8	5.32	0.248	1	-94.5	5.54	0.314	\$83.59
20121226-S11	D		500	SAT	24		100 g (20 wt%)			1-DAY	NT	477.4	2.58	1	-92.7	4.52	0.171	2-DAY	PASS	468.2	2.62	1	-73.3	4.48	0.194	PASS	460.1	2.72	1	-134.5	4.93	0.218	1	39.1	4.86	0.326	1	-64.2	5.34	<0.250	\$111.45
20121226-S11	E		500	SAT	24		Env 25/75			1-DAY	PASS	254.3	9.01	2	-161.9	6.35	1.15	2-DAY	PASS	219.6	9.28	2	-152.9	6.12	1.03	PASS	-221.0	9.14	2	-154.7	5.21	0.721	2	1.5	5.05	0.828	2	-51.5	5.64	0.831	\$32.50
20121226-S11	F		500	SAT	24		25g (5 wt%)			1-DAY	NT	100.4	9.01	2	-165.5	6.68	0.801	2-DAY	PASS	119.5	9.10	2	-197.3	6.63	0.828	PASS	-234.5	9.31	2	-166.1	5.65	0.382	2	-1.6	5.25	0.410	2	-88.0	5.93	0.472	\$65.00
20121226-S11	G		500	SAT	24		75 g (15 wt%)			1-DAY	NT	104.9	8.84	2	-165.9	6.71	0.502	2-DAY	PASS	135.0	8.82	2	-197.8	6.67	0.491	PASS	-205.4	8.90	2	-163.0	5.50	0.187	2	-2.2	5.37	0.219	2	-70.4	5.72	<0.250	\$97.50
20121226-S11	H		500	SAT	24		100 g (20 wt%)			1-DAY	NT	98.6	5.31	1	-158.4	6.26	0.189	2-DAY	PASS	134.7	6.26	1	-189.2	6.39	0.174	PASS	-231.6	7.66	2	-163.4	5.48	0.155	2	5.1	5.14	0.169	1	-159.6	6.94	0.271	\$130.00
20121226-S11	I		500	SAT	24		25g (5 wt%)	12.5g (2.5 wt%)		1-DAY	NT	103.4	9.07	1	-160.1	6.35	0.917	2-DAY	PASS	130.3	8.23	2	-168.2	5.76	0.513	PASS	-248.7	8.65	2	-170.4	5.96	0.645	2	16.3	4.88	0.767	2	-105.7	5.49	0.820	\$36.25
20121226-S11	J	500	SAT	24		50 g (10 wt%)	12.5g (2.5 wt%)		1-DAY	NT	114.6	7.78	2	-149.8	6.00	0.293	2-DAY	PASS	131.1	7.86	1	-176.3	6.36	0.356	PASS	-211.2	8.32	1	-172.3	6.93	0.411	2	13.3	5.05	0.365	2	-89.3	5.42	0.316	\$68.75	
20121226-S11	K	500	SAT	24		75 g (15 wt%)	12.5g (2.5 wt%)		1-DAY	NT	105.9	6.31	1	-156.9	6.31	0.241	2-DAY	PASS	135.3	7.48	1	-175.7	6.31	0.204	PASS	-208.0	6.55	2	-151.9	5.32	0.204	2	13.4	5.08	0.220	2	-51.0	5.34	<0.250	\$101.25	
20121226-S11	L	500	SAT	24		100 g (20 wt%)	12.5g (2.5 wt%)		1-DAY	NT	100.5	5.77	1	-158.2	6.28	0.161	2-DAY	PASS	139.1	7.27	2	-173.6	6.00	0.116	PASS	-215.0	6.48	2	-154.8	5.24	0.178	2	12.3	4.99	0.208	2	-57.4	5.48	<0.250	\$133.75	
		Tues. 1/8/13	60% Fe2(SO4)3																																						
20121226-S11	M		500	SAT	24		25g (5 wt%)	12.5g (2.5 wt%)		1-DAY	NT	82.4	9.95	1	-166.8	6.65	2.83	2-DAY	PASS	123.8	10.22	2	-173.6	6.27	2.11	PASS	-234.9	9.87	2	-141.5	5.13	1.11	1	-34.5	6.42	2.59	2	-90.2	5.45	2.21	\$16.40
20121226-S11	N		500	SAT	24		50 g (10 wt%)	12.5g (2.5 wt%)		1-DAY	NT	99.9	6.59	1	-146.1	6.13	0.388	2-DAY	PASS	135.0	7.38	1	-161.6	6.16	0.415	PASS	-204.7	8.25	1	-164.2	6.26	0.516	1	-26.6	6.17	0.605	1	-79.0	6.22	0.616	\$29.62
20121226-S11	O	500	SAT	24		75 g (15 wt%)	12.5g (2.5 wt%)		1-DAY	NT	101.6	5.58	1	-136.6	5.70	0.212	2-DAY	PASS	137.1	6.98	1	-155.6	5.95	0.277	PASS	-214.3	7.82	1	-159.0	6.18	0.290	1	-13.3	5.81	0.249	1	-97.9	5.92	0.341	\$42.85	
		Tues. 1/8/13	Suite C Ferix-3 PC Ca-Bent																																						
20130108-S11	A		500	SAT	24		25g (5 wt%)	12.5g (2.5 wt%)		1-HR	NT	-123.9	7.20	1	-1.7	5.77	1.4	1-DAY	PASS	-100.3	9.12	1	-323.2	5.78	1.76	PASS	-210.4	9.13	2	-245.0	4.90	1.56	1	-133.2	6.16	2.26	2	-58.1	5.05	1.36	\$31.04
20130108-S11	B	500	SAT	24		25g (5 wt%)		12.5g (2.5 wt%)		1-HR	NT	-7.7	4.43	1	22.7	5.28	0.461	1-DAY	PASS	28.9	5.41	1	-312.4	5.40	0.43	PASS	-178.4	7.63	1	-269.6	5.67	0.468	1	-128.6	5.66	0.700	1	-102	5.77	0.652	\$31.61
		Thurs. 1/17/2013	Suite D Ferix-3							Sample period skipped																															
20130117-S11	A		500	SAT	24		12.5g (2.5wt%)			1-DAY	NT	53.9	7.66	2	107.3	4.69	2.01								PASS	7.															

