FINAL

Work Plan for a Pilot Study and Feasibility Study at RVAAP-50 Atlas Scrap Yard

Camp Ravenna
Ravenna, Ohio

19 February 2016

Contract No. W912QR-14-D-0001
Delivery Order No. 0004

Prepared for:

US Army Corps of Engineers
Louisville District
600 Martin Luther King Jr. Place
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14. ABSTRACT

This Work Plan presents the field activities, and procedures to be implemented during field operations for a Pilot Study and Feasibility Study (FS) at the Atlas Scrap Yard area of concern (AOC) [Ravenna Army Ammunition Plant (RVAAP)-50]. This Work Plan details the field activities and procedures to be followed, and includes the Quality Assurance Project Plan, and the Site Safety and Health Plan for this pilot test, and FS.

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Work Plan, Site Safety and Health Plan, Quality Assurance Project Plan, Pilot Study, field activities and procedures.

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CONTRACTOR STATEMENT OF INDEPENDENT TECHNICAL REVIEW
COMPLETION OF INDEPENDENT TECHNICAL REVIEW

Alliant has completed the Work Plan – FINAL for a Pilot Study and Feasibility Study (FS) for impacted soils at the Atlas Scrap Yard area of concern (AOC) [former Ravenna Army Ammunition Plant (RVAAP)-50] at Camp Ravenna, Portage and Trumbull Counties, Ohio. Notice is hereby given that an independent technical review that is appropriate to the level of risk and complexity inherent in the project, has been conducted. During the independent technical review, compliance with established policy principles and procedures, utilizing justified and valid assumptions was verified. This included review of assumptions; methods, procedures, and material used in the analyses; alternatives evaluated; the appropriateness of data used and level obtained; and reasonableness of the results, including whether the deliverable meets the customer's needs consistent with law and existing Corps policy. Any comments resulting from the independent technical review have been resolved.

2/19/2016

Mark Maki, P.G. Alliant Corporation
Independent Technical Review Team Leader

CERTIFICATION OF INDEPENDENT TECHNICAL REVIEW

All Concerns resulting from independent technical review of the deliverable have been fully resolved.

Belinda Price

19-FEB 2016

Belinda Price, P.G., Alliant Corporation
Project Manager

Ohio
Ohio Environmental
Protection Agency

John R. Kasich, Governor
Mary Taylor, Lt. Governor
Craig W. Butler, Director

March 3, 2016

Mr. Mark Leeper
Army National Guard Directorate
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111 South George Mason Drive
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Re: US Army Ammunition PLT RVAAP
Remediation Response
Project Records
Remedial Response
Portage County
267000859106

Subject: Ravenna Army Ammunition Plant, Portage/Trumbull Counties. Final, Work Plan for a Pilot Study and Feasibility Study at RVAAP-50 Atlas Scrap Yard at the Ravenna Army Ammunition Plant, Ravenna, Ohio, Dated February 19, 2016

Dear Mr. Leeper:

The Ohio Environmental Protection Agency (Ohio EPA) has received and reviewed the "Final, Work Plan for a Pilot Study and Feasibility Study at RVAAP-50 Atlas Scrap Yard" at the Ravenna Army Ammunition Plant (RVAAP), Ravenna, Ohio, dated February 19, 2016 and received at Ohio EPA's Northeast District Office (NEDO), Division of Environmental Response and Revitalization (DERR) on February 23, 2016. The work plan was prepared for the US Army Corps of Engineers (USACE) Louisville District by Alliant Corporation under Contract Number W912QR-14-D-0001. The work plan has been reviewed by various personnel at Ohio EPA.

The Work Plan is approved.

Related to this Work Plan and the Vapor Energy Generation (VEG) project, Ohio EPA received the Draft of the second part of the VEG study regarding the lead immobilization bench test study via email on February 17, 2016. In summary, due to the organic content of the soils at the Atlas Scrap Yard, the lead immobilization will not be as effective as anticipated. This will be discussed in the forthcoming Feasibility Study.

Northeast District Office • 2110 East Aurora Road • Twinsburg, OH 44087-1924
epa.ohio.gov • (330) 963-1200 • (330) 487-0769 (fax)

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03-08-2016

If you have any questions, please call me at (330) 963-1207.

Sincerely,

Vicki Deppisch

Vicki Deppisch
Hydrogeologist/Project Coordinator
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Final Work Plan
for a Pilot Study and Feasibility Study
at RVAAP-50 Atlas Scrap Yard

Camp Ravenna
Ravenna, Ohio

19 February 2016

Contract No. W912QR-14-D-0001
Delivery Order No. 0004

US Army Corps of Engineers
Louisville District
600 Martin Luther King Jr. Place
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Eric Cheng, USACE – Louisville District Contracting Officer's Representative (COR)	3	1

ARNG = Army National Guard
EPA DERR = Ohio Environmental Protection Agency Division of Environmental Response and Revitalization
EPA CO = Ohio Environmental Protection Agency Central Office
NEDO = Northeast District Office
OHARNG = Ohio Army National Guard
REIMS = Ravenna Environmental Information Management System
RVAAP = Ravenna Army Ammunition Plant
USACE = United States Army Corps of Engineers

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LIST OF ACRONYMS

Acronym	**Description**
Alliant	Alliant Corporation
AHA	activity hazard analysis
AOC	area of concern
ARNG	Army National Guard
bgs	below ground surface
BMP	Best Management Practices
BRACD	Base Realignment and Closure Division
BSV	background screening value
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
CERCLIS	Comprehensive Environmental Response, Compensation, and Liability Information System
COC	chemicals of concern
COR	Contracting Officer’s Representative
CY	cubic yard
DFFO	Director’s Final Findings and Order
DO	Delivery Order
DoD	Department of Defense
DQO	Data Quality Objective
EDD	Electronic Data Deliverable
Endpoint	Endpoint Consulting, Inc.
ERIS	Environmental Restoration Information System
FS	Feasibility Study
ft	foot
FWCUG	Facility-Wide Cleanup Goals
FWSAP	Facility-Wide Sampling and Analysis Plan
FWSHP	Facility-Wide Safety and Health Plan
FWQAPP	Facility-Wide Quality Assurance Plan
IDW	Investigation Derived Waste
Leidos	Leidos Engineering of Ohio, Inc.
LCG	Louisville Chemistry Guideline
mg/kg	milligrams per kilogram
NGB	National Guard Bureau
OHARNG	Ohio Army National Guard
Ohio EPA	Ohio Environmental Protection Agency
ORC	Ohio Revised Code
PAH	polycyclic aromatic hydrocarbon
PBR	Permit-By-Rule
PWS	Performance Work Statement

Acronym	**Description**
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
REIMS	Ravenna Environmental Information Management System
RI	Remedial Investigation
RSLs	residential screening levels
RVAAP	Ravenna Army Ammunition Plant
SAIC	Science Applications International Corporation
SSHP	Site Safety and Health Plan
TAT	turnaround time
TCLP	Toxicity Characteristic Leaching Procedure
UFP-QAPP	Uniform Federal Policy for Quality Assurance Project Plans
USACE	U.S. Army Corps of Engineers
USEPA	United States Environmental Protection Agency
VEG©	Vapor Energy Generation©
YD	yard

EXECUTIVE SUMMARY

This Work Plan presents the field activities, and procedures to be implemented during field operations for Alliant's task order under Contract No. W912QR-14-D-0001, Delivery Order (DO) No. 0004 for a Pilot Study and Feasibility Study (FS) at the Atlas Scrap Yard area of concern (AOC) [former Ravenna Army Ammunition Plant (RVAAP)-50] at Camp Ravenna, Portage and Trumbull Counties, Ohio. The DO was issued by the United States Army Corps of Engineers, Louisville District on September 17, 2015. In accordance with the Performance Work Statement (PWS) dated August 26, 2015 Alliant is tasked with executing a pilot test and FS. This Work Plan details the field activities and procedures to be followed, and includes the Quality Assurance Project Plan, and the Site Safety and Health Plan for this pilot test, and modification of the FS.

1.0 BACKGROUND

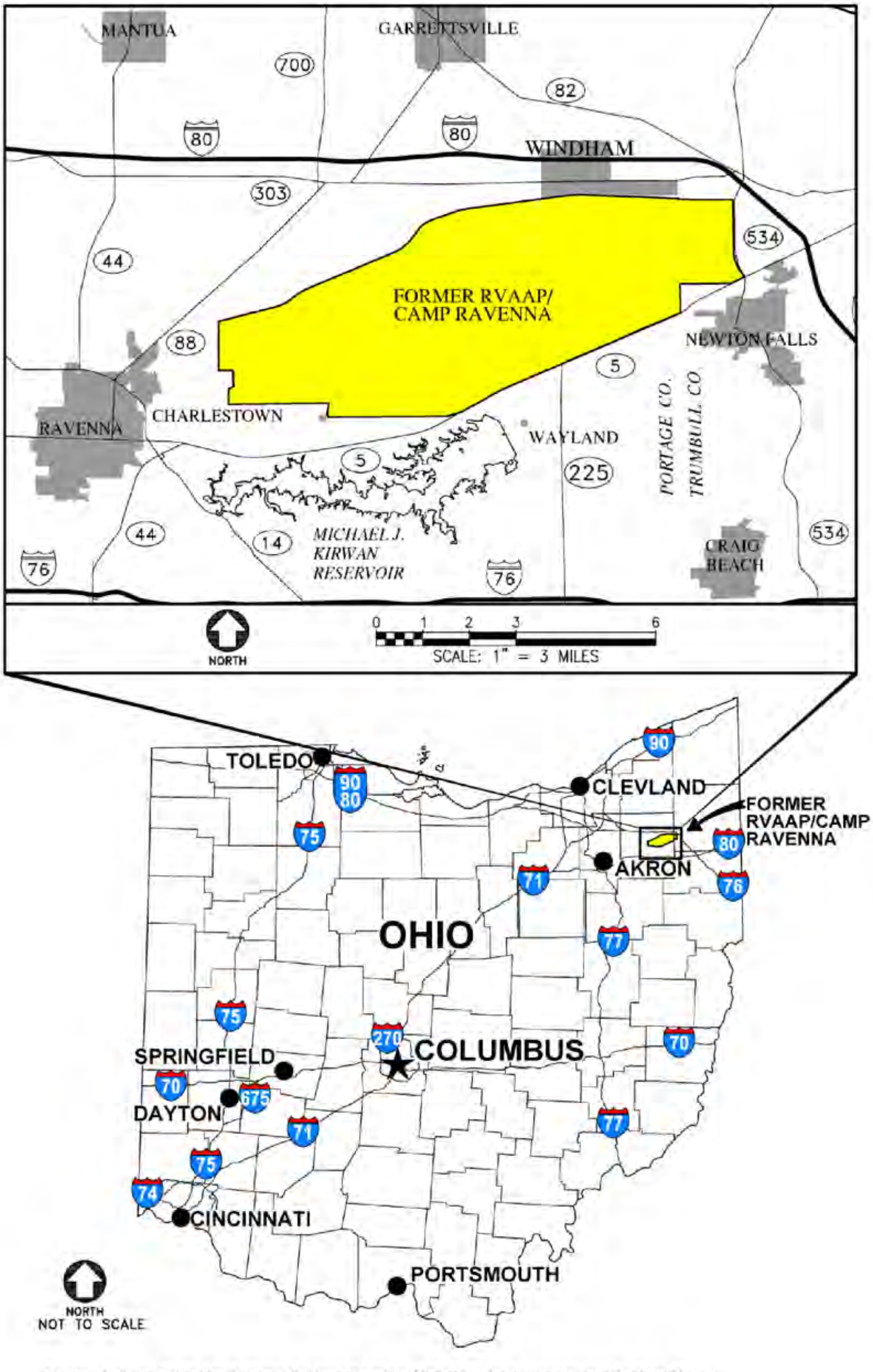
This Work Plan outlines the activities to be conducted for a Pilot Study and Feasibility Study (FS) for impacted soils at the Atlas Scrap Yard area of concern (AOC) [former Ravenna Army Ammunition Plant (RVAAP)-50] at Camp Ravenna, Portage and Trumbull Counties, Ohio (Figure 1-1).

Alliant Corporation (Alliant) has been tasked by the U. S. Army Corps of Engineers (USACE) to conduct the pilot study and update the FS Report, and is submitting this Work Plan to the U.S. Army in accordance with the Performance Work Statement (PWS), Contract No. W912QR-14-D-0001, Delivery Order (DO) No. 0004. The DO was issued by the United States Army Corps of Engineers, Louisville District on 17 September 2015 (USACE 2015a). The draft version of this Work Plan has been reviewed by the Ohio Environmental Protection Agency (EPA), Army Personnel, and USACE project representatives. Alliant has provided a response for each comment, and has received approval by USACE and/or Ohio EPA for all responses to the reviewer's individual comments. The reviewer's comments and Alliant's responses are presented in Appendix D. The following subsections present descriptions for the installation and the Atlas Scrap Yard AOC.

1.1 INSTALLATION DESCRIPTION

The former Ravenna Army Ammunition Plant (RVAAP), now known as the Camp Ravenna Joint Military Training Center (Camp Ravenna), located in northeastern Ohio within Portage and Trumbull Counties, is approximately three (3) miles east/northeast of the City of Ravenna and one (1) mile north/northwest of the City of Newton Falls. The facility is approximately 11 miles long and 3.5 miles wide. The facility is bounded by State Route 5, the Michael J. Kirwan Reservoir, and the CSX System Railroad to the south; Garret, McCormick, and Berry Roads to the west; the Norfolk Southern Railroad to the north; and State Route 534 to the east. In addition, the facility is surrounded by the communities of Windham, Garrettsville, Charlestown, and Wayland.

The facility was formerly used as a load, assemble, and pack facility for munitions production. As of September 2013, administrative accountability for the entire 21,683-acre facility has been transferred to the United States Property and Fiscal Officer (USP&FO) for Ohio and the property was subsequently licensed to the Ohio Army National Guard (OHARNG) for use as a military training site, Camp Ravenna. The facility restoration program involves cleanup of former production/operational areas throughout the facility related to former activities conducted under the RVAAP. References in this document to RVAAP relate to previous activities at the facility as related to former munitions production activities or to activities being conducted under the restoration/cleanup program. RVAAP is bound to the Director's Final Findings and Orders (DFFOs) issued June 10, 2004 by the Ohio EPA pursuant to the authority vested under Chapters 3734, 3745, and 6111 of the Ohio Revised Code (ORC). The objective of the Orders is to ensure that the public health, safety, and welfare, as well as the environment, is protected from the disposal, discharge, or release of contaminants. RVAAP is not on the United States Environmental Protection Agency (USEPA) National Priorities List, although it is in the USEPA Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS) database. The Ohio EPA is the lead environmental regulator for the RVAAP restoration program. The Installation is bound to the DFFOs, issued on 10 June 2004 by the Ohio EPA. The DFFOs form the basis



Source: Leidos, 2015, Draft Remedial Investigation Work Plan for Sediment and Surface Water

Figure 1-1. Location of Former RVAAP or Camp Ravenna for the implementation of a Comprehensive Environmental Response Compensation and Liability Act (CERCLA) based environmental remediation program at the Installation.

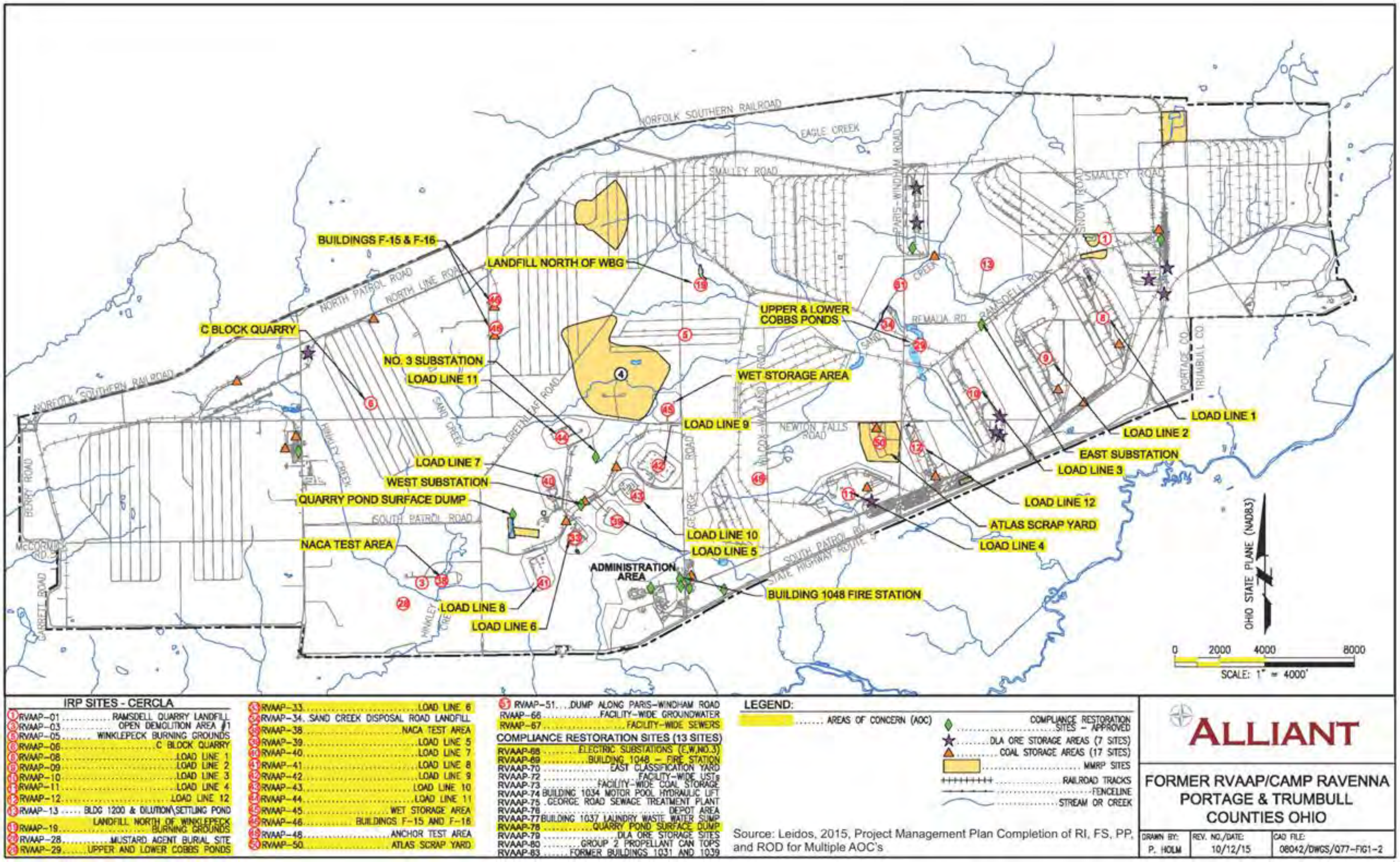
1.2 SITE DESCRIPTION

The Atlas Scrap Yard AOC (RVAAP-50), formerly known as the construction camp, is approximately 73 acres and is located in the southeastern portion of Camp Ravenna (Figure 1-2). The Atlas Scrap Yard has served several operational functions over the history of the former RVAAP, but the AOC was never used for munitions production activities. From 1940 to 1945, the Atlas Scrap Yard operated as a construction camp to house workers and their families while the facility was being constructed. By the end of World War II, the majority of buildings and structures at the Atlas Scrap Yard were demolished or relocated to other areas of the facility. The structures that remained were used to support roads and grounds maintenance activities. These remaining structures were razed after the Vietnam War. After the Vietnam War, the AOC became a stockpile storage area for bulk materials, including gravel, railroad ballasts, sand, and culvert pipes. Coal, used for building process heat, was piled in several areas of the AOC. The central-east portion of the AOC was a staging area for salvaged ammunition boxes from demilitarized Vietnam War-era munitions. The Atlas Scrap Yard also included an incinerator, underground storage tanks, and was a storage area for numerous treated railroad ties.

There is no fence around the AOC as a perimeter boundary, but the AOC is bordered by Newton Falls Road to the north and Paris-Windham Road to the east. Load Line 4 is located to the south of the AOC. The interior of the AOC is currently vegetated with shrub/scrub vegetation in unpaved areas and is forested around its perimeter. The north-central portion of the AOC is sparsely vegetated and has extensive gravel cover.

The Remedial Investigation (RI) [Leidos Engineering of Ohio, Inc. (Leidos), 2015a] concluded that the Atlas Scrap Yard was adequately characterized. The RI identified five (5) polycyclic aromatic hydrocarbons (PAHs) as chemicals of concern (COCs) at the site. The identified PAHs are benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and dibenz(a,h)anthracene. The PAH COCs were primarily identified in the 0-1 foot (ft) below ground surface (bgs) interval with the most contaminated areas being located southeast of the former T-4703 Roads and Grounds Maintenance Building, in the approximate vicinity of the stockpiled railroad ties. Additionally, a small area in the southern part of the site in the vicinity of the former incinerator has been characterized by elevated lead concentrations, and constitutes a lead "hot spot."