Table B-4
Stabilization/Solidification Mix Design Results for SCM 10 Source Materials
Tyco Fire Products, Marinette, WI

TYCO Mix Designs SCM 10 Total As 884 mg/kg Initial ORP -243.7
CH2M HILL MC= 81% TCLP-As 2.04 mg/L Initial pH 7.98

12114-02

Treatment	Sample	Launch	Sample	Target	Actual	Suite				1st Cure Period (400 ml)								2nd Cure Period (400 ml)								3-Day							7-Day				28-Day				Reagent Cost																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
			wt	MC	MC		Reagent 1	Reagent 2	Reagent 3	Interval	Paint	ORP	pH	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Interval	Paint	ORP	pH	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Paint	ORP	pH	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As		Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH	TCLP-As	Fluid	TCLP-ORP	TCLP-pH

Master legend precedes Tables B-1 through B-4

Attachment 3
White Papers

Rapid Assessment of Total Arsenic in Tyco Fire Products LP (Marinette, Wisconsin Project) Dredged Material Using Portable XRF Device

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Dennis Grubb/CH2M HILL

DATE: February 1, 2013

In fall 2012, CH2M HILL internally funded a series of *Technology Innovation Grants* that were focused on technology development, groundbreaking ideas, and research and development that would aid CH2M HILL in better serving its clients. A team led by Dr. Dennis Grubb was awarded an Innovation Grant related to rapid field characterization techniques to support field project processing operations. This technical memorandum is the project deliverable for the Innovation Grant.

This innovation grant focused on the use of a portable X-ray fluorescence (XRF) device to accurately and rapidly measure the total arsenic content (milligram per kilogram [mg/kg] basis) in wet dredged material (DM) collected from the Tyco Fire Products LP (Tyco) Sediment Removal Project in Marinette, Wisconsin, and evaluated by the CH2M HILL Applied Sciences Laboratory in Corvallis, Oregon. The primary objective of the study was to develop a rapid assessment tool to directly measure the total arsenic content of the wet DM without the drying typically required when measuring total metals content by U.S. Environmental Protection Agency (USEPA) Method 6200. The main concern was that XRF approaches are prone to signal interference when analyzing high moisture content samples, so a comparison was made between the accuracy of the XRF versus ICP-OES (USEPA Method 6010) to determine the level of sample preparation required for the XRF results to be accurate. Samples were shipped to the laboratory in mid-December 2012, and focused XRF testing was performed the week of January 7, 2013.

Tyco DM Source Materials

Two main types of DM have been identified at the project site. The soft, fresh DM that is primarily comprised of fine-grained material and organic matter (taken from three different locations and denoted as Surrogates B6, B4, and S2/7) typically has the highest total and TCLP arsenic content, up to 7,000 mg/kg and up to 40 milligrams per liter (mg/L), respectively. The semi-consolidated material (SCM series or Surrogates SCM11LOW, SCM10), are more silty-sandy materials having moderate total arsenic contents (up to 2,000 mg/kg), but elevated leaching (up to TCLP arsenic 30 mg/L). These materials were selected to evaluate the ability of the XRF to accommodate high variability in terms of soil type and total arsenic of the DM characteristic of the project site. Table 1 summarizes the basic soil indices and environmental quality of the DM source materials used in this study.

TABLE 1
Summary of DM Source Material Soil Indices

Media	Moisture Content [SM 2540B] %	L.O.I. [ASTM D2974] (550°C) %	USCS Description [ASTM D2487]	Gradation [ASTM D422] weight %					Atterberg Limits [ASTM D4318]		
				Gravel	Sand			Silt/ Clay	LL	PL	PI
					Coarse	Med.	Fine				
B6	169	15.4	Silty sand (SM)	0.00	0.00	1.41	69.6	28.5	95	52	43
B4	206	18.9	Silty sand (SM)	0.00	0.06	0.79	57.7	40.8	114	68	47
S 2/7	252	14.9	Silty sand (SM)	0.00	0.16	0.54	61.6	36.5	125	86	39
SCM 11 LOW	24.0	2.13	Well-graded sand with silt (SW-SM)*	5.58	5.53	42.2	40.0	5.93	ND	ND	NP
SCM 10	81.0	8.64	Poorly-graded sand (SP)	11.4	12.8	42.1	30.2	2.99	ND	ND	NP

Moisture Content and L.O.I. presented on a dry soil (105°C) basis. NP = Non-Plastic

* Silt/clay determination estimated by Practice D2488. ND = Limits could not be determined due to non-plastic sample properties

XRF Testing Method

Each DM sample with varying moisture content was analyzed for total arsenic on an as-received basis and an oven-dried basis using the XRF device.

A Thermo Fisher Niton XRF Model XL3t 600 positioned in its test stand was used for testing (Figures A-1 and A-2). Each as-received DM was homogenized with a wood spatula, then placed in a sample cup with a Mylar film cover (Premier Lab Supply). The sample cups were partially filled, as shown on Figure A-3. For analysis, each replicate was sequentially placed on the XRF test stand, and the total arsenic content was measured in the *soils* mode with the sample time integrated over 30 seconds. The first five DM source materials identified in Table B-1 were analyzed by XRF using five replicates (1 through 5) at their as-received moisture content. The second set of five DM source materials from Table B-1 (SB-1 to SB-5) were blends of the original DM materials, and only one replicate of each was analyzed by XRF.

The same 10 DM samples were dried at 105 degrees Celsius for 2.5 hours, then ground using a mortar and pestle following typical standard XRF sample preparation methods. The dried sample then was placed in the sample cup and analyzed in the same manner as the as-received material.

Results

Two sets of experiments were conducted and are summarized in the attached tables. The first series of experiments involved total arsenic content determinations of the wet DM source materials. The second series of tests were identical, but using oven-dried DM source materials to gauge the effect of moisture content on the portable XRF device.

Table B-1 summarizes the comparison of the XRF and ICP-OES total arsenic measurements performed on the as-received (wet) DM samples, on a dry weight basis. Each DM source material was analyzed based on five replicates (1 through 5), and the average and standard deviation of the measured arsenic contents were reported. The moisture contents measured as part of USEPA Method SM 2540B during the ICP-OES testing suite were used to convert both data sets to a dry total arsenic basis. The results are plotted on Figure 1 with a linear curve fit to the raw data as well as a 1:1 correlation (dashed line) shown for visual comparison purposes. The R^2 value

(0.9966) indicates a strong correlation between the rapid XRF method and USEPA Method 6010 total arsenic measurements with an average negative bias of 11 percent.

Table B-2 shows the XRF total measurements performed on oven-dried samples are consistently higher than the wet XRF measurements. An R^2 value of 0.9912 was obtained (average positive bias of 6 percent), which again suggests a strong correlation between the standard XRF method (which includes sample preparation) and USEPA Method 6010 total arsenic measurements. Figure 2 plots both the wet and dry DM sample XRF measurements versus the arsenic totals content determined by USEPA Method 6010.

Figure 2 conveys two main points. First, there is a high correlation between wet and/or dry XRF measurements and those analyzed by USEPA Method 6010. Second, since the bias is consistent, there is no significant value in drying materials or additional sample preparation before XRF analysis. This will enable rapid total arsenic content determination (approximately 2 minutes) once the calibration curve is determined for the suite of solids at the project site. Review of the testing data shown in Table B-1 suggests finer DM will be associated with a more negative bias under wet and dry conditions, whereas the coarser DM (10, 11, SB series) exhibit positive bias under dried conditions.

Use of portable XRF devices to rapidly assess the total arsenic content of the DM can be accomplished accurately, rapidly, and potentially much more cost effectively than ICP-OES. In this regard, the XRF approach can serve as a strong complement to the rapid TCLP assessment tool developed for the same site and conditions. However, the wet XRF sample must be well homogenized and free of large debris such as rocks or twigs. It also is recommended that split samples be analyzed by USEPA Method 6010 (or the equivalent) at prescribed intervals during field operations to identify potential equipment drift, systematic errors, changes in the XRF/ICP correlation because of significant differences in DM characteristics, etc.