A Preliminary Draft FS for the Atlas Scrap Yard was completed (Leidos, 2015b). However, since the completion of the Preliminary Draft FS Report, an additional technology has been identified as a potential remedial alternative. Therefore, the FS will be updated as a part of this project.



Source: Leidos, 2015, Project Management Plan Completion of RI, FS, PP, and ROD for Multiple AOC's

Figure 1-2. Map of the Former RVAAP or Camp Ravenna

2.0 PROJECT DESCRIPTION

2.1 PURPOSE

The purpose of this Work Plan is to provide the details and procedures necessary to conduct a pilot study and to obtain the data necessary to update the FS Report for the Atlas Scrap Yard AOC (RVAAP-50).

Contaminated soils at the site will be tested for the suitability of using Vapor Energy Generation© (VEG©) technology to treat PAH-impacted soil in a sequence of a bench and pilot tests. Additionally a bench test only using steel slag will be conducted to test treatment of lead-impacted soil. The actual tests will be conducted by Alliant's subcontractor, Endpoint Consulting, Inc. (Endpoint), a California-based environmental company. VEG© technology is a sustainable, green remediation technology that involves ex-situ thermal treatment of impacted soils in an enclosed treatment chamber using steam. A process diagram is presented in the subcontractor Work Plan in Appendix C. As an internal auger rotates the soil, the steam causes the contaminants to be released and captured by a vacuum system inside the chamber which then filters the gases out. The goal is to reduce contaminants to non-detect levels or to below regulatory standards. Using steel slag for treatment of lead-impacted soils involves mixing of the contaminated soils with steel slag to induce immobilization of lead through pH control, long term soil pH buffering, and the creation of insoluble lead compounds.

A Preliminary Draft FS Report was previously prepared for the Atlas Scrap Yard AOC (RVAAP-50) (Leidos, 2015b). Since completion of the FS Report, additional technologies as discussed above have been identified as potential remedial alternatives. Therefore, the results from the pilot- and bench-scale studies will be used to update the FS Report.

2.2 SCOPE

The scope of this Work Plan is to outline the activities to be conducted for the planned bench-scale and pilot-scale tests for impacted soils at the Atlas Scrap Yard AOC (RVAAP-50). This Work Plan also details health and safety specifications to minimize the potential for personnel injury or illness, and provides the quality assurance (QA) and quality control (QC) requirements to ensure data are usable and defensible.

This Work Plan was developed in accordance with the FWSAP and Facility-wide Quality Assurance Project Plan (FWQAPP) (SAIC 2011a), as well as the Facility-wide Safety and Health Plan (FWSHP) (SAIC 2011b). The project-specific Site Safety and Health Plan (SSHP) (Appendix A) presents the potential hazards, project-specific staff organization, qualifications, responsibilities, training requirements, activity hazard analyses (AHAs), and monitoring requirements that may be encountered during implementation of the Work Plan. The project-specific Quality Assurance Project Plan (QAPP) (Appendix B) has been prepared in accordance with the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP) and presents the data quality objectives (DQOs) for sampling, laboratory analysis, and reporting, which will provide results to be used in finalizing the FS Report.

3.0 PROJECT ACTIVITIES

The project activities include performing bench-scale and pilot-scale studies for treatment of PAH and lead-impacted soils, preparing a Technical Memorandum which presents the results and conclusions of the tests, and modification of the FS Report. The FS will be updated separately from the Technical Memorandum and in accordance with CERLA guidance.

The following subsections describe the project activities that will be conducted including the planned bench-scale and pilot-scale tests, and associated reporting, and completion of the FS Report. More detailed information concerning conduct of the bench- and pilot-scale tests may be found in the subcontractor Work Plan (Endpoint 2015) provided in Appendix C.

3.1 BENCH SCALE TESTING

The bench-scale portion of the activities will be conducted at the laboratories of Alliant's subcontractor, Endpoint. Bench-scale testing will include thermal treatment of PAH-impacted soils using VEG© remediation technology, and stabilization of lead in impacted soils via mixing with steel slag. The objectives of the bench-scale tests are to assess the potential applicability and effectiveness of the treatment options, and to identify optimal treatment conditions.

3.1.1 Pre-Treatment Sampling

To provide Endpoint with soil for the bench tests, Alliant will ship one 55-gallon drum of PAH-impacted soils, and two 5-gal buckets (10-gallons total) of lead-impacted soils to the bench-test laboratories. Soil in the drum will be obtained by Army personnel from the PAH-impacted area of the site as identified in Section 1.2. Soil in the two 5-gallon containers will be obtained by Army and Alliant personnel from the lead impacted area of the site. Samples will be collected from the soils before shipping to characterize the soils prior to treatment. Profiles for shipping the contaminated soils will be based on previous analytical data obtained from the site and/or samples collected from the soils prior to shipment. Table 3-1 shows the Work Plan bench test and pilot study sample categories, analytical parameters, analytical methods, sample types and preservatives scheduled for the study.

One 7-aliquot (or more) composite sample will be collected from soil contained in the 55-gallon drum. This sample will be submitted to the laboratory for analysis for PAHs using EPA Method 8270D SIM. Prior to shipment, two 7-aliquot composite samples will be collected from soil contained in the 5-gallon buckets. These samples will be submitted to TestAmerica laboratory for analysis of: pH using method 9045; lead using Method 6020A; and for Leachable Lead using Methods 1311 (extraction) and 6010C (Lead by ICP). Upon arrival at Endpoint's testing laboratory, additional 7-aliquot composite samples will be collected from the 5-gallon buckets and submitted to the laboratory for analysis of Toxicity Characteristic Leaching Procedure (TCLP) by EPA Method 1311, and for Synthetic Precipitation Leaching Procedure (SPLP) by EPA Methods 1312.

The aliquots will be collected from seven different locations in the drum and buckets. The soil samples will be collected by dipping the containers directly into the soil and obtaining equal portions of soil each time the container is dipped. The soil samples will be properly labeled, and preserved at 4ºC. Sample packaging, shipping and chain of custody will be conducted in accordance with the requirements of the project-specific QAPP (Appendix B). Additionally, laboratory analytical data will be subject to QC and

Table 3-1. Atlas Scrap Yard AOC (RVAAP-50) Bench and Pilot Study Soil Sampling

Sample Category	Parameter	Analytical Method	No. of Samples	Duplicates(1)	Sample Type(2)	Preservative	Turnaround Time
Pre-Treatment Sampling							
55-gal Drum Sample	PAHs	8270D SIM	1	N/A	7-Point Composite	Cool 4ºC	15 Days
10-gal Container Sample(3)	Lead	6020A/6010C	1/1	N/A	7-Point Composite	Cool 4ºC	15 Days
10-gal Container Sample(3)	pH	9045	1	N/A	Discrete	Cool 4ºC	15 Days
10-gal Container Sample(3)	TCLP Lead	1311/6010C	1	N/A	7-Point Composite	Cool 4ºC	28 Days
10-gal Container Sample(3)	Long-Term Leachable Lead	SPLP 1312	2	N/A	7-Point Composite	Cool 4ºC	90 Days
VEG© Technology Bench Scale Study							
Initial Post-Treatment Sampling (3 Stockpiles)	PAHs	8270D SIM	3 (1/ stockpile)	None	7-Point Composite	Cool 4ºC	24 hours
VEG© Technology Pilot Scale Study							
Pre-Treatment Sampling (3 Stockpiles)	PAHs	8270D SIM	3 (1/ stockpile)	None	7-Point Composite	Cool 4ºC	24 hours
Post-Treatment Sampling (3 Stockpiles)	PAHs	8270D SIM	3 (1/ stockpile)	None	7-Point Composite	Cool 4ºC	24 hours
Steel Slag Mixing Bench-Scale Study							
Initial Post-Treatment Sampling Basic Oxygen Furnace Slag	Long-term leachable Lead	SPLP 1312	5 (1/mix design)	5 (1/mix design)	7-Point Composite	Cool 4ºC	90 Days
Initial Post-Treatment Sampling Stainless-Steel Slag	Long-term leachable Lead	SPLP 1312	5 (1/mix design)	5 (1/mix design)	7-Point Composite	Cool 4ºC	90 Days
Final Post-Treatment Sampling Basic Oxygen Furnace Slag (2 Mix Designs)	Long-term leachable Lead	SPLP 1312	2 (1/mix design)	N/A	7-Point Composite	Cool 4ºC	90 Days
Final Post-Treatment Sampling Stainless-Steel Slag (2 Mix Designs)	Long-term leachable Lead	SPLP 1312	2 (1/mix design)	N/A	7-Point Composite	Cool 4ºC	90 Days

Table 3-1. Atlas Scrap Yard AOC (RVAAP-50) Bench and Pilot Study Soil Sampling (Continued)

(1) No other field QC samples are planned other than duplicate samples. Laboratory QC samples will be performed in accordance with USACE Quality Systems Manual Version 5.

(2) The number of points is a minimum number, additional points may be collected.

(3) Split between 2 x 5-gallon buckets for shipping

N/A	not applicable	SPLP	Synthetic Precipitation Leaching Procedure
PAHs	polycyclic aromatic hydrocarbons	TCLP	Toxicity Characteristic Leaching Procedure
SIM	Selective Ion Method	USACE	U.S. Army Corps of Engineers

certification in accordance with Department of Defense (DoD) requirements as described in the project-specific QAPP (Appendix B).

3.1.2 Bench-Scale Testing for Treatment of PAHs in Soils

Bench-scale ex-situ thermal treatment of PAHs in site soils will be conducted by testing a series of treatment temperatures and treatment residence times within the VEG© Technology remediation system as described in the subcontractor Work Plan (Appendix C). The objective of the bench-scale tests is to determine the optimal system treatment temperatures and residence times for effective treatment of the PAH-impacted soils.

Endpoint will evenly distribute the soil in the drum into three stockpiles using a shovel. Each stockpile will be used to test treatment options for the PAH-impacted soil. Variables for the bench-scale treatment of PAH-impacted soils include temperature and residence time. Temperature will range from of 600 to 800°F and residence times in the treatment chamber will range from 15 to 30 minutes. The first stockpile will be treated at a temperature of 600°F for 15 minutes. Temperatures and residence times for the subsequently treated stockpiles will be adjusted based on the results of the first treatment run.

Upon completion of the tests, Endpoint will conduct post-treatment sampling of the soils. Post-treatment samples will consist of 7-point composites (Table 3-1) and will be collected as described in the following paragraph. The composite samples will be collected from the bench-scale study stockpiles using the sample containers. The soil samples will be collected by dipping the containers directly into the soil and obtaining equal portions of soil each time the container is dipped. Soils will be collected from seven different locations in the post-treatment soil stockpiles. The samples will be properly labeled, and cooled to 4ºC. Soil samples will be submitted to TestAmerica, a DoD approved laboratory for 24-hour turnaround time (TAT) analysis of PAHs by EPA Method 8270D SIM (Table 3-1). Sample packaging, shipping and chain of custody will be conducted in accordance with the requirements of the project-specific QAPP (Appendix B). Additionally, laboratory analytical data will be subject to QC and certification in accordance with DoD requirements as described in the project-specific QAPP (Appendix B).

3.1.3 Bench-Scale Testing for Treatment of Lead in Soils

Bench-scale testing activities for treatment of lead in soils will be conducted at the subcontractor's laboratory. No bench- or pilot-scale studies for treatment of lead in soils will be conducted at the Atlas Scrap Yard AOC. Bench-scale studies will be conducted by testing various soil/steel slag mixing ratios, and slag particle sizes as specified in the subcontractor Work Plan (Appendix C). The objective of bench-scale tests for steel slag mixing is to determine the optimal mixing ratio for soils and slag that will effectively render lead immobile (non-leachable) in site soils. The slag will be leveraged for its residual lime content and soluble silica to immobilize lead by pH control and precipitation of a variety of insoluble carbonates and silicates. Steel slag relies on a combination of chemical precipitation, metals complexation, and hydraulic conductivity reduction to bond metals in place. Articles concerning immobilization of lead in soils via mixing with steel slag are presented in Appendix E.

A series of five mix designs will be conducted on soils in the bucket using two different sources of regionally available steel slag fines. Once the five mix designs are complete, post-treatment sampling of the soils will be conducted. The initial samples will consist of five 7-point composite samples from each of the two steel slag types, and will be collected following methods described in Section 3.1.2, and submitted to TestAmerica for analysis of SPLP by EPA Method 1312 (Table 3-1).

The types of steel slag that may be used for the bench-scale tests include basic oxygen furnace slag, stainless steel slag, and/or electric arc furnace slag. Based on a combination of leaching performance, dose and expected cost, two leading candidate mix designs will be advanced to a final stage of testing. The final round of testing will include analysis of five samples each from the two leading mix designs using USEPA SPLP Method 1312 to assess long-term leaching. The final composition of the steel slag to be used for soil cleanup will depend on the blending results of the bench-scale tests, especially relative to the buffer capacity of the soil. The final composition of the steel slag chosen for the site, and the potential negative consequences of treating site soils with steel slag will be thoroughly discussed in the updated FS.

Sample packaging, shipping and chain of custody will be conducted in accordance with the requirements of the project-specific QAPP (Appendix B). Additionally, laboratory analytical data will be subject to QC and certification in accordance with DoD requirements (Appendix B).

3.2 PILOT SCALE TESTING

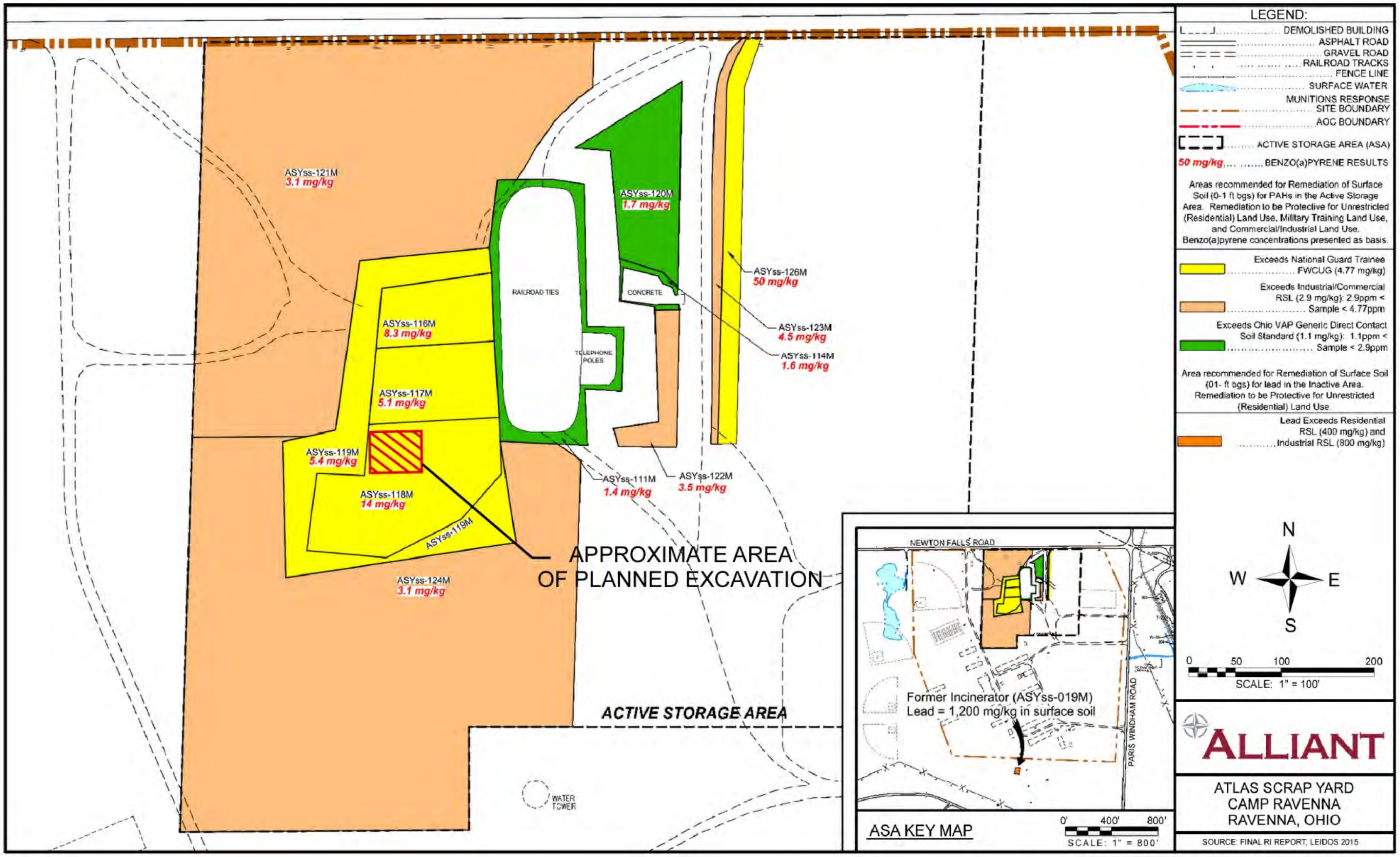
The specifics of the pilot-scale study at the Atlas Scrap Yard AOC (RVAAP-50) will be based on the results of the VEG© bench-scale study. Alliant's subcontractor (Endpoint) will conduct the pilot testing in the field, and Alliant will provide oversight and field documentation services during the field effort. The objective of the pilot-scale test is to demonstrate the effectiveness of the VEG© technology for effective treatment of PAH-impacted site soils.

Endpoint will mobilize to Camp Ravenna all necessary equipment and resources to excavate and manage (i.e, profile soils and provide erosion protection) up to 100 cubic yards (CY) of PAH-impacted soils, thermally treat (using the ex-situ component of Endpoint's VEG© Technology) up to 100 CY of soils, and to perform post-treatment soil sampling and associated laboratory analysis to evaluate the efficacy of the technology to treat PAH-impacted soils.

3.2.1 Soil Excavation

Up to 100 CYs of soil will be excavated using a backhoe for pilot-scale testing of the VEG© technology. Soils will be excavated from one of the most contaminated areas near the stockpiled railroad ties. Figure 3-1 shows the general area of the pilot study excavation location, and Figure 3-2 presents an aerial view of the location. Alliant and Endpoint will walk down the site with Army personnel to confirm the field location of the PAH soil source area before excavation begins. The excavation will be conducted to a depth of no greater than 1 ft bgs in an 18 yard (YD) x 18 YD area. Because the excavation depth will not exceed 1 ft, no excavation permit is required. The location for the excavation was selected by Endpoint in conjunction with Ohio EPA, USACE, Army National Guard (ARNG), and Army personnel. The area is readily accessible, and the intended area of the excavation will be delineated using wooden stakes prior to the start of the excavation activities. Surveying of the excavation will use Global Positioning System coordinates collected at each of the four corners of the excavation to document the actual location.

Excavated soils will be stockpiled immediately adjacent to the VEG© system into two 50-CY stockpiles. The treated soils will be stockpiled on an 11-ml-thick tarp, and covered with plastic sheeting during times of inactivity, as necessary. The excavation area will be barricaded off to ensure safety.



SOURCE: FINAL RI REPORT, LEIDOS 2015

Figure 3-1. Approximate Location of the Planned Excavation at the Atlas Scrap Yard

SOURCE: GOOGLE MAPS, JANUARY 2016

Figure 3-2. Aerial View of Pilot Study Location at the Atlas Scrap Yard

Baseline levels of PAHs at the site will be determined prior to the treatment process by collecting soil samples from both of the soil stockpiles (one from each 50-CY stockpile). Baseline (pre-treatment) samples will consist of 7-point composites (Table 3-1).

Soils will be collected from three different locations in the stockpiles using the sample containers. The soil samples will be collected by dipping the containers directly into the soil and obtaining equal portions of soil each time the container is dipped The samples will be properly labeled, and cooled to 4ºC. Stockpile soils will be sampled and submitted to TestAmerica for analysis of PAHs using EPA Method 8270D SIM (Table 3-1). Sample packaging, shipping and chain of custody will be conducted in accordance with the requirements of the project-specific QAPP (Appendix B). Additionally, laboratory analytical data will be subject to QC and certification in accordance with DoD requirements as described in the project-specific QAPP (Appendix B).

3.2.2 Onsite Treatment

Following pre-treatment sampling, soils from each 50-CY soil stockpile will be independently loaded into the VEG© system, and thermally treated using the ex-situ component of Endpoint's VEG© Technology. The estimated CO2 emissions from the VEG© system (with and without Endpoint's patented CO2 filter) have been calculated and are provided in Attachment C of the subcontractor Work Plan (Appendix C).