FIGURE 1

Total Arsenic Correlation of Wet, as-received DM Analyzed by XRF and ICP-OES

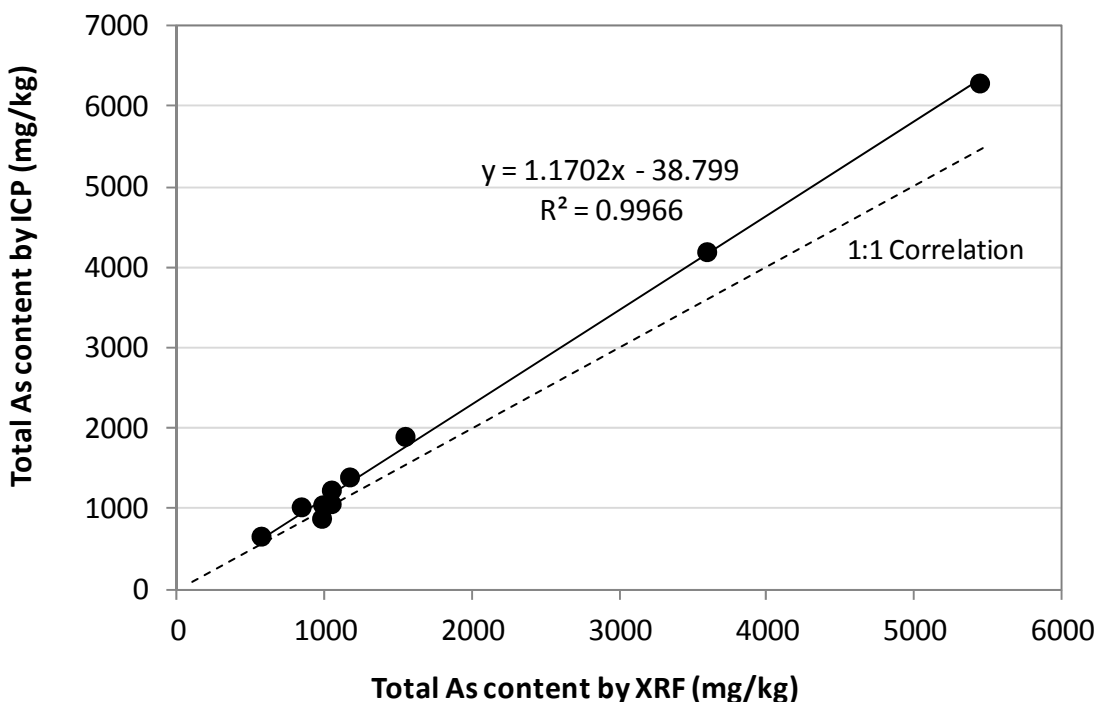
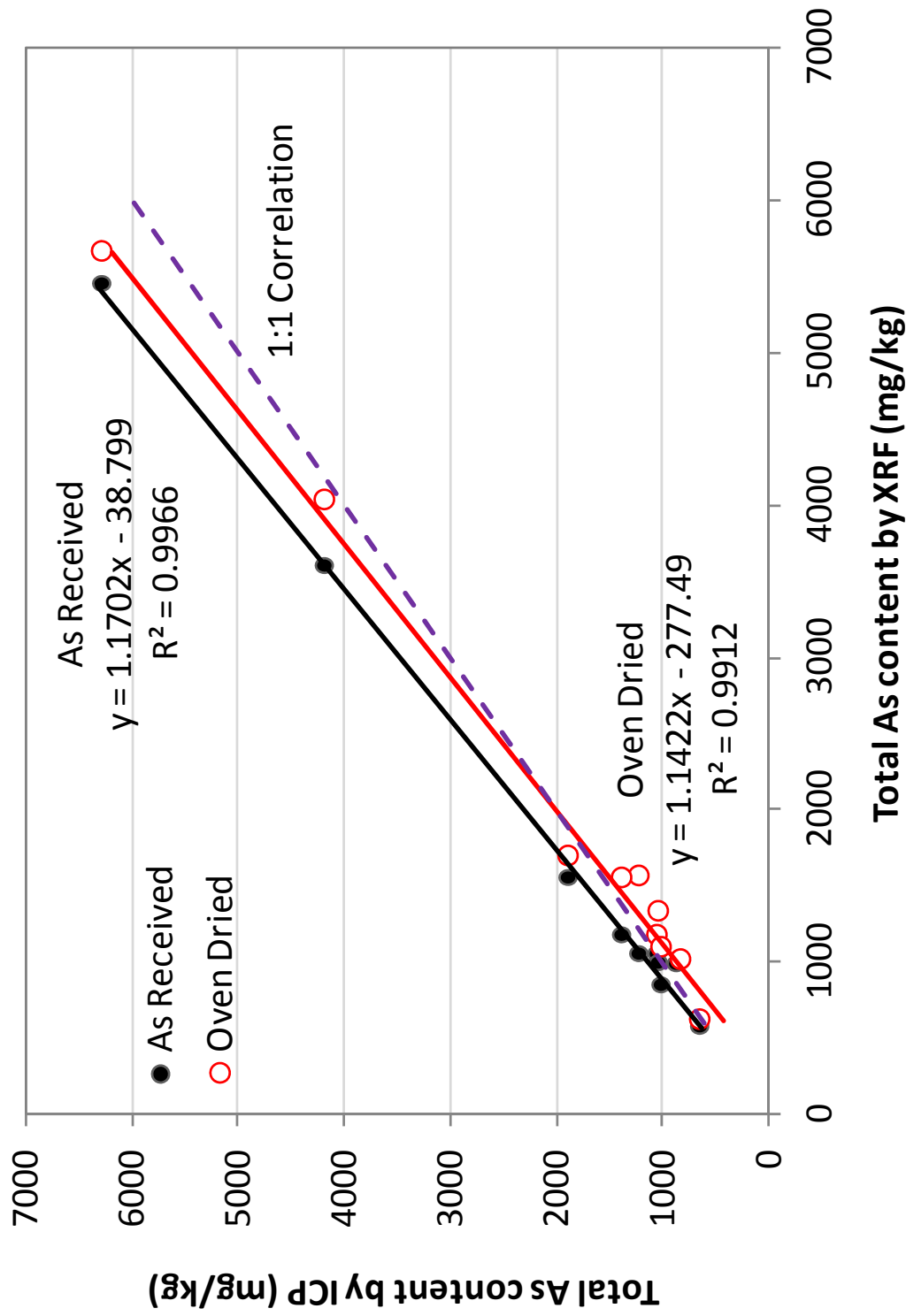


FIGURE 2
Total Arsenic Correlation of As-Received and Oven-Dried DM by XRF and ICP-OES