The duration of the pilot testing is estimated at 3 to 5 days. The pilot-scale test will be targeted for a period of time where weather conditions are expected to be dry. If inclement weather conditions are encountered during the field effort, testing may be temporarily suspended, and the stockpiles covered until dry conditions prevail. Prior to loading of soils, the system will be pre-heated to the optimal treatment temperature based on the bench-scale tests. Soil will be fed directly into the preheated chamber either using a shovel or by being placed onto a conveyor. Soil will be treated via steam in the treatment chamber which will be generated by heating air and water with propane as a fuel source. Water for the pilot test will be obtained from Canton Water Works and will consist of public water used by the city of Canton, Ohio. Residence times for soils in the treatment chamber will be set as determined by the bench-scale testing. Soil treatment rates are expected to range from 10 to 30 CY/hour depending upon soil moisture, and weather conditions. After treatment, the soils will be independently re-stockpiled into two 50-CY stockpiles on uncontaminated 11-ml-thick tarp, and covered with plastic sheeting until analytical results determine if the soil meets the remedial objectives.

Endpoint will perform post-treatment soil sampling to evaluate the efficacy of the technology to treat PAH-impacted soils to non-detect levels, or to levels below residential screening levels (RSLs). Post-treatment samples will include collecting one 7-point composite sample from each 50-CY stockpile to be submitted to the laboratory for analysis for PAHs using EPA Method 8270D SIM (Table 3-1). The 7-point composite samples will be collected as described in Section 3.2.1. Sample packaging, shipping and chain of custody will be conducted in accordance with the requirements of the Project-Specific QAPP (Appendix B). Additionally, laboratory analytical data will be subject to QC and certification in accordance with DoD requirements as described in the QAPP (Appendix B).

3.2.3 Soil Backfilling and Demobilization

Upon completion of the pilot testing, soils will be placed back into the excavation pit using a backhoe. The plan is to treat the excavated soils until clean based on the results obtained from the bench-scale study. The excavated area will be included in any future remediation at the site whether or not the soils are still contaminated after treatment. The soils will be compacted using the excavation equipment so that the ground surface elevation of the backfilled area is even with the surrounding area. Any water inadvertently collected in the excavation pit will be pumped out and containerized prior to backfilling the excavation. The likelihood of dewatering the pit is low since the pilot testing will be conducted during a dry period. However, any water removed from the excavation pit will be drummed, profiled, and shipped offsite for disposal. Following backfilling of the excavation, the subcontractor will re-vegetate the area using Camp Ravenna Seed Mix.

Decontamination and demobilization activities will include removing of excess soils from all equipment used prior to removal from the site. This process will maximize the use of dry, clean steam from the vapor energy generator system inherent to the VEG© technology, thereby eliminating any rinsate or other investigation derived wastes (IDW) during decontamination procedures. Therefore, no waste water should be generated from decontamination activities. Any liquid IDW will be drummed, profiled, and shipped offsite. Some waste water may be generated due to dewatering of the pit but this is not likely. The majority of the liquid waste (approximately one 55-gallon drum) is anticipated to be generated from the VEG© system filters. Camp Ravenna Waste Management Guidelines as presented in Appendix D will be followed for any IDW generated at the site.

3.3 REPORTING

Alliant and its subcontractor, Endpoint, will prepare and submit to the Army a Draft Technical Memorandum outlining all procedures, results, and conclusions relative to bench-scale and pilot-scale tests performed. Any IDW generated during the field operations will be summarized in the memorandum. The memorandum will include information on the feasibility of the VEG© technology to treat PAHs and related optimal treatment conditions which may in turn be used for full-scale applications at the site. Similarly, the feasibility of the use of steel slag to stabilize lead impacted soils at the site at full-scale will be evaluated, with related conclusions and recommendations set forth in the memorandum. Alliant will respond to informal Army comments and prepare the Final Technical Memorandum which will incorporate the responses to those comments, The Final Technical Memorandum shall be included as an appendix to the FS Report, and will follow the normal review process as a part of the Revised Preliminary Draft FS.

3.4 FEASIBILITY STUDY REPORT

Alliant will prepare a Revised Preliminary Draft, Draft, and Final FS Reports for RVAAP-50, Atlas Scrap Yard. The current Preliminary Draft FS (Leidos, 2015b) will be revised to include the information obtained during the bench- and pilot-scale tests. Alliant will prepare a Revised Preliminary Draft FS Report for Army review and respond to Army comments. Alliant will then prepare a Draft FS Report for Ohio EPA review and respond to Ohio EPA comments. Alliant will prepare a Final FS Report which incorporates the responses to Ohio EPA comments. The FS format will adhere to the USACE Submission Format Guidelines (Leidos 2015c).

4.0 ENVIRONMENTAL PROTECTION PLAN

The environmental resources within the project boundaries and those affected outside the limits of the activities under this contract will be protected during this field effort. The following subsections present the plans for protection against sediment and erosion, spill control and prevention, protection of threatened and endangered species, potential wetlands (if any), and cultural and natural resources.

4.1 AIR PERMITTING AND FUGITIVE DUST

Alliant contacted the Ohio EPA to apply for an air permit for the planned site operations. However, the Ohio EPA deemed that the size and scope of the project was not large enough to warrant a permit at this time provided the use of best management practices (BMP) is employed. However, a Permit-By-Rule (PBR) was granted for the pilot study. The Permit Number is PBR 14548 and the Facility ID number is 1667000109. Alliant and its subcontractor will employ BMPs to control visible emissions.

During field operations fugitive dust will be watched for and if necessary dust emissions will be controlled. Dust emissions will be controlled by employing BMPs such as halting excavation activities, and covering soil piles during periods of high wind, and/or ensuring that soil and mud have been removed from the backhoe before entering road ways.

4.2 SEDIMENT AND EROSION CONTROL

BMPs will be implemented during the project to reduce and control sediment and erosion from the excavated area, as necessary. BMPs include installing straw bales and/or silt fence barriers in the potential path of stormwater flow to prevent impacted soils or sediments from entering on site storm sewers. If necessary, diversion ditches will be dug to divert stormwater towards barriers, and away from the excavation and/or storm grates. If installed, regular maintenance and inspection will be performed on barriers. This may include removal of collected soils and sediments and repair or replacement of damaged sections.

Soil stockpiles will be placed on 11-mil thick tarpaulins, and covered with plastic sheeting during periods of inactivity to prevent rainwater infiltration. The purpose for this is to isolate contaminated soils from stormwater runoff and to prevent contamination movement via stormwater. Stockpile covers will be weighted and secured to prevent storm damage. Covers will extend over the edges of the stockpiles to prevent stormwater from impacting stockpiled soil. Straw bales will be placed, and diversion ditches will be constructed as necessary to control stormwater flow. Additionally, Alliant’s subcontractor will avoid excavating wet soil.

The most likely source of erosion at the site will be from erosion of the soil stockpiles if the plastic sheeting is disturbed during a period of inactivity. The stockpile plastic sheeting will be secured as described above before any periods of unanticipated inactivity that may occur. Also movement of project vehicles and the backhoe may disturb soils causing damage such as ruts. During on-site activities, the area will be inspected and ruts and soft areas will be smoothed out and leveled with the backhoe and/or shovels as necessary to maintain a smooth surface to prevent soil erosion.

4.3 SPILL CONTROL AND PREVENTION

No chemicals will be used for the ex-situ thermal soil treatment activities. The most likely spills or leaks would occur during operation or refueling of the backhoe. The backhoe will arrive on site fully fueled to circumvent accidental spillage during refueling operations. If the backhoe requires refueling, plastic sheeting will be placed under the equipment during refueling operations to prevent accidental spills from reaching the ground surface. Additionally, the backhoe will be inspected at arrival and daily for signs of hydraulic or fuel leaks. If leaks are observed then the backhoe will be removed from service immediately and repaired. In the event of a spill, Camp Ravenna Range Control at (614) 336-6041 will be contacted and the procedures on the Camp Ravenna First Responder Form (Appendix D) will be followed. A spill kit will be kept on site.

4.4 THREATENED OR ENDANGERED SPECIES

Alliant and their subcontractor will perform all site activities in such a manner as to avoid or minimize adverse effects on any rare or protected plant/wildlife species and resources discovered on the site. The AOC has not been specifically surveyed for threatened or endangered species but none are not to exist at the site. Listings of threatened and endangered species are provided in the document entitled *Camp Ravenna Integrated Natural Resources Management Plan* (USACE. 2015b). Most of the work is being performed in an overgrown area.

4.4 POTENTIAL WETLANDS

There are no wetlands in the area of the pilot test.

4.5 CULTURAL AND ARCHAEOLOGICAL RESOURCES

In the event that cultural materials, artifacts, or human remains are encountered during the excavation activities the COR will be contacted and all excavation activities will be suspended. Based upon results of previous cultural resource surveys, prior disturbance associated with previous industrial activities, and the minimal disturbance planned, the project will have no effect on cultural resources at the facility. In the event that cultural materials are inadvertently discovered, Alliant will stop work and follow the OHARNG Procedures for Inadvertent Discovery of Cultural Materials at Camp Ravenna (Appendix D).

5.0 PROJECT DOCUMENTATION AND SAMPLE QA/QC

Alliant will ensure that the quality of all work performed or produced under this DO meets Army approval through the COR. Documentation of the pilot-test activities will consist of entries in a field logbook and field forms as appropriate. The logbook and forms will be reviewed for accuracy and completeness by the Field Oversight representative.

Chemical QC will be provided whenever sampling or analysis for chemical constituents is required in order to achieve milestones. The laboratory to be used by Alliant’s subcontractor will be DoD-approved, will perform testing in accordance with requirements of the DoD Quality Systems Manual Version 5 (or the latest approved version), and will be compliant with the Louisville Chemistry Guideline (LCG) where it does not conflict. All samples collected and analyzed under this DO will be generated in Electronic Data Deliverable (EDD) format compatible with uploading requirements for Environmental Restoration

Information System (ERIS) and other required databases. The EDD will accurately reflect all analytical quality requirements. All electronic data submitted by the contract laboratory is required to be error-free and in complete agreement with the hard copy data. Laboratories will provide the appropriate Chemical Abstracts Services number to a specific analyte. A Load Summary Report and a transmittal letter from the laboratory will accompany the hard copy data report, certifying that the EDD is in agreement with hard copy data reports and was found to be free of errors.

6.0 DISPOSITION OF INVESTIGATION DERIVED WASTE

6.1 BENCH-SCALE TESTING SOILS DISPOSITION

Soils used in the bench-scale studies, regardless of the levels of PAHs detected, will be considered as IDW. Alliant's subcontractor (Endpoint) will place these soils back into the original drums and dispose of them at an appropriate landfill using the post-treatment sample results as the profile for disposal. Endpoint will confirm the disposal approach with USACE and Alliant prior to offsite transport by Safety Kleen. In addition, Endpoint will provide the waste manifest confirming transport and disposal of the soil drums at the landfill to Alliant and USACE.

6.2 PILOT-SCALE TESTING SOILS DISPOSITION

Upon receipt of the post treatment results from the pilot study, the site excavation will be backfilled with the treated soils. Some waste water may be generated due to dewatering of the pit but this is not likely. The majority of the liquid waste (approximately one 55-gallon drum) is anticipated to be generated from the VEG© system filters, Camp Ravenna Waste Management Guidelines as presented in Appendix D will be followed for any IDW generated at the site. Additionally, Alliant will collect and dispose of any non-soil IDW (i.e., personal protective equipment and/or trash generated during the pilot study) in accordance with facility procedures and regulations.

7.0 CLEAN UP LEVELS AND BACKGROUND CONCENTRATIONS

Cleanup levels for PAHs and lead at the Atlas Scrap Yard AOC will be in accordance with Facility-Wide Cleanup Goals (FWCUGs) for this project. USEPA RSL cleanup levels will be used only if an FWCUG does not exist. Facility-wide background soil sampling was conducted at the former RVAAP in 1998 to determine background screening values (BSVs) for inorganic constituents (SAIC 2001). Although no background concentrations were determined for PAHs at the former RVAAP, several PAHs were detected in background sampling locations at concentrations ranging from a low of 0.0078 milligrams per kilogram (mg/kg) (dibenzo[a,h]anthracene) to a high of 51 mg/kg (benzo[b]fluoranthene). The BSV for lead in soil was determined to be 26.1 mg/kg.

8.0 DELIVERABLES

Project Deliverables are presented in the Project Management Plan (Alliant 2015).

9.0 REFERENCES

Alliant Corporation, 2015. Draft Project Management Plan for a Pilot Study and Feasibility Study at RVAAP-50 Atlas Scrap Yard, Camp Ravenna, Ravenna, Ohio, 30 September 2015.

Endpoint Consulting, Inc. 2015. Work Plan for Bench- and Pilot-Scale Testing- Ex-Situ Thermal Desorption of Polycyclic Aromatic Hydrocarbons in Soils, and Bench-Scale Testing of Lead Stabilization in Soils, RVAAP-50 Atlas Scrap Yard, Former Ravenna, Army Ammunition Plant, Ravenna, OH, 7 October 2015.

Leidos Engineering of Ohio, Inc. 2015a. Final Remedial Investigation Report for Soil, Sediment, and Surface Water at RVAAP-50 Atlas Scrap Yard, Ravenna Army Ammunition Plant, Ravenna, Ohio, dated 26 June.

Leidos Engineering of Ohio, Inc. 2015b. Preliminary Draft Feasibility Study Report for Soil, Sediment, and Surface Water at RVAAP-50 Atlas Scrap Yard, Ravenna Army Ammunition Plant, Ravenna, Ohio.

Leidos Engineering of Ohio, Inc., 2015c. Submission Format Guidelines for the Ravenna Army Ammunition Plant Restoration Program, Version 21, Ravenna, Ohio, dated 21 October 2015.

Ohio Environmental Protection Agency (Ohio EPA) 2004. Director’s Final Findings and Orders (DFFO) for RVAAP, dated 10 June.

SAIC 2001. Phase II Remedial Investigation Report for the Winklepeck Burning Grounds at the Ravenna Army Ammunition Plant, Ravenna, Ohio, April 2001.

SAIC 2011a. Facility-Wide Safety and Health Plan for Environmental Investigations at the Ravenna Army Ammunition Plant, Ravenna, Ohio, dated 24 February.

SAIC 2011b. Facility-Wide Sampling and Analysis Plan and Facility-wide Quality Assurance Project Plan for Environmental Investigations at the Ravenna Army Ammunition Plant, Ravenna, Ohio, dated 24 February.

USACE 2015a. Performance Work Statement for Pilot Study and Feasibility Study at the Atlas Scrap Yard Camp Ravenna, Portage and Trumbull Counties, Ohio, dated 26 August.

USACE 2015b. Camp Ravenna Integrated Natural Resources Management Plan.

Vista Sciences Corporation 2012. Submission Format Guidelines Ravenna Army Ammunition Plant Version 20, dated 23 March.

APPENDIX A
PROJECT-SPECIFIC SITE SAFETY AND HEALTH PLAN

FINAL

Site Safety and Health Plan for a Pilot Study and Feasibility Study at RVAAP-50 Atlas Scrap Yard

Camp Ravenna
Ravenna, Ohio

19 February 2016

Contract No. W912QR-14-D-0001
Delivery Order No. 0004

Prepared for:

US Army Corps of Engineers
Louisville District
600 Martin Luther King Jr. Place
Louisville, Kentucky 40202

FINAL

Site Safety and Health Plan for a Pilot Study and Feasibility Study at RVAAP-50 Atlas Scrap Yard

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Louisville District
600 Martin Luther King Jr. Place
Louisville, Kentucky 40202

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ACRONYMS AND ABBREVIATIONS

Acronym	**Description**
ACGIH	American Conference of Governmental Industrial Hygienists
AHA	Activity hazard analysis
Alliant	Alliant Corporation
AOC	Area of Concern
Camp Ravenna	Camp Ravenna Joint Military Training Center
CDC	Center for Disease Control
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	*Code of Federal Regulations*
CIH	Certified Industrial Hygienist
COR	Contracting Officer's Representative
CPR	Cardiopulmonary Resuscitation
DEET	n,n-diethyl-m-toluamide
FWSAP	Facility-Wide Sampling and Analysis Plan
HAZWOPER	Hazardous Waste Operations and Emergency Response
IDW	Investigation Derived Waste
MSDS	Material Safety Data Sheet
NIOSH	National Institute of Occupational Safety and Health
OHARNG	Ohio Army National Guard
Ohio EPA	Ohio Environmental Protection Agency
OJT	On-the-Job Training
OSHA	Occupational Safety and Health Administration
PAH	Polycyclic Aromatic Hydrocarbon
PPE	Personal Protective Equipment
RCRA	Resource Conservation and Recovery Act
RVAAP	Ravenna Army Ammunition Plant
SSHO	Site Safety and Health Officer
SSHP	Site Safety and Health Plan
TLV	Threshold Limit Value
USACE	United States Army Corps of Engineers
UXO	Unexploded Ordnance
WBGT	Wet Bulb Globe Temperature

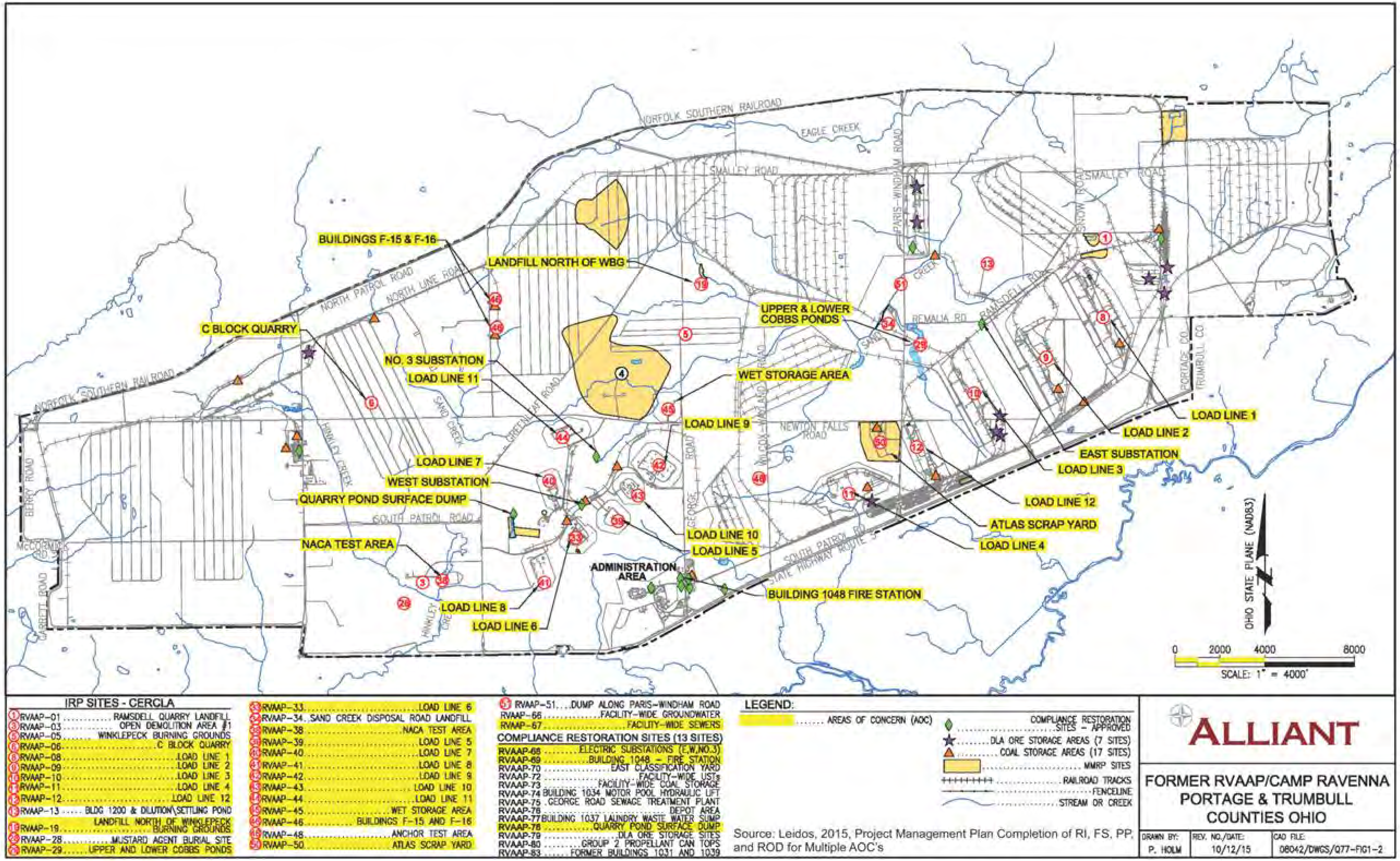
1.0 INTRODUCTION

Alliant Corporation (Alliant) prepared this Project-Specific Site Safety and Health Plan (SSHP) for the Pilot Study to be conducted as a part of the Pilot Study and Feasibility Study (FS) at the Atlas Scrap Yard area of concern (AOC) [former Ravenna Army Ammunition Plant (RVAAP)-50] at Camp Ravenna, Portage and Trumbull Counties, Ohio under Contract No. W912QR-14-D-0001, Delivery Order (DO) No. 0004.

The pilot study will consist of testing contaminated soils at the site for the suitability of using Vapor Energy Generator© (VEG©) technology to treat Polycyclic Aromatic Hydrocarbon (PAH)-impacted soil. VEG© technology involves ex-situ thermal treatment of impacted soils in an enclosed treatment chamber using steam. As an internal auger rotates the soil, the steam causes the contaminants to be released and captured by a vacuum system inside the chamber which then filters the gases out. The goal of the treatment is to reduce contaminants to non-detect levels or to below regulatory standards.

Figure 1-1 depicts Camp Ravenna and the location of the Atlas Scrap Yard AOC (RVAAP-50) in the south-central portion of the facility. This Project-Specific SSHP was developed in accordance with U.S. Army and Ohio Environmental Protection Agency (Ohio EPA) guidance documents to meet the requirements under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); the Resource Conservation and Recovery Act (RCRA); and other federal or state regulations that govern environmental restoration activities at the former RVAAP. This SSHP accompanies, and is to be used in conjunction with the Work Plan, and Project-Specific Quality Assurance Project Plan (QAPP) in addition to installation-wide plans to provide consistent programmatic and technical requirements for the field activities to be conducted for this project at the former RVAAP.

This SSHP sets forth the minimum requirements for protecting personnel involved in environmental field activities at Camp Ravenna. Standard procedures must be used to minimize the potential for personnel injury or illness. These will include on-site training, routine inspections, and enforcement of the health and safety requirements by project management. This plan follows and addresses requirements in the U. S. Army Corps of Engineers (USACE's) Safety and Occupational Health Requirements for Hazardous, Toxic, and Radioactive Waste and Ordnance and Explosive Waste Activities (USACE 2007). This SSHP complies with the requirements of the USACE Safety and Health Requirements Manual (USACE 2008); relevant Occupational Safety and Health Administration (OSHA) regulations; and other applicable federal, state, and local government safety and health requirements. This plan provides guidance on health and safety hazards and controls. A copy of this SSHP will be present at the work site.



Source: Leidos, 2015, Project Management Plan Completion of RI, FS, PP, and ROD for Multiple AOC's

Figure 1-1. Map of the Former RVAAP or Camp Ravenna

2.0 FACILITY DESCRIPTION AND CONTAMINATION CHARACTERIZATION

2.1 FACILITY DESCRIPTION

The former RVAAP, now known as the Camp Ravenna Joint Military Training Center (Camp Ravenna), located in northeastern Ohio within Portage and Trumbull Counties, is approximately three (3) miles east/northeast of the City of Ravenna and one (1) mile north/northwest of the City of Newton Falls (Figure 2-1). The facility is approximately 11 miles long and 3.5 miles wide. The facility is bounded by State Route 5, the Michael J. Kirwan Reservoir, and the CSX System Railroad to the south; Garret, McCormick, and Berry Roads to the west; the Norfolk Southern Railroad to the north; and State Route 534 to the east. In addition, the facility is surrounded by the communities of Windham, Garrettsville, Charlestown, and Wayland.

The facility was formerly used as a load, assemble, and pack facility for munitions production. As of September 2013, administrative accountability for the entire 21,683-acre facility has been transferred to the United States Property and Fiscal Officer (USP&FO) for Ohio and the property was subsequently licensed to the Ohio Army National Guard (OHARNG) for use as a military training site, Camp Ravenna. The facility restoration program involves cleanup of former production/operational areas throughout the facility related to former activities conducted under the RVAAP. References in this document to RVAAP relate to previous activities at the facility as related to former munitions production activities or to activities being conducted under the restoration/cleanup program. RVAAP is bound to the Director's Final Findings and Orders (DFFOs) issued 10 June 2004 by the Ohio Environmental Protection Agency (Ohio EPA) pursuant to the authority vested under Chapters 3734, 3745, and 6111 of the Ohio Revised Code (ORC). The objective of the Orders is to ensure that the public health, safety, and welfare, as well as the environment, is protected from the disposal, discharge, or release of contaminants. RVAAP is not on the United States Environmental Protection Agency (USEPA) National Priorities List, although it is in the USEPA Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS) database. The Ohio EPA is the lead environmental regulator for the RVAAP restoration program. The Installation is bound to the DFFOs, issued on 10 June 2004 by the Ohio EPA. The DFFOs form the basis for the implementation of a Comprehensive Environmental Response Compensation and Liability Act (CERCLA) based environmental remediation program at the Installation.

2.2 SITE DESCRIPTION

The Atlas Scrap Yard AOC (RVAAP-50), formerly known as the construction camp, is approximately 73 acres and is located in the southeastern portion of Camp Ravenna (Figure 1-2). The Atlas Scrap Yard has served several operational functions over the history of the former RVAAP, but the AOC was never used for munitions production activities. From 1940 to 1945, the Atlas Scrap Yard operated as a construction camp to house workers and their families while the facility was being constructed. By the end of World War II, the majority of buildings and structures at the Atlas Scrap Yard were demolished or relocated to other areas of the facility. The structures that remained were used to support roads and grounds maintenance activities. These remaining structures were razed after the Vietnam War. After the Vietnam War, the AOC became a stockpile storage area for bulk materials, including gravel, railroad ballasts, sand, and culvert pipes. Coal, used for building process heat, was piled in several areas of the AOC. The central-east portion of the AOC was a staging area for salvaged ammunition boxes from demilitarized Vietnam War-era munitions.

There is no fence around the AOC as a perimeter boundary, but the AOC is bordered by Newton Falls Road to the north and Paris-Windham Road to the east. Load Line 4 is located to the south of the AOC. The interior of the AOC is currently vegetated with shrub/scrub vegetation in unpaved areas and is forested around its perimeter. The north-central portion of the AOC is sparsely vegetated and has extensive gravel cover.

2.3 CONTAMINANTS

The Remedial Investigation (RI) [Leidos Engineering of Ohio, Inc. (Leidos), 2015] concluded that the Atlas Scrap Yard AOC was adequately characterized. The RI identified five (5) PAHs as chemicals of concern (COCs) at the site. The identified PAHs are benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and dibenz(a,h)anthracene. The PAH COCs were primarily identified in the 0-1 foot (ft) below ground surface (bgs) interval with the most contaminated areas being located southeast of the former T-4703 Roads and Grounds Maintenance Building, in the approximate vicinity of the stockpiled railroad ties. Additionally, a small area in the southern part of the site in the vicinity of a former incinerator has been characterized by elevated lead concentrations, and constitutes a lead “hot spot.”

Lead COCs will not be encountered during the field activities at the site. The onsite field activities will consist of conduction of a pilot-study for testing the efficacy of remediating PAH-impacted soils. The pilot study activities will take place in the northern area of the Atlas Scrap Yard AOC. Lead-impacted soils were discovered in the southern portion of the site in an area well away from the planned pilot study.

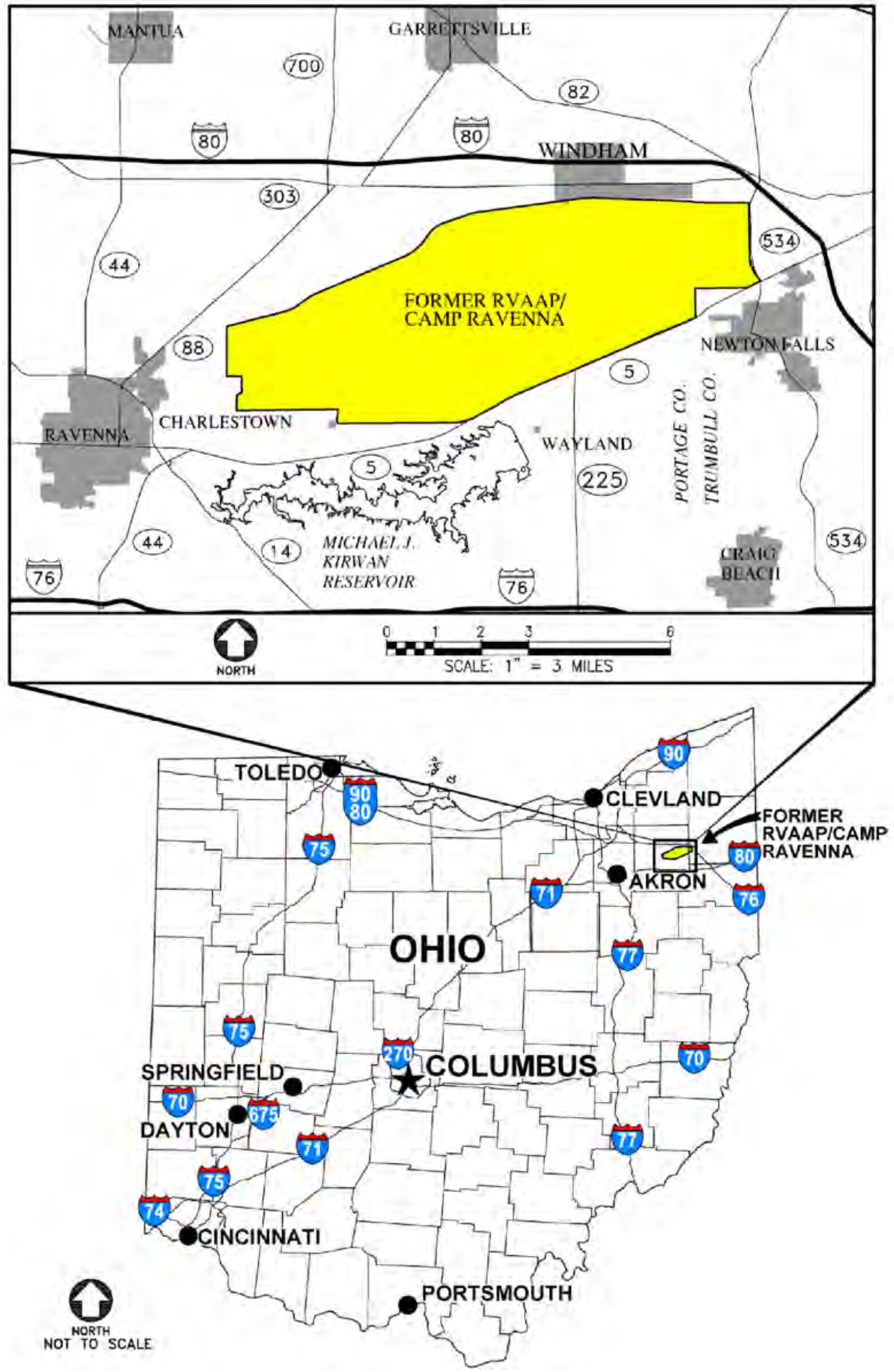


Figure 2-1. General Location and Orientation of Former RVAAP/Camp Ravenna

3.0 HAZARD/RISK ANALYSIS

The activity hazard analysis (AHA) identifies and assesses potential hazards that may be encountered by personnel and prescribes the required controls. The AHAs provide the project-specific hazards based on completion of a hazard inventory. The tasks are expected to consist of excavating site soils (to a maximum depth of 1 ft, operating a backhoe and an ex-situ thermal treatment system for treatment of site soils. collecting stockpile soil samples; decontaminating equipment (as necessary), and managing investigation derived waste (IDW). In general, given these tasks, the potential for unacceptable exposure to contaminants appears to be low. Expected tasks present a variety of physical hazards including biological, contact with equipment or falls into the excavations, noise, and heat/cold stress.

3.1 TASK-SPECIFIC ACTIVITY HAZARD ANALYSIS

Tables 3-1 and 3-2 present the AHAs, including task-specific job steps, hazards, actions to eliminate or minimize hazards, equipment to be used, and inspection, and training requirements, if appropriate, for all of the planned field activities during the pilot test. Specific tasks considered in this document are as follows:

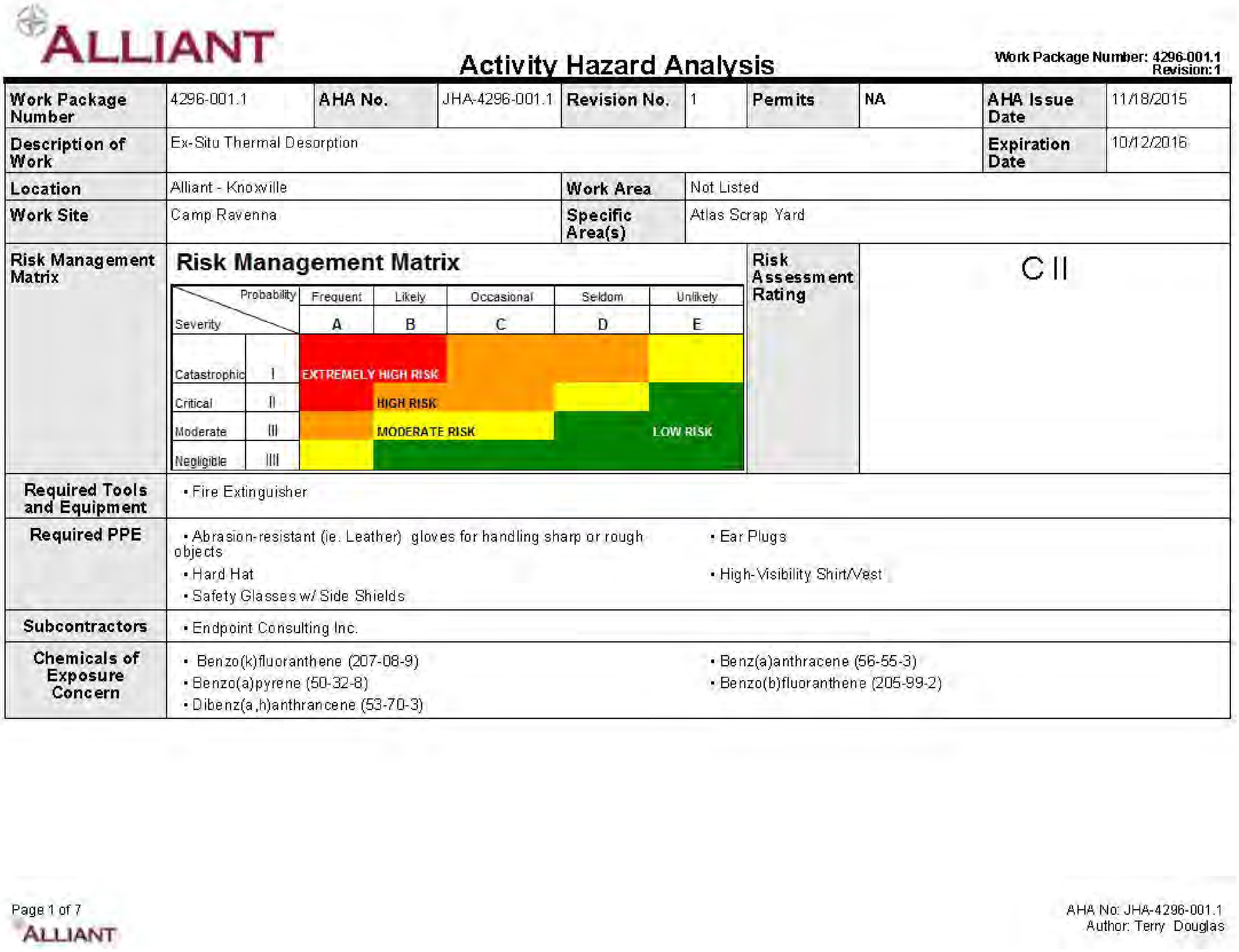
- Site mobilization and demobilization;
- Soil excavation and preparation of soil stockpiles using a backhoe;
- Soil sampling using spoons or scoops;
- Operation of the VEG treatment system;
- IDW handling; and
- Equipment decontamination.

The hazard assessments for each of these tasks are based on USACE expectations, as presented in the *USACE Safety and Health Requirements Manual* (USACE 2008), and some assumptions regarding the planned activities. Ultimately, the Alliant and the subcontractor will be responsible for ensuring that the hazards of each activity are adequately controlled.

3.2 POTENTIAL EXPOSURES

Table 3-3 provides information on potential exposures from the COCs (PAHs), and the chemicals that may be used during this field effort.

Table 3-1. Activity Hazard Analysis – Ex-Situ Thermal Desorption



ALLIANT

Activity Hazard Analysis

Work Package Number: 4296-001.1
Revision: 1

Work Package Number	4296-001.1	**AHA No.**	JHA-4296-001.1	**Revision No.**	1	**Permits**	NA	**AHA Issue Date**	11/18/2015
Description of Work	Ex-Situ Thermal Desorption							**Expiration Date**	10/12/2016
Location	Alliant - Knoxville			**Work Area**	Not Listed				
Work Site	Camp Ravenna			**Specific Area(s)**	Atlas Scrap Yard				
Risk Management Matrix	Risk Management Matrix (below)					**Risk Assessment Rating**	C II		
Required Tools and Equipment	• Fire Extinguisher								
Required PPE	• Abrasion-resistant (ie. Leather) gloves for handling sharp or rough objects • Hard Hat • Safety Glasses w/ Side Shields					• Ear Plugs • High-Visibility Shirt/Vest			
Subcontractors	• Endpoint Consulting Inc.								
Chemicals of Exposure Concern	• Benzo(k)fluoranthene (207-08-9) • Benzo(a)pyrene (50-32-8) • Dibenz(a,h)anthrancene (53-70-3)					• Benz(a)anthracene (56-55-3) • Benzo(b)fluoranthene (205-99-2)			

Risk Management Matrix

Severity \ Probability		Frequent A	Likely B	Occasional C	Seldom D	Unlikely E
Catastrophic	I	🟥 EXTREMELY HIGH RISK	🟥	🟧	🟧	🟨
Critical	II	🟥	🟧 HIGH RISK	🟧	🟨	🟩
Moderate	III	🟧	🟨 MODERATE RISK	🟨	🟩	🟩 LOW RISK
Negligible	IIII	🟨	🟩	🟩	🟩	🟩

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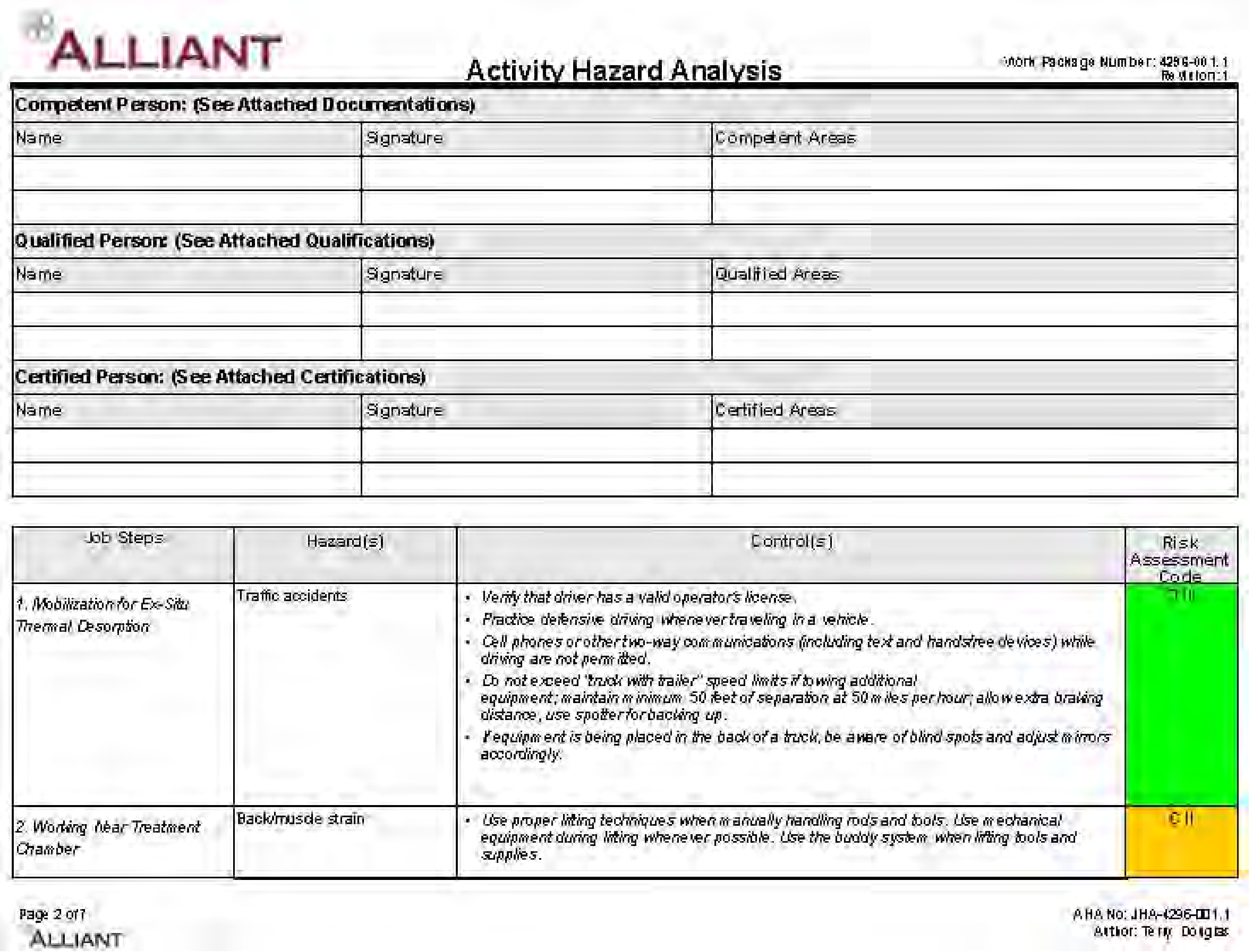
AHA No: JHA-4296-001.1
Author: Terry Douglas