Attachment A

FIGURE A-1
Thermo Fisher Niton X-Ray Fluorescence
Model XL3t 600



FIGURE A-2
XRF in Table Stand



FIGURE A-3
XRF Sample Preparation



Attachment B

Table B-1

XRF Analysis of as received Sample - Total As (mg/kg)

DM	Wet Weight Basis						Std. Dev.	% RSD	% Moisture	As (mg/kg) Dry Weight Basis
	1	2	3	4	5	Average				
B6	1950	1926	1966	1998	2274	2023	143	7%	169%	5441
B4	1205	1136	1203	1179	1143	1173	33	3%	206%	3590
S2/7	156	162	168	149	168	161	8	5%	252%	565
S11	816	832	816	837	899	840	34	4%	24%	1042
S10	456	572	539	565	565	539	48	9%	81%	976
SB-1	527					527	NA		59%	838
SB-2	600					600	NA		64%	984
SB-3	686					686	NA		52%	1043
SB-4	617					617	NA		89%	1166
SB-5	738					738	NA		109%	1542

ICP-OES Total As (mg/kg)

DM	Wet Weight Basis						Std. Dev.	% RSD	% Moisture	As (mg/kg) Dry Weight Basis
	1	2	3	4	5	Average				
B6	2330	2270	2650	2260	2190	2340	180	8%	169%	6295
B4	1440	1470	1370	1270	1310	1372	84	6%	206%	4198
S 2/7	187	190	174	196	195	188	9	5%	252%	663
S 11	915	858	829	850	848	860	33	4%	24%	1066
S 10	578	401	488	437	539	489	72	15%	81%	884
SB-1	643	700	621	619	647	646	33	5%	59%	1027
SB-2	648	658	661	610	635	642	21	3%	64%	1054
SB-3	877	815	786	753	836	813	47	6%	52%	1236
SB-4	761	712	712	750	765	740	26	4%	89%	1399
SB-5	885	920	910	940	898	911	21	2%	109%	1903

Percent Difference on as received sample for Arsenic between XRF and ICP-OES

DM	Wet weight Basis (mg/kg)			Dry weight Basis (mg/kg)		
	XRF	ICP	%D	XRF	ICP	%D
B6	2023	2340	-14%	5441	6295	-14%
B4	1173	1372	-14%	3590	4198	-14%
S2/7	161	188	-15%	565	663	-15%
S11	840	860	-2%	1042	1066	-2%
S10	539	489	10%	976	884	10%
SB-1	527	646	-18%	838	1027	-18%
SB-2	600	642	-7%	984	1054	-7%
SB-3	686	813	-16%	1043	1236	-16%
SB-4	617	740	-17%	1166	1399	-17%
SB-5	738	911	-19%	1542	1903	-19%
Average						-11%

Table B-2

Percent Difference on oven dried sample of Arsenic between XRF and ICP (mg/kg)

DM	XRF * Single Reading	ICP (Dry Weight basis) Average of 5 readings	%D
B6	5655	6295	-10%
B4	4024	4198	-4%
S2/7	613	663	-8%
S11	1167	1066	9%
S10	1007	844	19%
SB-1	1088	1027	6%
SB-2	1324	1054	26%
SB-3	1556	1236	26%
SB-4	1543	1399	10%
SB-5	1687	1903	-11%
Average			6%

* Samples Dried at 105C for 2.5 hours, then ground

2013 Tyco Dredged Material Rapid TCLP Study Report

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Jeff Danko/CH2M HILL
PREPARED BY: Dennis Grubb/CH2M HILL
Dusty Berggren/CH2M HILL
DATE: February 1, 2013
PROJECT NUMBER: 464642

During December 2012 to January 2013, the CH2MHILL Applied Sciences Laboratory in Corvallis, Oregon, performed an assessment to determine if short duration and reduced volume toxicity characteristic leaching procedure (TCLP) testing on dredged material (DM) from the Tyco Fire Products LP (Tyco) facility in Marinette, Wisconsin, could be used in a screening mode to conservatively estimate the full volume and duration TCLP testing result of the fresh DM at the site according to U.S. Environmental Protection Agency (USEPA) Method 1311 (without deviation). This technical memorandum reports on the rapid TCLP assessment that was performed as part of the Tyco winter 2012 DM treatability study scope of work.

The main objective was to develop a rapid assessment tool to determine the environmental quality of incoming DM in an effort to optimize the overall reagent dose, based on knowledge of the TCLP arsenic (this report) and/or total arsenic concentrations (see X-ray fluorescence [XRF] report). In addition to the raw materials testing results and the associated discussion, CH2M HILL has prepared a recommended guidance on how to potentially use the rapid TCLP assessment technique in the field (e.g., mobile laboratory). Accordingly, the CH2M HILL technical memorandum regarding the rapid XRF assessment of DM also should be reviewed to fully understand real time decision-making tools available for determining reagent dosing.

Tyco Dredge Material Source Material Characterization

This work was conducted in two phases. Phase 1 used six representative samples of DM source materials (B6, B4, S2/7, SCM11LOW, and SCM10) where the soft DM material is primarily comprised of fine-grained material and organic matter (e.g., B6, B4, and S 2/7), and the SCM denotes the semi-consolidated materials (SCM 11LOW; SCM10), which is silty/sandy sediment found below the soft DM sediment that is highly impacted by arsenic. The use of these DM samples is consistent with the sediment testing and mix design work conducted by Waste Stream Technology (a wholly owned subsidiary of Severson) in fall 2012, as well as the ongoing winter 2012/2013 mix design work conducted by CH2M HILL.