Table 3-1. Activity Hazard Analysis – Ex-Situ Thermal Desorption (Continued)



ALLIANT

Activity Hazard Analysis

Work Package Number: 4296-001.1
Revision: 1

Competent Person: (See Attached Documentations)		
Name	Signature	Competent Areas
Qualified Person: (See Attached Qualifications)		
Name	Signature	Qualified Areas
Certified Person: (See Attached Certifications)		
Name	Signature	Certified Areas

Job Steps	Hazard(s)	Control(s)	Risk Assessment Code
1. Mobilization for Ex-Situ Thermal Desorption	Traffic accidents	• *Verify that driver has a valid operator's license.* • *Practice defensive driving whenever traveling in a vehicle.* • *Cell phones or other two-way communications (including text and handsfree devices) while driving are not permitted.* • *Do not exceed "truck with trailer" speed limits if towing additional equipment; maintain minimum 50 feet of separation at 50 miles per hour; allow extra braking distance, use spotter for backing up.* • *If equipment is being placed in the back of a truck, be aware of blind spots and adjust mirrors accordingly.*	🟩 [illegible] II
2. Working Near Treatment Chamber	Back/muscle strain	• *Use proper lifting techniques when manually handling rods and tools. Use mechanical equipment during lifting whenever possible. Use the buddy system when lifting tools and supplies.*	🟨 C II

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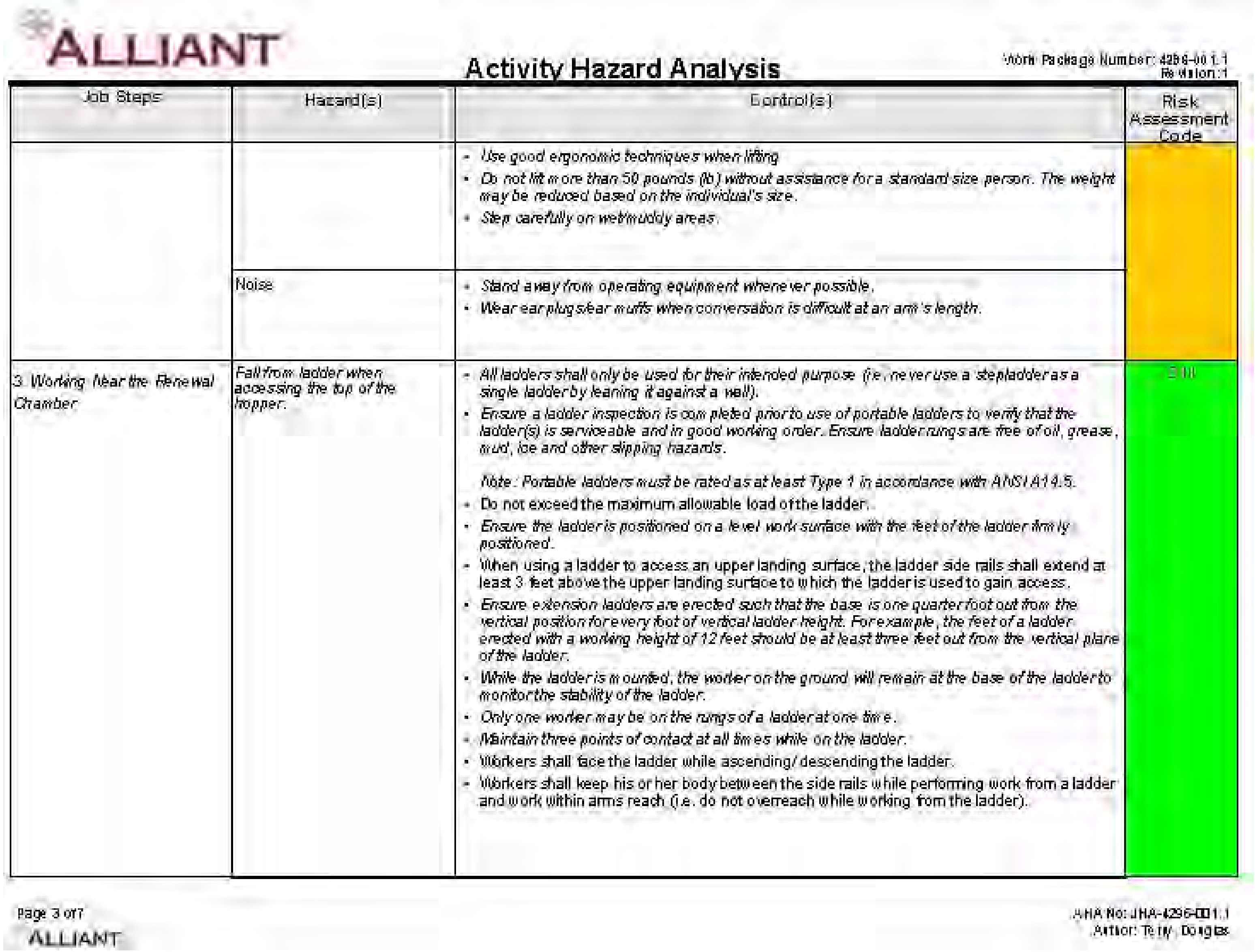
AHA No: JHA-4296-001.1
Author: Terry Douglas

Table 3-1. Activity Hazard Analysis – Ex-Situ Thermal Desorption (Continued)



ALLIANT

Activity Hazard Analysis

Work Package Number: 4296-001.1
Revision: 1

Job Steps	Hazard(s)	Control(s)	Risk Assessment Code
		• *Use good ergonomic techniques when lifting* • *Do not lift more than 50 pounds (lb) without assistance for a standard size person. The weight may be reduced based on the individual's size.* • *Step carefully on wet/muddy areas.*	🟧
	Noise	• *Stand away from operating equipment whenever possible.* • *Wear ear plugs/ear muffs when conversation is difficult at an arm's length.*	
3. Working Near the Renewal Chamber	*Fall from ladder when accessing the top of the hopper.*	• *All ladders shall only be used for their intended purpose (i.e., never use a stepladder as a single ladder by leaning it against a wall).* • *Ensure a ladder inspection is completed prior to use of portable ladders to verify that the ladder(s) is serviceable and in good working order. Ensure ladder rungs are free of oil, grease, mud, ice and other slipping hazards.* *Note: Portable ladders must be rated as at least Type 1 in accordance with ANSI A14.5.* • Do not exceed the maximum allowable load of the ladder. • *Ensure the ladder is positioned on a level work surface with the feet of the ladder firmly positioned.* • When using a ladder to access an upper landing surface, the ladder side rails shall extend at least 3 feet above the upper landing surface to which the ladder is used to gain access. • *Ensure extension ladders are erected such that the base is one quarter foot out from the vertical position for every foot of vertical ladder height. For example, the feet of a ladder erected with a working height of 12 feet should be at least three feet out from the vertical plane of the ladder.* • *While the ladder is mounted, the worker on the ground will remain at the base of the ladder to monitor the stability of the ladder.* • *Only one worker may be on the rungs of a ladder at one time.* • *Maintain three points of contact at all times while on the ladder.* • Workers shall face the ladder while ascending/descending the ladder. • Workers shall keep his or her body between the side rails while performing work from a ladder and work within arms reach (i.e. do not overreach while working from the ladder).	3 III

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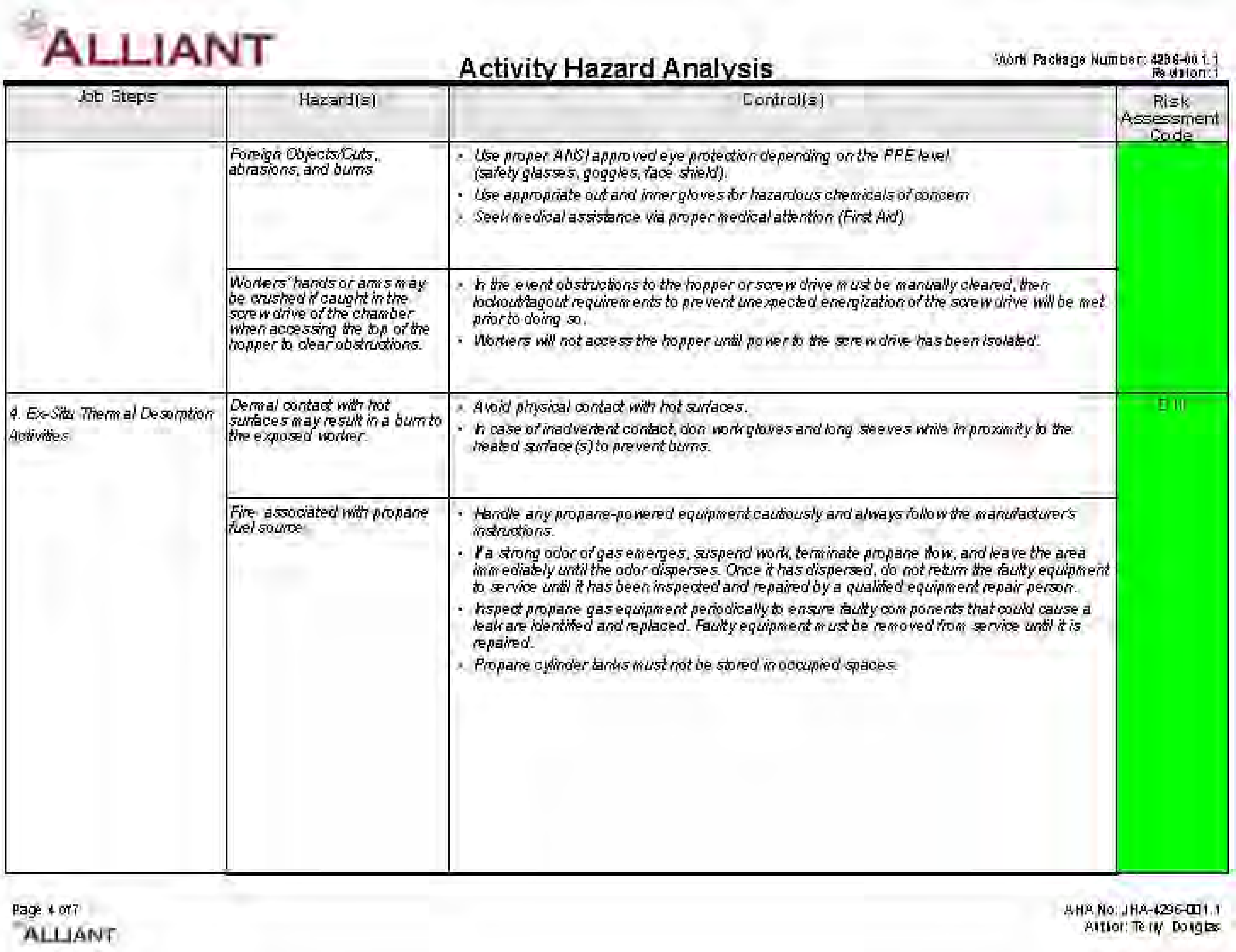
AHA No: JHA-4296-001.1
Author: Terry Douglas

Table 3-1. Activity Hazard Analysis – Ex-Situ Thermal Desorption (Continued)



ALLIANT

Activity Hazard Analysis

Work Package Number: 4296-001.1
Revision: 1

Job Steps	Hazard(s)	Control(s)	Risk Assessment Code
	Foreign Objects/Cuts, abrasions, and burns	- Use proper ANSI approved eye protection depending on the PPE level (safety glasses, goggles, face shield). - Use appropriate out and inner gloves for hazardous chemicals of concern - Seek medical assistance via proper medical attention (First Aid)	
	Workers' hands or arms may be crushed if caught in the screw drive of the chamber when accessing the top of the hopper to clear obstructions.	- In the event obstructions to the hopper or screw drive must be manually cleared, then lockout/tagout requirements to prevent unexpected energization of the screw drive will be met prior to doing so. - Workers will not access the hopper until power to the screw drive has been isolated.	
4. Ex-Situ Thermal Desorption Activities	Dermal contact with hot surfaces may result in a burn to the exposed worker.	- Avoid physical contact with hot surfaces. - In case of inadvertent contact, don work gloves and long sleeves while in proximity to the heated surface(s) to prevent burns.	[illegible]
	Fire associated with propane fuel source.	- Handle any propane-powered equipment cautiously and always follow the manufacturer's instructions. - If a strong odor of gas emerges, suspend work, terminate propane flow, and leave the area immediately until the odor disperses. Once it has dispersed, do not return the faulty equipment to service until it has been inspected and repaired by a qualified equipment repair person. - Inspect propane gas equipment periodically to ensure faulty components that could cause a leak are identified and replaced. Faulty equipment must be removed from service until it is repaired. - Propane cylinder tanks must not be stored in occupied spaces.	

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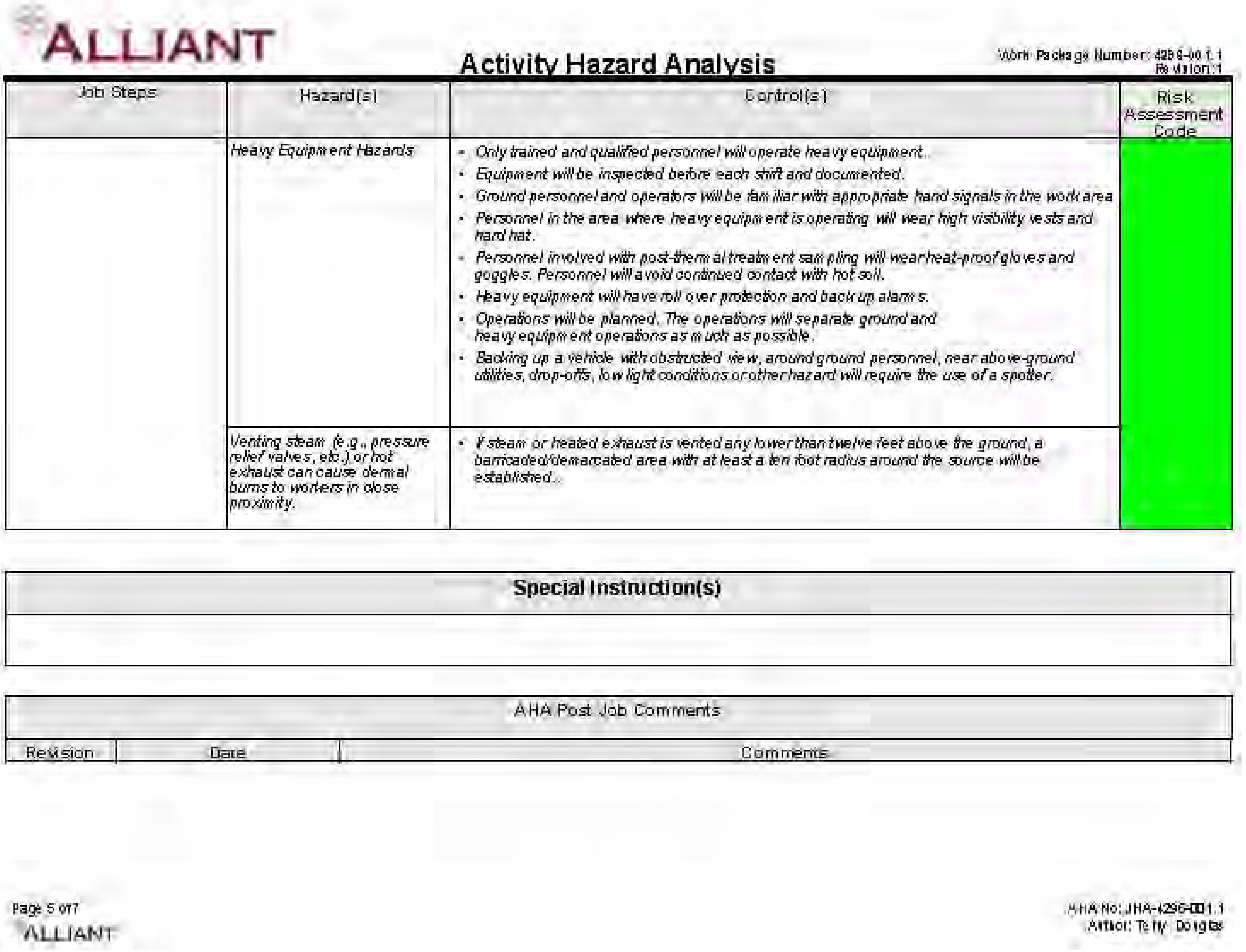
AHA No: JHA-4296-001.1
Author: Terry Douglas

Table 3-1. Activity Hazard Analysis – Ex-Situ Thermal Desorption (Continued)



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Activity Hazard Analysis

Work Package Number: 4296-001.1
Revision: 1

Job Steps	Hazard(s)	Control(s)	Risk Assessment Code
	Heavy Equipment Hazards	*Only trained and qualified personnel will operate heavy equipment..* *Equipment will be inspected before each shift and documented.* *Ground personnel and operators will be familiar with appropriate hand signals in the work area* *Personnel in the area where heavy equipment is operating will wear high visibility vests and hard hat.* *Personnel involved with post-thermal treatment sampling will wear heat-proof gloves and goggles. Personnel will avoid continued contact with hot soil.* *Heavy equipment will have roll over protection and back up alarms.* *Operations will be planned. The operations will separate ground and heavy equipment operations as much as possible.* *Backing up a vehicle with obstructed view, around ground personnel, near above-ground utilities, drop-offs, low light conditions or other hazard will require the use of a spotter.*	🟩
	Venting steam (e.g., pressure relief valves, etc.) or hot exhaust can cause dermal burns to workers in close proximity.	*If steam or heated exhaust is vented any lower than twelve feet above the ground, a barricaded/demarcated area with at least a ten foot radius around the source will be established..*	

Special Instruction(s)

AHA Post Job Comments		
Revision	Date	Comments

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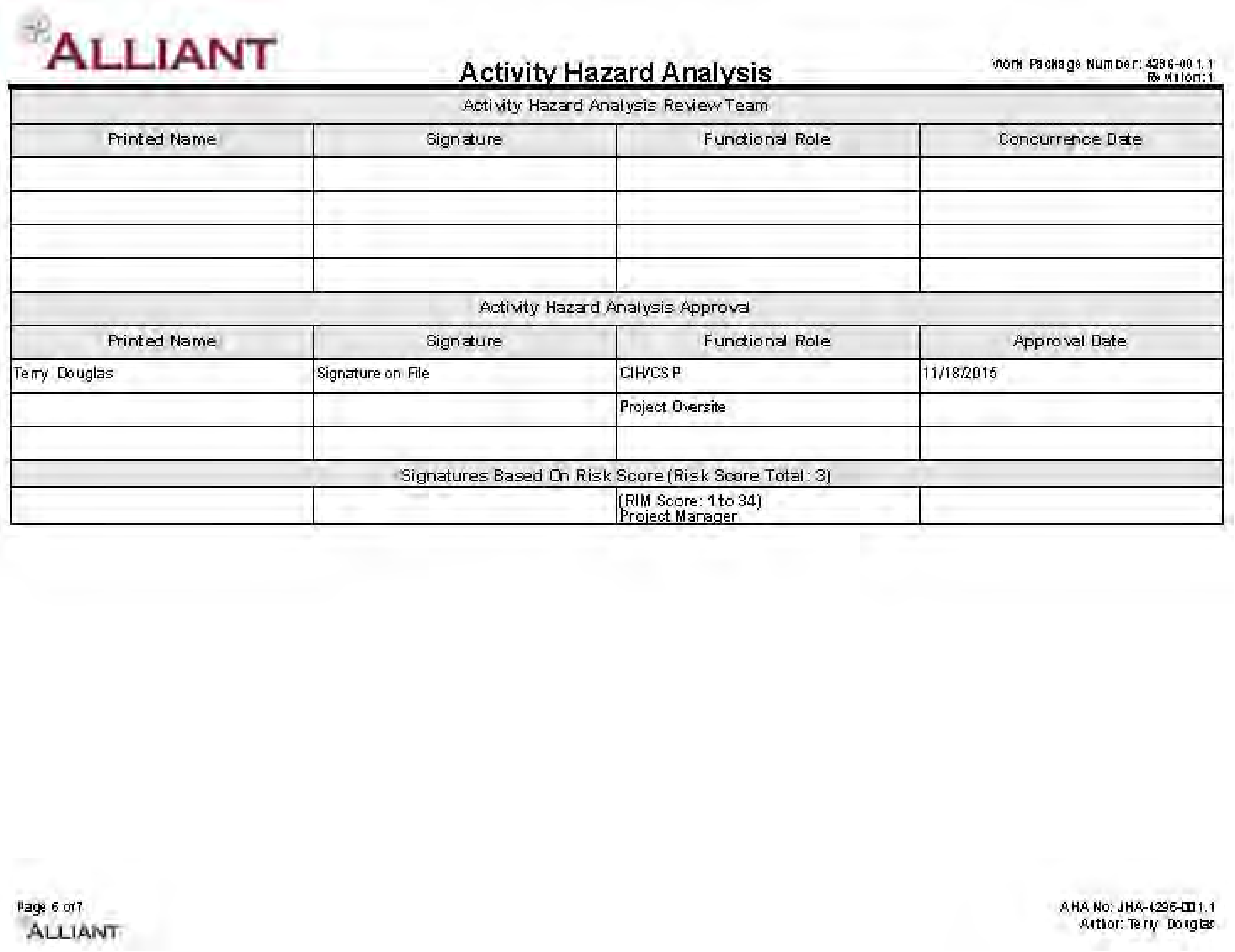
AHA No: JHA-4296-001.1
Author: Terry Douglas

Table 3-1. Activity Hazard Analysis – Ex-Situ Thermal Desorption (Continued)



ALLIANT

Activity Hazard Analysis

Work Package Number: 4296-001.1
Revision: 1

Activity Hazard Analysis Review Team			
Printed Name	**Signature**	**Functional Role**	**Concurrence Date**

Activity Hazard Analysis Approval			
Printed Name	**Signature**	**Functional Role**	**Approval Date**
Terry Douglas	Signature on File	CIH/CSP	11/18/2015
		Project Oversite	

Signatures Based On Risk Score (Risk Score Total: 3)			
		(RIM Score: 1 to 34) Project Manager	

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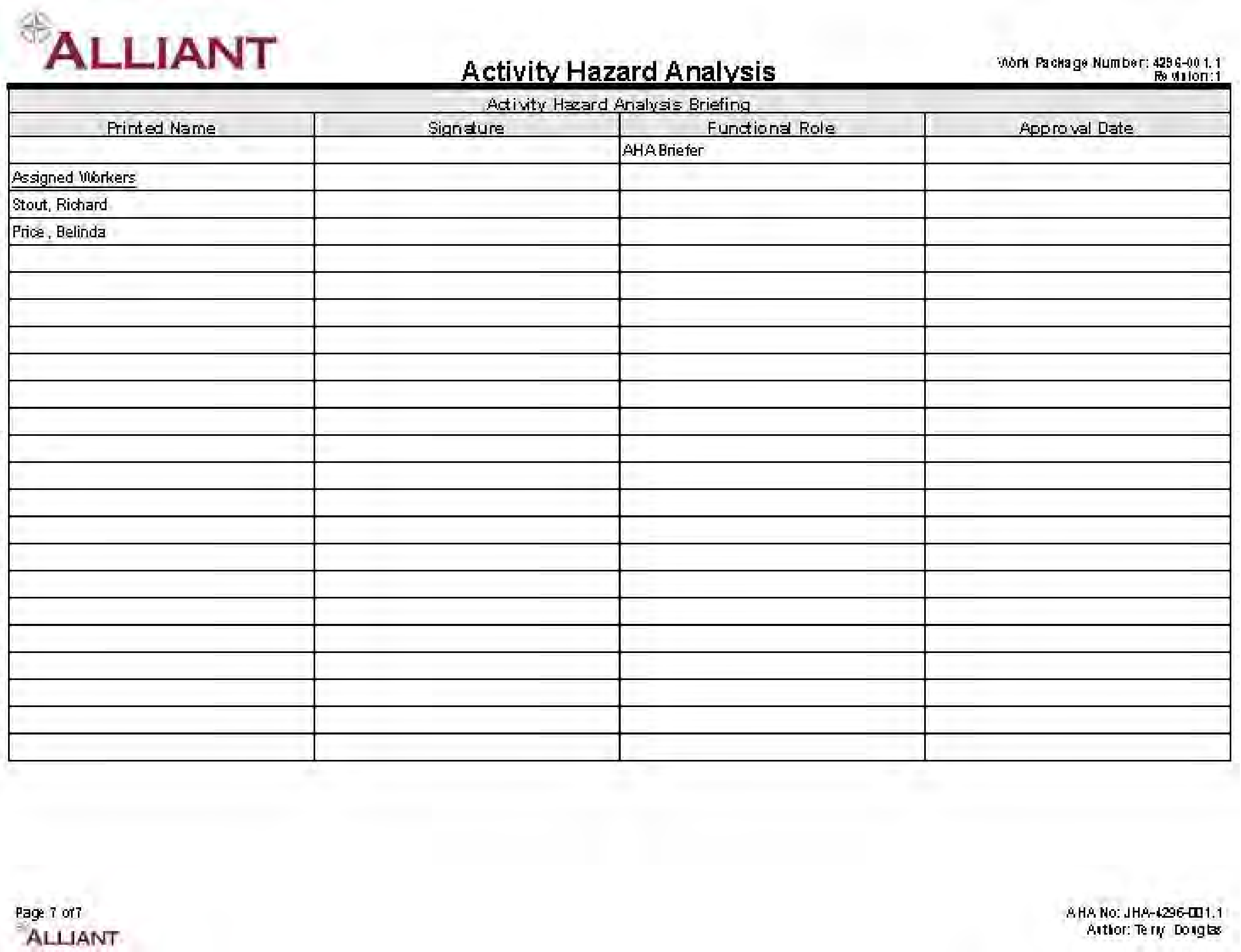
AHA No: JHA-4296-001.1
Author: Terry Douglas

Table 3-1. Activity Hazard Analysis – Ex-Situ Thermal Desorption (Continued)



ALLIANT

Activity Hazard Analysis

Work Package Number: 4296-001.1
Revision: 1

Activity Hazard Analysis Briefing

Printed Name	Signature	Functional Role	Approval Date
		AHA Briefer	
Assigned Workers			
Stout, Richard			
Price , Belinda			

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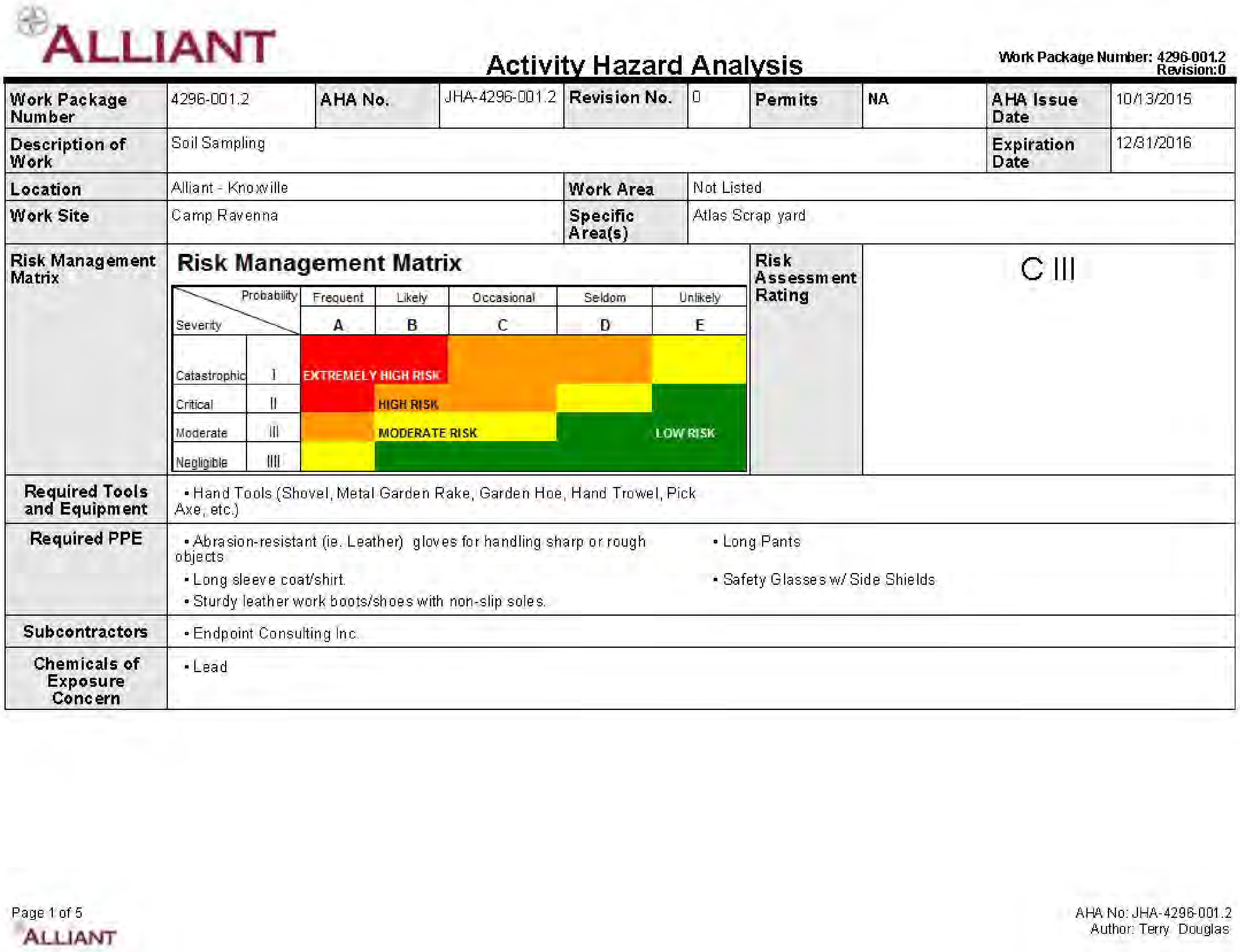
ALLIANT

AHA No: JHA-4296-001.1
Author: Terry Douglas

Table 3-2. Activity Hazard Analysis – Soil Sampling



ALLIANT

Activity Hazard Analysis

Work Package Number: 4296-001.2
Revision:0

Work Package Number	4296-001.2	**AHA No.**	JHA-4296-001.2	**Revision No.**	0	**Permits**	NA
AHA Issue Date	10/13/2015						
Description of Work	Soil Sampling						
Expiration Date	12/31/2016						
Location	Alliant - Knoxville	**Work Area**	Not Listed				
Work Site	Camp Ravenna	**Specific Area(s)**	Atlas Scrap yard				

Risk Management Matrix

Risk Management Matrix

Severity \ Probability		Frequent A	Likely B	Occasional C	Seldom D	Unlikely E
Catastrophic	I	🟥 EXTREMELY HIGH RISK	🟥	🟧	🟧	🟨
Critical	II	🟥	🟧 HIGH RISK	🟧	🟨	🟩
Moderate	III	🟧	🟨 MODERATE RISK	🟨	🟩	🟩 LOW RISK
Negligible	IIII	🟨	🟩	🟩	🟩	🟩

Risk Assessment Rating: C III

Required Tools and Equipment	• Hand Tools (Shovel, Metal Garden Rake, Garden Hoe, Hand Trowel, Pick Axe, etc.)
Required PPE	• Abrasion-resistant (ie. Leather) gloves for handling sharp or rough objects • Long sleeve coat/shirt. • Sturdy leather work boots/shoes with non-slip soles. • Long Pants • Safety Glasses w/ Side Shields
Subcontractors	• Endpoint Consulting Inc.
Chemicals of Exposure Concern	• Lead

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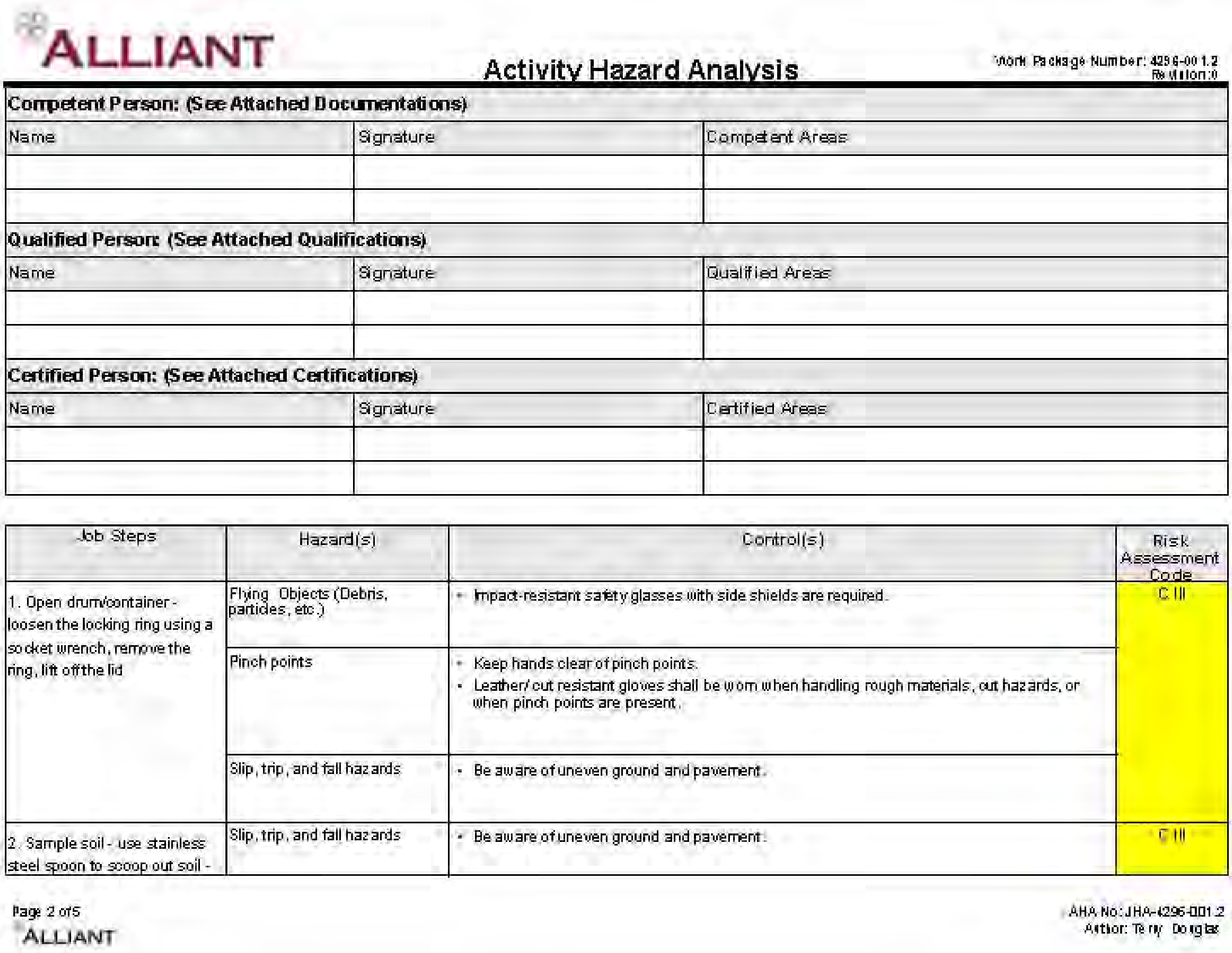
AHA No: JHA-4296-001.2
Author: Terry Douglas

Table 3-2. Activity Hazard Analysis – Soil Sampling (Continued)



ALLIANT

Activity Hazard Analysis

Work Package Number: 4296-001.2
Revision: 0

Competent Person: (See Attached Documentations)		
Name	Signature	Competent Areas
Qualified Person: (See Attached Qualifications)		
Name	Signature	Qualified Areas
Certified Person: (See Attached Certifications)		
Name	Signature	Certified Areas

Job Steps	Hazard(s)	Control(s)	Risk Assessment Code
1. Open drum/container - loosen the locking ring using a socket wrench, remove the ring, lift off the lid	Flying Objects (Debris, particles, etc.)	• Impact-resistant safety glasses with side shields are required.	C III
	Pinch points	• Keep hands clear of pinch points. • Leather/ cut resistant gloves shall be worn when handling rough materials, cut hazards, or when pinch points are present.	
	Slip, trip, and fall hazards	• Be aware of uneven ground and pavement.	
2. Sample soil - use stainless steel spoon to scoop out soil -	Slip, trip, and fall hazards	• Be aware of uneven ground and pavement.	C III

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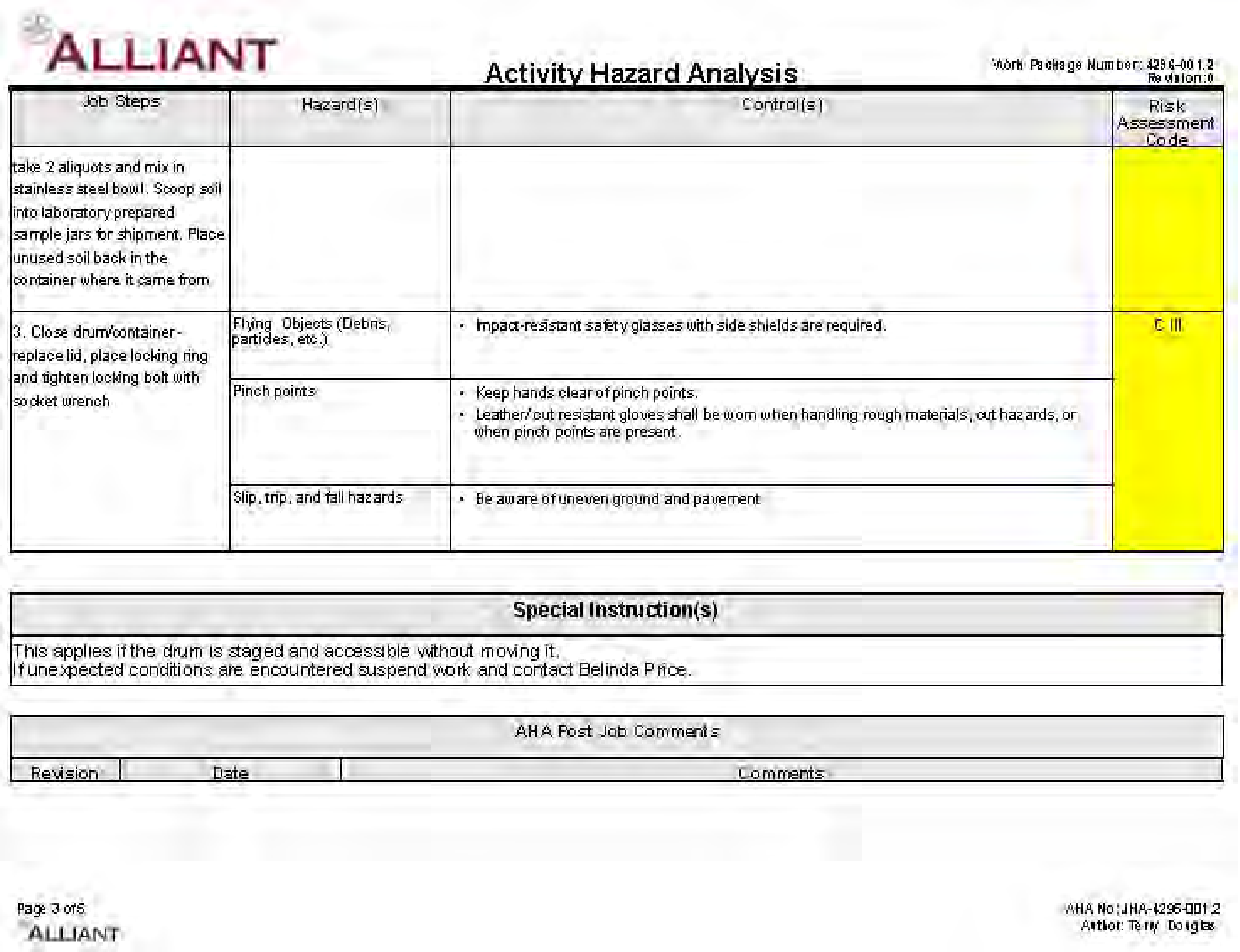
AHA No: JHA-4296-001.2
Author: Terry Douglas

Table 3-2. Activity Hazard Analysis – Soil Sampling (Continued)



ALLIANT

Activity Hazard Analysis

Work Package Number: 4296-001.2
Revision: 0

Job Steps	Hazard(s)	Control(s)	Risk Assessment Code
take 2 aliquots and mix in stainless steel bowl. Scoop soil into laboratory prepared sample jars for shipment. Place unused soil back in the container where it came from			
3. Close drum/container - replace lid, place locking ring and tighten locking bolt with socket wrench	Flying Objects (Debris, particles, etc.)	• Impact-resistant safety glasses with side shields are required.	C III
	Pinch points	• Keep hands clear of pinch points. • Leather/cut resistant gloves shall be worn when handling rough materials, cut hazards, or when pinch points are present.	
	Slip, trip, and fall hazards	• Be aware of uneven ground and pavement	

Special Instruction(s)

This applies if the drum is staged and accessible without moving it.
If unexpected conditions are encountered suspend work and contact Belinda Price.