For characterization purposes, moisture content determinations were made in accordance with ASTM D2216 on the homogenized, blended DM source materials. The pH and oxidation-reduction potential (ORP) determinations were made in conjunction with TCLP fluid determination step in accordance with USEPA Method 1311 (20:1 liquid to solid ratio). Total arsenic determinations (milligrams per kilogram [mg/kg]) made on five replicates (R1 to R5) of the homogenized DM source materials were completed in accordance with USEPA Method 6010B and are summarized in Table 1. The raw data are contained in Attachment A.

Phase 2 involved blending of select DM samples (from Table 1) in an attempt to simulate DM having TCLP arsenic values in the range of 2 to 20 milligrams per liter (mg/L) to assess the accuracy, sensitivity, and usefulness of the rapid TCLP method in close proximity to the USEPA TCLP arsenic criterion of 5 mg/L. Table 2 summarizes the total arsenic determinations made on five replicates of the Phase 2 DM blends.

TABLE 1

Total Arsenic Summary of Dredged Material Source Material Samples from the Tyco Marinette Facility

Media	MC	pH	ORP	Total As (mg/kg, dry)							TCLP-As
	(%)	SU	mV	R 1	R 2	R 3	R 4	R 5	Average	Std Dev.	mg/L
B6	169%	7.92	-309.1	6,268	6,106	7,129	6,079	5,891	6,295	458	39.3
B4	206%	7.45	-283.8	4,406	4,498	4,192	3,886	4,009	4,198	258	13.5
S2/7	252%	7.50	-308.2	658	669	612	690	686	663	31	0.952
SCM11LOW	24%	8.68	-251.4	1,135	1,064	1,028	1,054	1,052	1,066	40	32
SCM 10	81%	7.98	-243.7	1,046	726	883	791	976	884	131	2.04

As - arsenic

TABLE 2

Total Arsenic Summary of Blend Dredged Material Source Material Samples

Media	Blend Ratio (%)			MC	pH	ORP	Total As (mg/kg, dry)		TCLP-As
	B4	SCM11LOW	SCM10	(%)	SU	mV	Average	Std Dev.	mg/L
SCMB1	-	12.5	87.5	59	6.97	42.3	1,029	52	2.89
SCMB2	-	25	75	64	7.89	-33.7	1,054	34	4.37
SCMB3	-	50	50	52	8.23	-109.5	1,235	72	9.92
SCMB4	12.5	-	87.5	89	7.95	-116.1	1,401	50	2.67
SCMB5	25	-	75	109	7.81	-103.7	1,907	44	2.66

As - arsenic

Rapid TCLP Testing Program

Three different approaches to TCLP testing were evaluated as part of this scope of work. Each testing suite was evaluated for the following time intervals: 0.5, 1, 2, 3, and 18 hours. One full TCLP was performed for each time interval and DM source material. The mini-TCLPs were conducted using four replicates and sample splits to evaluate variability. A standard operating protocol (SOP) for this testing program is included as Attachment B.

The three TCLP testing suites were:

- **Full TCLP, Digestion:** TCLP extraction (e.g., standard procedure, full volume and solids [2 liters; 100 g]) in accordance with USEPA Method 1311. Approach includes both filtering and standard digestion (with heating). Required timing: Add 3 hours to the extraction interval to reach the inductively couple plasma (ICP) analysis and 10 minutes for each replicate to obtain the ICP result.
- **Mini TCLP, Digestion:** Smaller TCLP extraction (e.g., standard procedure, reduced volume and solids [400 milliliters {mL}; 20 g]) in accordance with USEPA Method 1311. Approach includes both filtering and standard digestion (with heating). Required timing: Add 3 hours to the extraction interval to reach ICP analysis and 10 minutes for each replicate to obtain ICP result.
- **Mini TCLP, Screening:** Smaller TCLP extractions (e.g., standard procedure, reduced volume and solids [400 mL; 20 g]) in accordance with USEPA Method 1311. Approach includes filtering and acidification, not digestion. Required timing: Add 1 hour (maximum) to the extraction interval to reach ICP analysis and 10 minutes for each replicate to obtain ICP result.