AHA Post Job Comments

Revision	Date	Comments

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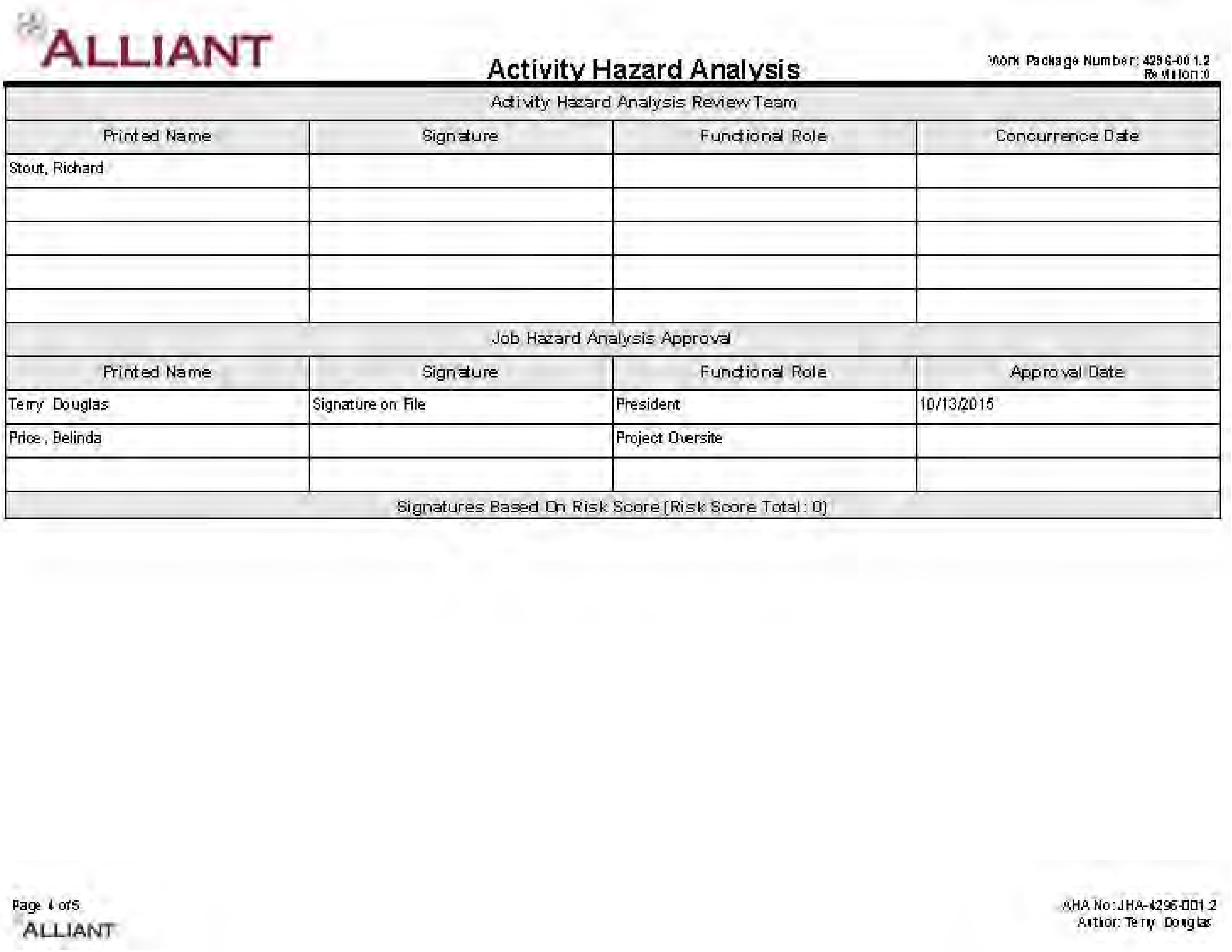
AHA No: JHA-4296-001.2
Author: Terry Douglas

Table 3-2. Activity Hazard Analysis – Soil Sampling (Continued)



ALLIANT

Activity Hazard Analysis

Work Package Number: 4296-001.2
Revision:0

Activity Hazard Analysis Review Team

Printed Name	Signature	Functional Role	Concurrence Date
Stout, Richard			

Job Hazard Analysis Approval

Printed Name	Signature	Functional Role	Approval Date
Terry Douglas	Signature on File	President	10/13/2015
Price, Belinda		Project Oversite	

Signatures Based On Risk Score (Risk Score Total: 0)

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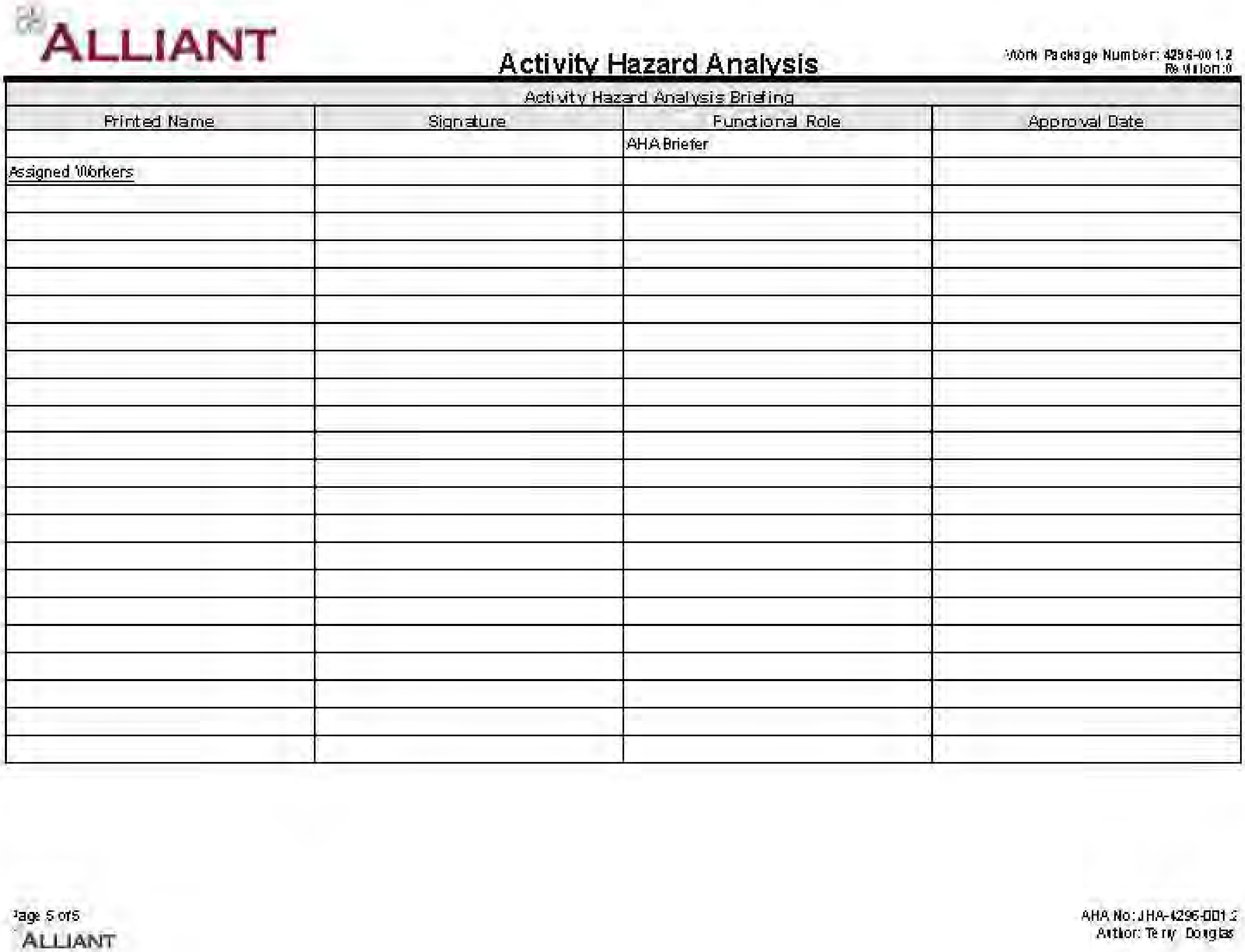
AHA No: JHA-4296-001.2
Author: Terry Douglas

Table 3-2. Activity Hazard Analysis – Soil Sampling (Continued)



ALLIANT

Activity Hazard Analysis

Work Package Number: 4296-001.2
Revision:0

Activity Hazard Analysis Briefing			
Printed Name	Signature	Functional Role	Approval Date
		AHA Briefer	
Assigned Workers			

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ALLIANT

AHA No: JHA-4296-001.2
Author: Terry Douglas

Table 3-3. Potential Exposures

Chemical	Health Effects/Potential Hazards[a]	Chemical and Physical Properties[a]	Exposure Route(s)[a]
Benzo(a)anthracene	Known animal carcinogen, may cause skin irritation, cataracts, kidney and liver damage, and jaundice.	Yellow-blue solid; VP: $2.2\text{x}10^{-8}$ mmHg; FP: no data; IP: N/A	Absorption Ingestion Contact
Benzo(a)pyrene	Known animal carcinogen, may cause skin irritation, cataracts, kidney and liver damage, and jaundice.	Colorless solid; VP: $5.7\text{x}10^{-9}$ mmHg; FP: no data; IP: N/A	Inhalation Ingestion Contact
Benzo(b)fluoranthene	Known animal carcinogen, may cause skin irritation, cataracts, kidney and liver damage, and jaundice.	Colorless solid (needles); VP: $5.0\text{x}10^{-7}$ mmHg; FP: no data; IP: N/A	Inhalation Ingestion Contact
Benzo(k)fluoranthene.	Known animal carcinogen, may cause skin irritation, cataracts, kidney and liver damage, and jaundice.	Pale Yellow solid (needles); VP: $9.59\text{x}10^{-11}$ mmHg; FP: no data; IP: N/A	Inhalation Ingestion Contact
Dibenz(a,h)anthracene.	Known animal carcinogen, may cause skin irritation, cataracts, kidney and liver damage, and jaundice.	Colorless solid; VP: $1.0\text{x}10^{-10}$ mmHg; FP: no data; IP: N/A	Inhalation Ingestion Contact
Other Potential Exposures			
Propane (for fueling the treatment system)	Dizziness, confusion, excitation, asphyxia, liquid: frostbite	Colorless, odorless liquid/gas (may have odorant added)	Inhalation Ingestion Contact
Diesel (used for fuel for heavy equipment)	Irritation of skin and inflammation, respiratory system; dizziness; headache; nausea; central nervous system	Brown, slightly viscous liquid, with characteristic odor; FP: 125.6°F	Inhalation Ingestion Contact
Diesel Exhaust	Irritation of eyes and respiratory system; potential occupational carcinogen	Appearance odor and properties vary depending upon the specific diesel exhaust component	Inhalation Contact
Gasoline (used for fuel)	Potential carcinogen per NIOSH, dizziness, eye irritation, dermatitis	Liquid with aromatic odor; FP: -45°F; VP: 38-300 mm	Inhalation Absorption Ingestion Contact

[a] From http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=122&tid=25

PAH = Polycyclic aromatic hydrocarbon.
SVOC = Semi-volatile organic compound.
VP = Vapor pressure.
FP = Flash point.
IP = Ionization potential.
NA = Not available.
NIOSH = National Institute of Occupational Safety and Health.

4.0 STAFF ORGANIZATION, QUALIFICATION AND RESPONSIBILITIES

This section presents the general lines of authority, responsibilities, and communication procedures concerning site safety and health and emergency response. It includes key positions.

- Project Manager;
- Certified Industrial Hygienist (CIH);
- Field oversight representative;
- Site Safety and Health Officer (SSHO); and
- All subcontractors and suppliers.

4.1 PROGRAM MANAGER

The Program Manager will ensure conformance with corporate and USACE policies and procedures. Specific responsibilities of the Program Manager are as follows:

- Coordinate with USACE personnel;
- Ensure project managers satisfy USACE health and safety requirements;
- Ensure project staff implement the SSHP;
- Ensure projects have the necessary resources to operate safely; and
- Ensure project personnel have the appropriate regard for safe job performance.
- Exercise Stop Work Authority if unsafe work conditions develop.

4.2 CERTIFIED INDUSTRIAL HYGIENIST

The CIH manages the health and safety program. This includes establishing health and safety policies and procedures, supporting project and office activities, and verifying safe work practices and conditions. The specific responsibilities of the CIH are as follows:

- Coordinate with USACE health and safety personnel;
- Review and approve SSHPs;
- Approve downgrades in personal protective equipment (PPE) or protective procedures; and
- Interface with project personnel through routine communications and audits of selected projects.
- Exercise Stop Work Authority if unsafe work conditions develop.

4.3 PROJECT MANAGER

The Project Manager will be responsible for overall project execution. The responsibilities of the Project Manager are as follows:

- Coordinate with USACE personnel, including reporting accidents and incidents to the USACE Project Manager immediately and submitting written reports within 2 working days;
- Ensure implementation of this SSHP and all project-specific addenda;
- Maintain auditable project documentation of all required records;
- Ensure that a qualified SSHO is designated; and
- Maintain a current copy of this SSHP and the project-specific addenda.

- Exercise Stop Work Authority if unsafe work conditions develop.

4.4 FIELD OVERSIGHT REPRESENTATIVE

The field oversight representative will oversee the field activities associated with a project and is responsible for site accessibility, safety, and quality assurance. He will enforce the field requirements of this SSHP and project-specific addenda. Specific responsibilities of the Field oversight representative are as follows:

- Enforce compliance with this SSHP and the project-specific addenda;
- Coordinate on-site operations, including subcontractor activities;
- Ensure that subcontractors follow the requirements of this SSHP and the project-specific addenda;
- Coordinate and control any emergency response actions;
- Ensure that at least one person per field team, who is currently certified in first aid and cardiopulmonary resuscitation (CPR), is on-site during site operations; and
- Maintain current copies of this SSHP, the project-specific addenda, and the USACE Safety and Health Requirements Manual (USACE 2008) on-site.
- Exercise Stop Work Authority if unsafe work conditions develop.

4.5 CONTRACTOR SITE SAFETY AND HEALTH OFFICER

The Alliant field oversight representative/SSHO will implement this SSHP, make health and safety decisions for specific health and safety activities, and verify the effectiveness of the health and safety program. The SSHO's qualifications include, at a minimum, experience with similar projects, knowledge of and understanding of this SSHP and the project-specific addenda, and the ability to use the required monitoring equipment. The SSHO's primary responsibilities will be as follows:

- Stop work or upgrade protective measures (including protective clothing) if uncontrolled health and safety hazards are encountered. Indications of uncontrolled health and safety hazards include monitoring instrument readings in excess of the established action limits, heavy equipment without back-up alarms, exposed unexploded ordnance (UXO), unguarded moving/rotating equipment, exposed electrical connections, non-compliance with health and safety requirements, encountering liquids other than water, soil staining suggestive of unexpectedly high concentrations of non-volatile contaminants. The SSHO authorizes resumption of work following correction of the adverse condition(s).
- Implement and verify compliance with this SSHP and the project-specific addenda and report to the field oversight representative, Project Manager, and Health and Safety Manager any deviations from anticipated conditions.
- Conduct daily safety inspections using the form provided in Appendix A.
- Document deficiencies identified in the daily inspections and responsible parties, procedures, and timetables for correction.
- Ensure that site personnel have access to this plan and are aware of its provisions.
- Conduct a site-specific pre-entry health and safety briefing covering potential chemical and physical hazards, safe work practices, and emergency procedures.
- Maintain on-site auditable documentation of:

  - Material Safety Data Sheets (MSDS) for applicable materials utilized at the site;
  - Daily tailgate and health and safety training for site workers and visitors (Appendix A);
  - Calibration/maintenance of field instruments such as photoionization detectors, combustible gas indicators;
  - Calibration standards tracking;
  - Environmental and personal exposure monitoring results (Appendix A);
  - Notification of accidents/incidents (Appendix A);
  - Reports of any overexposure or excessive levels;
  - Notification of employees of exposure data; and
  - Medical surveillance.

- Confirm that all on-site personnel have received the required training (see Section 5.0).
- Issue respirators, as necessary, and ensure that all respirator users have received medical clearance within the last year, have been properly trained, and have been successfully fitted for respiratory protection (respiratory protection is not anticipated for this field effort).
- Verify that this SSHP's and the project-specific addenda's emergency points of contact are correct and supply correcting information as necessary.
- Ensure that all monitoring equipment is operating according to the manufacturer's specifications and perform field checks of instrument calibration.
- Ensure monitoring for potential on-site exposures is conducted in accordance with this SSHP and its project-specific addenda.
- Investigate accidents and near accidents and report (in concert with the field oversight representative) findings to the Project Manager and CIH.
- Conduct daily "tailgate" safety briefings using the form provided in Appendix A.
- Control visitor access to the exclusion zone.
- Exercise Stop Work Authority if unsafe work conditions develop.

5.0 TRAINING

Personnel participating in the investigation of an AOC are subject to the training requirements presented in Table 5-1 and discussed below.

The following paragraphs briefly summarize the training requirements. These summaries include a course description and guidance on who must take each course.

5.1 OFF-SITE TRAINING

The 40-hr Hazardous Waste Site Worker course is required for hazardous, toxic, and radioactive waste activities in the exclusion (contamination) zone, contamination reduction (buffer) zone, or other hazardous areas on-site including areas of sample preparation and packaging. Three days of relevant field experience are required in conjunction with this training.

Table 5-1. Training Requirements

Training	Worker	Supervisor	Site Visitor (exclusion zone)
HAZWOPER (40-hr, 3-day OJT)	√	√	√
HAZWOPER Annual Refresher (8 hr)	√	√	√
HAZWOPER Supervisors Training (8 hr)		√	
CPR and First Aid Training (required for a minimum of one person per field team)	√	√	√
General Hazard Communication Training (contained in 40- and 8-hr courses)	√	√	√
Respiratory Protection Training (required only if respirators are worn; contained in 40-hr course)	√	√	√
Hearing Conservation Training (for workers in hearing conservation program; contained in 40- and 8-hr courses)	√	√	√
Pre-entry Briefing	√	√	√
Site-specific Hazard Communication (contained in pre-entry briefing)	√	√	√
Safety Briefing (daily and whenever conditions or tasks change)	√	√	√
Equipment-specific Training (equipment operators)	√	√	

√ = Required
CPR = Cardiopulmonary Resuscitation
HAZWOPER = Hazardous Waste Operations and Emergency Response
OJT = On-the-Job Training

The 8-hr Hazardous Waste Refresher course is required annually to maintain currency in the 40-hr course.

General Hazard Communication Training is required for all site workers. This training must communicate the risks and protective measures for chemicals that employees may encounter. This requirement is met by taking the 40-hr Hazardous Waste Site Worker course and the site-specific hazard communication training addressing the chemicals in use on the project. MSDSs must be kept on-site during field investigations for all chemicals expected to be encountered or used on-site.

At least one on-site employee must be certified in CPR and first aid. For multiple field teams working under the required buddy system, at least one field team member must be certified in CPR and first aid. The 43.5-hr American Red Cross Emergency Response training is no longer required.

Respiratory Protection Training is required for all individuals who wear respirators. This requirement can be met by taking the 40-hr Hazardous Waste Site Worker course, annual refreshers, and site-specific training covering the types of respirators to be used on-site. Respirator fit-test certifications must be kept on-site for anyone who might wear one.