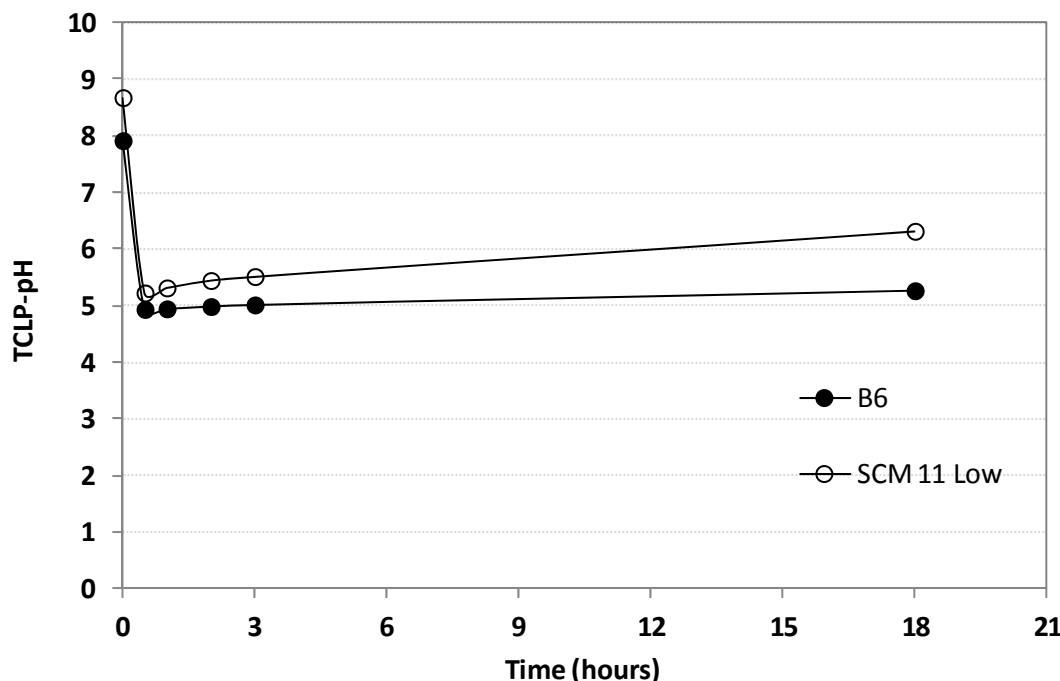
Rapid TCLP Testing Results

Phase 1

The rapid TCLP testing results for the soft fresh DM (samples B6, B4, and S2/7) are summarized on Figures A-1 to A-3. The supporting data tables (as well as the figures) indicate the standard deviation on replicates is small, so the testing protocol is repeatable. The general trend is that all TCLP values decrease with time, and for highly contaminated soft DM (B6, B4), the biggest change in TCLP arsenic concentrations appears to occur within a 3-hour equilibration time. This behavior is consistent with the pH response of poorly buffered soils and soil-like media, as shown on Figure 1. Such rapid changes in pH allow for the use of shorter test duration as pH strongly influences the solubility and adsorption behavior of many metals and metalloids, including arsenic.

FIGURE 1

Evolution of TCLP-pH During TCLP Extraction of Dredge Material Source Materials



In each case, for a wide range in total arsenic contents and TCLP arsenic values (Table 1), Figures A-1 to A-3 support the interpretation that the 3-hour mini-TCLP screening values are approximately equal to (typically within 2 mg/L) the 18-hour full TCLP value (Figures A-1,-2), or are conservative compared to the TCLP arsenic criterion of 5 mg/L (Figure A-3). In highly contaminated soft fresh DM (B6, B4), the 3-hour mini screening and 18-hour full digested TCLP values are so remote from the TCLP arsenic criterion that the minor differences in their values will not alter the decision to apply S/S reagents. For compliant (TCLP arsenic less than 5 mg/L) soft fresh DM, the 18-hour full TCLP value is less than the 3-hour mini-TCLP screening value, and the trend is decreasing (Figure A-3). The same mini/full TCLP trends are observed with SCM, as shown on Figures A-4 to A-5, for highly contaminated and TCLP arsenic compliant SCM source materials.

Phase 2

In Phase 2, additional data were plotted for the testing suite that included a full TCLP in screening mode. Identical to the mini-TCLP screening samples, but using the sample size specified by USEPA Method 1311, it was acidified and directly analyzed by ICP without heating.

SCM Blends 1 through 3 were prepared using various ratios of the SCM11LOW and SCM10 DM source materials shown in Table 1. The results are shown on Figures A-6 to A-8, and the TCLP arsenic range is much closer to the TCLP arsenic criterion of 5 mg/L. In each case, the 3-hour mini-TCLP screening values are typically 2 to 4 mg/L

greater than the 18-hour full TCLP value, allowing them to be used as a conservative (maximum) pre-screening tool for in field determinations.

SCM Blends 4 and 5 were prepared using various ratios of the SCM10 DM and B4 source materials shown in Table 1. The reason for selecting B4 over B6 for blending was driven by the goal to achieve borderline TCLP values compared to the 5 mg/L criterion for the soft DM/SCM interface, with the recognition that if the overlying soft DM was highly contaminated, SCM at the interface likely would resemble SCM11LOW, which would fail the TCLP (less than 5 mg/L). It was believed that the B4/SCM10 combination might better simulate more mildly contaminated DM conditions away from the hotspots. This could be determined spatially based on the prior site delineation work and the global positioning system location of the dredging horizon during barge filling operations.

The results are shown on Figures A-9 and A-10 for total arsenic contents in the range of 1,400 to 1,900 mg/kg, which is somewhat above the expected range for SCM alone (Figure A-4 and A-5). The higher total arsenic contents are attributable to the inclusion of up to 25 percent soft DM B4. Such conditions might occur in the vicinity of the soft DM/SCM interface during dredging.

On Figures A-1 through A-8, there appears to be a tighter clustering of the suite of TCLP curves than those observed on Figures A-9 and A-10, especially at the 3-hour interval. Here, the spread in the results appears to be on the order of 10 percent of the average 0.5-hour value. On Figures A-9 and A-10, the offset of the full digested TCLP results from the mini screening values is almost 100 percent (up to 3 mg/L TCLP arsenic), suggesting the difference in behavior is related to the sample volume, not the digestion process. This offset creates a condition where using either 3-hour mini-TCLP test results may not present a conservative estimate of the 18-hour full TCLP value (Figure A-10). This difference only takes on real significance from a DM processing and treatment perspective when the TCLP values are borderline compliant. In such instances, the 3-hour full volume test value remains conservative. Thus, if it is relatively clear that one is dealing with a soft DM/SCM sample, it seems prudent to run both a 3-hour mini and full volume TCLP sample in screening mode (no digestion) to bracket the magnitude of the 18-hour full TCLP value.

Rapid TCLP Testing Summary

This summary is based on the blends tested as part of this scope; live updating should be implemented during field operations. TCLP arsenic values tend to decrease with time, with typical differences between the 3-hour mini-TCLP screening and 18-hour full TCLP values being on the order of 2 to 3 mg/L, but less than 5 mg/L, even for the highly contaminated arsenic scenarios. This makes the 3-hour mini-TCLP value a good candidate method for implementation and rapid decision making for DM at the site. Moreover, testing can be initiated and completed in approximately 4 hours before it is unloaded.

As the TCLP arsenic criterion of 5 mg/L is approached, the 3-hour mini TCLP value ranges between approximately 1 mg/L less than, and up to 3 mg/L greater than, the 18-hour full TCLP value. Blends containing soft DM/SCM seem to be linked to the occasions where the 3-hour mini-TCLP screening value is not a conservative estimate of the 18-hour full TCLP value (i.e., when its value is less than that of the 18-hour full TCLP). These mixtures would be potentially encountered when the soft DM/SCM interface is removed during dredging operations.

As this seems to be the only scenario where the 3-hour mini-TCLP screening value is not a conservative estimate of the 18-hour full TCLP value, resolving this issue only takes on meaningful significance when the TCLP value is borderline compliant (4 to 5 mg/L). There are three ways to check if soft DM/SCM mixing may be affecting the 3-hour mini-TCLP screening value: knowledge of the dredging horizon, physical inspection of the samples (fines vs. silty sandy), and from rapid total arsenic content tests performed on the same DM sample (total arsenic greater than approximately 1,300 mg/kg suggests the presence of soft DM).

Should a mixture of soft DM/SCM be likely or actually encountered, the use of 3-hour full volume TCLPs in a screening mode appears both appropriate and conservative for decision making. These substituted or duplicate tests should only be run on an as-needed basis, since the disadvantage of performing full volume TCLPs decrease the availability of TCLP rotator positions (4 minis = 1 full volume).

Based on this scope of work and the results presented herein, consideration of the following implementation approach is recommended:

- Collect up to 10 representative samples of DM during the barge filling operation using 1 gallon pails or the equivalent. Homogenize each pail before performing rapid TCLP (or XRF) testing in an onsite laboratory.
- Physically inspect samples to ascertain and report the likely source of DM (soft DM and/or SCM). Measure and report moisture content, pH, and ORP for each replicate.
- Perform up to ten 3-hour mini-TCLP screening tests on DM per barge according to the attached SOP. If it appears soft DM/SCM is mixed, consider performing one or two 3-hour full volume TCLP extractions in screening mode. Report individual results and barge statistics. If results are highly variable, consider effects of homogenization implied by DM processing equipment (rapid TCLP approach can be used to assess this too; or will be self-evident based on bin certification tests).
- Implement treatment recommendations based on joint consideration of rapid TCLP and rapid XRF testing results with DM processing related information and experience. Where the rapid TCLP results are concerned, the following criteria are appropriate based on the 3-hour mini-TCLP screening results:
 - TCLP arsenic greater than 7.5 mg/L. S/S treatment required, consult individual mix design results for soft DM and SCM, as it will not likely become compliant.
 - TCLP arsenic greater than 5 mg/L but less than 7.5 mg/L. S/S treatment decision by field project manager. Consider no treatment or low dosing schemes outlined by individual mix design results for soft DM and SCM.
 - TCLP arsenic less than 5 mg/L. No chemical treatment, solidification (drying) only to the pass paint filter test.

The prior delineation of arsenic contamination in sediment, while well documented and useful, has not translated to the ability to accurately predict the characteristics of DM when it arrives dockside for unloading and subsequent treating. These rapid TCLP testing results indicate the 3-hour mini-TCLP screening approach can provide a perspective on the quality of DM of incoming barges. Coupled with the rapid XRF testing results and the tiered mix design results for different characteristic DM source materials, there is a tangible opportunity to optimize reagent dosing by DM type, including the potential for no treatment whatsoever.

The approach will not be foolproof, and failures should be expected because of DM variability and homogeneity issues alone. However, the rapid TCLP approach has emerged as one of the most facile and direct rationale tools for assessing the arsenic leachability of DM at the site over a broad range of conditions. Accordingly, it should be strongly considered as a key component of a site management strategy for limiting the otherwise routine application of large reagent doses.

The decision criteria proposed above will likely be adjusted based on additional discussions with Tyco and Severson that may consider other factors such as maximizing throughput balanced against the need for reagents, contingency approaches for reprocessing, etc.