Hearing Conservation Training is required on an annual basis by 29 Code of Federal Regulations (CFR) 1910.95 for all employees enrolled in a hearing conservation program. This requirement includes all employees exposed to occupational noise in excess of 85 dB on a time-weighted average.

5.2 SITE-SPECIFIC TRAINING

Personnel on-site must receive the investigation-specific safety training. Two versions of this training will be used. The site worker version will contain full information regarding site hazards, hazard controls, and emergency procedures. A shortened version will be used for visitors who will be on-site for short times and who will not do hands-on work. This shortened version will contain the hazard information that is directly relevant to the purpose of the visit. Signatures of those attending and the type of briefing must be entered in the field logbook before site access will be granted. Note that casual visitors (e.g., package deliverers, observers) to the support zone will not be required to have the site-specific training. The site-specific training will include the following site-specific information:

- Names of site health and safety personnel and alternates;
- Contents of this SSHP and the appropriate addendum;
- Hazards and symptoms of contaminant exposure;
- Hazards and symptoms of exposure to chemicals present in the workplace;
- Physical hazards in the workplace;
- Recognition and avoidance of live ordnance;
- Site and task PPE (i.e., purpose, donning, doffing, and proper use);
- Safe work practices to minimize risks;
- Safe use of engineering controls and equipment;
- Medical surveillance requirements;
- Site control measures;
- Reporting requirements for spills and emergencies;
- Personnel decontamination procedures;
- Contingency plans (e.g., communications, phone numbers, emergency exits, assembly point);
- Spill containment procedures (e.g., reporting, cleanup methods); and
- Emergency equipment locations and use (e.g., fire extinguishers, spill kits).

Safety briefings will be held at least daily and also when conditions or tasks change. These briefings will be conducted by the field oversight representative/SSHO and will be attended by all site workers and supervisors. These briefings will address site-specific safety issues and are used as an opportunity to refresh workers on specific procedures and to address new hazards and controls.

5.3 DOCUMENTATION

Documentation of the required training must be maintained in the on-site project files. This documentation will include copies of 40-hr, 8-hr refresher, respirator fit-test certifications, and supervisor training certificates; copies of medical clearance reports; and entries in project logs showing the topics covered, trainer, and signatures of those attending on-site training.

6.0 PERSONAL PROTECTIVE EQUIPMENT

PPE for site tasks is based on potential site-specific hazards. In cases where multiple hazards are present, a combination of protective equipment will be selected so that adequate protection is provided for each hazard. When a conflict exists with the PPE requirements, the more restrictive shall apply. This section emphasizes the programmatic requirements for PPE. For task-specific equipment, see Section 3.0 (Hazard/Risk Analysis). All task-specific PPE requirements will be listed in the SSHP Addendum.

6.1 PERSONAL PROTECTIVE EQUIPMENT PROGRAM

PPE use must comply with 29 CFR 1910, Subpart I and Section 5 of the USACE Safety and Health Requirements Manual (USACE 2009). The level of protection and types of materials selected for a particular task must be based on the following:

- Potential for exposure because of work being done;
- Route of exposure;
- Measured or anticipated concentration in the medium of concern;
- Toxicity, reactivity, or other measure of adverse effect; and
- Physical hazards such as falling objects and flying projectiles.

In situations where the type of contamination, concentration, and probability of contact are not known, the appropriate protection is selected based on the CIH’s professional judgment until the hazards are further evaluated.

The SSHO may raise or lower the level of PPE worn by the teams depending upon the site-specific hazards encountered in the field. Prior to lowering the level of PPE, the field oversight representative and the CIH must be contacted/consulted and approval given and documented. If site conditions are such that the level of PPE is insufficient or work must be stopped, the SSHO will take appropriate action immediately, and the appropriate personnel (see above) will be contacted afterwards. The following criteria indicate a possible need for re-assessing the PPE selection:

- Introduction of new types of equipment;
- Commencement of an unplanned (hazard not previously assessed) work phase;
- Working in unplanned temperature extremes;
- Evidence of contamination such as discolored soil or elevated instrument readings near the soil;
- Exceeding the action limits; or
- Changing the work scope so that the degree of contact with contaminants changes.

6.2 TYPES OF EQUIPMENT

This section presents the types of protective clothing that may be used for the project. Requirements for task-specific levels of protective clothing are presented in Table 3-2. Levels of protection will be used to protect against chemical and physical hazards at this site are as follows:

- Level C Protective Equipment
  - Full-face respirator and air-purifying cartridges capable of filtering out organic vapors, acid gasses, and radionuclides. A half-face respirator with appropriate protective eyewear

(e.g., goggles and faceshield) may be deemed protective under certain conditions, but such a determination may only be made by the CIH and SSHO in accordance with the Contractor's health and safety procedures and policies, approved by USACE, and documented in the project-specific SSHP addendum or field change order. Half-face respirators may only be used in environments where contaminants are not an exposure hazard to the eyes or exposed skin;

  - Hooded chemical-resistant clothing (polyethylene-coated Tyvek® or equivalent) with all openings taped;
  - Two pairs of chemical-resistant gloves (nitrile and exam gloves);
  - Heavy duty leather, Kevlar, or equivalent gloves (in addition to chemical-resistant gloves) for materials handling or other tasks that pose physical hazards to the hands;
  - Safety boots;
  - Shoe covers; and
  - Hard hat (if overhead hazards are present).
- Level D+ Protective Equipment
  - Tyvek® or equivalent coveralls;
  - Nitrile or polyvinyl chloride gloves;
  - Heavy duty leather, Kevlar, or equivalent gloves (in addition to chemical-resistant gloves) for materials handling or other tasks that pose physical hazards to the hands;
  - Safety boots;
  - Boot covers;
  - Hard hat (if overhead hazards are present); and
  - Safety glasses with side shields.
- Level D Protective Equipment
  - Coveralls/field clothes;
  - Safety boots;
  - Safety glasses with side shields;
  - Hard hat (if overhead hazards are present);
  - Nitrile or equivalent gloves if contaminated materials are handled; and
  - Heavy duty leather, Kevlar, or equivalent gloves (in addition to chemical-resistant gloves) for materials handling or other tasks that pose physical hazards to the hands.

6.3 CLEANING, STORAGE, AND PROGRAM VERIFICATION

If site tasks require the use of chemical protective clothing, disposable clothing will be used and will be disposed as project-generated waste in accordance with Section 8.0 of the Facility-Wide Sampling and Analysis Plan (FWSAP). Unused chemical protective clothing will be stored in clean staging areas until needed. The SSHO will verify that the PPE in use is appropriate and is being used properly.

7.0 MEDICAL SURVEILLANCE

All employees performing on-site hazardous waste-related work will be enrolled in a medical surveillance program to meet the requirements of 29 CFR 1910.120(f), 1910.134, 1910.20 and to assess and monitor workers' health and fitness for employment in this field. Employees must be provided with summaries of medical examination results following each examination and must be provided more detailed information upon written request.

7.1 FREQUENCY OF EXAM

The frequency of employee medical exams will be as follows:

Prior to assignment to hazardous waste work that involves potential exposure above occupational exposure limits;

Once every 12 months for each employee covered unless the attending physician believes a shorter or longer interval (not to exceed 2 years) is appropriate;

At termination of employment or re-assignment to an area where the employee would not be covered if the employee has performed fieldwork since his/her last examination and has not had an examination within the last 6 months; and

As soon as possible upon notification by an employee that he/she has developed signs or symptoms indicating possible overexposure to hazardous substances or health hazards, or that the employee has been injured or exposed above the permissible exposure limit or published exposure levels in an emergency situation.

7.2 MEDICAL EXAM CONTENT

Medical examinations will include a medical and work history (or updated history if one is available in the employee's file) with special emphasis on symptoms related to the handling of hazardous substances. The examination will determine potential health impairments and fitness for duty, including the ability to wear any required PPE. As a minimum, the exam will include

- Collection of information on the employee's medical and work history;
- Hands-on examination;
- Audiometry;
- Blood screen such as Sequential Multiple Analyzer with Computer 24;
- Chest P/A X-ray at intervals specified by the attending physician;
- Complete blood count;
- Electrocardiogram for persons older than 45 or where medically indicated;
- Physical examination;
- Spirometry (forced expiratory volume/forced vital capacity); and
- Urinalysis (dipstick and microscopic).

8.0 EXPOSURE MONITORING/AIR SAMPLING PROGRAM

Airborne chemical concentrations will be assessed, as appropriate, to ensure exposures do not exceed acceptable levels, as specified in the most recent Threshold Limits Values and Biological Exposure Indices or by OSHA, whichever is more stringent. The USACE Safety and Health Requirement Manual identifies this more stringent value as the Occupational Exposure Limit (OEL). Airborne contaminants are not anticipated for this field effort. The site has been extensively investigated during the RI (Leidos, 2015), and no volatile organic compounds have been detected. Only low-level PAHs are present in the area of the pilot study. Therefore, no exposure monitoring or air sampling will be conducted for this field effort.

9.0 HEAT/COLD STRESS

9.1 INCLEMENT WEATHER

When warnings or indications of impending severe weather exist (e.g., heavy rains, thunderstorms, damaging winds, tornados, hurricanes, floods, lightning), the SSHO will monitor the weather conditions using a weather notification system. Appropriate precautions will be taken to protect personnel and property from the effects of the severe weather. In accordance with Section 6 of the USACE Safety and Health Requirements Manual (USACE 2008), project-specific SSHP addenda should include, at a minimum:

- Severe weather triggers to alert the Contractor SSHO to monitor weather conditions;
- Training on severe weather precautions and actions; and
- Identified area of retreat, preferably a substantial building.

9.2 HEAT/COLD STRESS MONITORING AND CONTROLS

Acclimatization, consumption of copious quantities of fluids, and appropriate work/rest cycles are important factors in preventing heat stress-induced illnesses. General controls will consist of making fluids readily available, using the buddy system, and taking scheduled and unscheduled breaks in a temperature-controlled environment as necessary. The following specific steps will be taken to reduce the potential for heat stress-induced illness:

- When possible, schedule work for cooler periods during the day.
- Provide site training to include controlling heat stress, recognizing heat stress-induced illness, and administering first aid for heat stress.
- Provide cool Gatorade™, equivalent drink, or water to site workers and encourage their consumption.
- Where employees are exposed to solar radiation for short periods and there is the potential for sunburn, or exposure for prolonged periods where long-term exposure could lead to health effects such as skin cancer, they shall be provided sun screen with a sun protection factor appropriate for their skin type and exposure. Sunscreens shall be used only in accordance with the manufacturer's recommendations.
- Instruct workers to monitor their own and their buddy’s condition relative to heat stress.
- Develop an initial work/rest cycle based on the site-specific conditions and the capabilities of the work crew. The American Conference of Governmental Industrial Hygienists (ACGIH) heat stress Threshold Limit Value (TLV) will be instituted per Table 9-1.

Table 9-1. Recommended Work/Rest Cycle

Work-Rest Regimen	Work Load		
	Light	Moderate	Heavy
Continuous work	86[b]	80	77
45 min work/15 min rest[a]	87	82	78
30 min work/30 min rest	89	85	82
15 min work/45 min rest	90	88	86

[a] Non-work, sitting in the shade or air conditioned area.

[b] Wet bulb globe temperature (WBGT) index expressed in degrees Fahrenheit or standard dry bulb temperature if WBGT is unavailable.

- Provide a cool environment, such as a vehicle with air conditioning, for breaks.
- Encourage and allow workers to take unscheduled breaks, if needed.
- Monitor workers wearing Tyvek® or other impermeable clothing for heat stress by taking their pulses at the beginning of each rest period. If any worker's heart rate exceeds 110 beats per minute, the next work period will be shortened by one third (NIOSH et al 1985).

Adequate clothing and staying dry are critical factors in preventing cold stress disorders. The SSHO/field oversight representative will ensure the capability to quickly move individuals who become wet to a sheltered, warm area. The following specific steps will be taken (adapted from ACGIH 2010).

- If ambient temperatures are less than 40°F, provide site training on preventing cold injury, recognizing cold injury symptoms, and administering cold injury first aid.
- Provide a heated break area if ambient temperatures are less than 32°F.
- Implement breaks in a warm area every 120 min, at a minimum, if ambient temperatures are less than 32°F.
- Allow workers to take unscheduled breaks, if needed, in a warm area.
- Outdoor work will not be performed if the equivalent chill temperature (temperature combined with the effect of wind) is less than -29°F.

9.3 HEAT/COLD STRESS-INDUCED ILLNESS SIGNS AND SYMPTOMS

Heat cramps are caused by heavy sweating and inadequate electrolyte replacement. Signs and symptoms are muscle spasms and pain in the hands, feet, and abdomen. Personnel exhibiting these symptoms should rest in a cool place and consume fluids and salt.

Heat exhaustion occurs from increased stress on various body organs. Signs and symptoms are:

- Pale, cool, moist skin;
- Heavy sweating;
- Dizziness and nausea; and
- Fainting.

Heat stroke is the most serious form of heat-related illness and should always be treated as a medical emergency. The body's temperature regulation system fails, and the body temperature rapidly rises to critical levels. Immediate action must be taken to cool the body before serious injury or death occurs. Signs and symptoms of heat stroke are:

- Red, hot, usually dry skin;
- Lack of or reduced perspiration;
- Nausea;
- Dizziness and confusion;
- Strong, rapid pulse and confusion; and
- Coma.

Hypothermia is the uncontrolled loss of body heat. As the body's core temperature decreases, bodily functions are slowed. The victim becomes weak and disoriented and may become comatose if steps are not taken to return the core temperature to the normal range. Hypothermia can occur whenever temperatures are below 45°F and is most common during wet, windy conditions, with temperatures between 40 and 30°F. The principal cause of hypothermia in these conditions is loss of insulating properties of clothing due to moisture, coupled with heat loss due to wind and evaporation of moisture on the skin.

Frostbite is the freezing of body tissue, which ranges from superficial freezing of surface skin layers to deep freezing of underlying tissue. Frostbite will only occur when ambient temperatures are below 32°F. The risk of frostbite increases as the temperature drops and wind speed increases.

10.0 STANDARD OPERATING SAFETY PROCEDURES

This section presents general safety rules applicable to the anticipated tasks. The provisions of the plan are mandatory for all on-site employees and visitors, including employees engaged in initial site reconnaissance, preliminary field investigations, mobilization, project operations, and demobilization. These standard operating procedures are offered for guidance. Alliant and subcontractors will be responsible for ensuring that the appropriate and sufficient procedures presented in project-specific SSHP addenda are used to protect employees.

10.1 SITE RULES

The following rules will apply to all site activities:

- All work will be conducted in compliance with the *USACE Safety and Health Requirements Manual* (USACE 2008).
- Daily safety briefings ("tailgate") will be held during field activities to inform personnel of new hazards or procedures.
- The field oversight representative/SSHO will conduct and document daily safety inspections.
- Personnel will notify the SSHO of any medical conditions (e.g., allergic to bee stings, diabetes, pregnancy) that require special consideration.
- Personnel will maintain proper workplace housekeeping to minimize the potential for tripping and other accidents.
- Contact with potentially contaminated substances will be avoided. Site personnel in the exclusion zone will avoid walking through puddles, pools, and mud; kneeling on the ground;

and placing equipment on the ground.

- Spills will be prevented to the extent possible. If a spill occurs, the material will be contained.
- All injuries and accidents requiring first aid will be reported to the SSHO, field oversight representative, CIH, and the USACE Project Manager.
- All workers will abide by a buddy system. Members of a buddy team will maintain verbal or visual contact.

10.2 DRIVING

All posted speed limits and state vehicle operation laws must be obeyed at all times. Personnel driving motor vehicles/equipment may not use hand-held cellular phones but may use hands-free telephones while the vehicle is in motion. Prior to using a hand-held cellular phone, drivers shall find a safe place to bring their vehicle to a stop. This requirement does not preclude passenger(s) from using cellular phones while the vehicle is in motion. Using headphones and earphones is prohibited while operating a motor vehicle/equipment.

10.3 PERMIT REQUIREMENTS

Alliant and subcontractors will coordinate with Camp Ravenna to obtain, as necessary, all permits necessary for the safe execution of this project, which will include, at a minimum, digging permits/clearance from local utilities prior to any excavation activities.

10.4 INVESTIGATION-DERIVED WASTE DRUM/CONTAINER HANDLING

Any drums used for the project will meet the requirements of the FWSAP and project-specific addenda. IDW movement from field sites to Building 1036 will be conducted by the subcontractor using a backhoe equipped with forks and drum dollies. No personnel will be allowed under lifted loads. Lifts of greater than 50 lb will be made with two or more personnel or with lifting equipment in compliance hazardous waste safety training and Sections 14 and 16 of the *USACE Safety and Health Requirements Manual*.

10.5 EXCAVATION AND TRENCH SAFETY

Trench excavation potentially poses the following hazards: contact with buried utilities, trench cave-in and engulfment, confined space hazards such as hazardous airborne concentrations of toxic chemicals, flammable concentrations of vapors or gases, and oxygen deficiency. The depth of the excavation and the nature of the excavated material significantly impact the potential hazard—the greater the depth, the greater the hazard. The excavation during this field effort will be a maximum of 1 ft in depth.

Prior to opening an excavation, the site will be verified free of underground utilities by contacting the local utility companies and/or appropriate base personnel. Notification will include submitting maps with planned excavation locations clearly marked for appropriate base personnel approval. If underground utilities are present, they will be located and protected from damage or movement.

Other location-specific hazards, such as the potential for UXO, building foundations, and unstable rocks will be controlled.

Cave-in hazards will be controlled by excluding personnel from inside or near (within 3 ft) excavations 5 ft or deeper. This restriction will not be applied to excavations less than 5 ft deep if the field oversight representative/SSHO has examined the excavations and determined there is no potential for cave-in.

If personnel must enter trenches deeper than 1.2 m (4 ft), the requirements of 29 CFR 1926.651 and Section 25 of the USACE Safety and Health Requirement Manual will be applied. This will include daily inspections of the excavation and shoring or sloping the trench sides. Shoring will be accomplished using a trench box with rigid sides to prevent engulfment. If a trench box is not utilized, the trench sides will be sloped at a 34° angle (one and one-half horizontal to one vertical). All spoils will be located at least 0.6 m (2 ft) from the edge of the excavation. Such entry also will be treated as confined space entry and procedures will comply with Section 10.5 (Confined Space Entry).

10.6 HAZARD COMMUNICATION

Hazard communication will be governed by 29 CFR 1910.1200 and Section 06.B of the *USACE Safety and Health Requirement Manual*. At a minimum, the following steps will be taken:

- All hazardous materials on-site will be labeled to comply with the hazard communication standard, and will include the following.
- Clear labeling as to the contents; and
- The appropriate hazard warning.
- MSDSs will be available on-site for all hazardous materials that are present.
- Site-specific training will be provided for the hazards posed by site chemicals, protective measures, and emergency procedures.
- Copies of MSDSs for all hazardous chemicals (chemicals brought on-site) will be maintained in the work area. MSDSs will be available to all employees for review during each work shift.

10.7 ILLUMINATION

All site fieldwork will be conducted during daylight hours (no earlier than 15 min after sunrise and no later than 15 min before sunset) and natural illumination will be used. Non-fieldwork conducted in buildings will be illuminated to meet the following minimums stated in Section 7 of the *USACE Safety and Health Requirement Manual*: general outdoors - 33 lx, stairs and ladders - 110 lx, offices - 540 lx, and first aid areas - 325 lx.

10.8 SANITATION

- Sanitation will comply with 29 *CFR* 1910.120(n) and Section 2 of the *USACE Safety and Health Requirement Manual*.
- Provide means at the work site for washing hands and faces prior to eating.
- Provide potable drinking water in closed, labeled (“Drinking Water”), sanitary dispensers and protect them from contamination.
- Post any containers or dispensers of non-potable water with “Caution – Water Unsafe for Drinking, Washing, or Cooking.”
- Provide a toilet. Toilet facilities must be lit, ventilated, and have areas for hand washing per Section 02.E of the *USACE Safety and Health Requirement Manual*.

10.9 HISTOPLASMOSIS

Histoplasmosis is an infectious disease caused by inhaling the spores of a fungus called *Histoplasma capsulatum*. Histoplasmosis is not contagious; it cannot be transmitted from an infected person or animal to someone else. Histoplasmosis primarily affects a person’s lungs, and its symptoms vary greatly. The vast majority of infected people are asymptomatic (have no apparent ill effects) or they experience symptoms so mild they do not seek medical attention and may not even realize that their illness was histoplasmosis. If symptoms do occur, they will usually start within 3 to 17 days after exposure, with an average of 10 days. Histoplasmosis can appear as a mild, flu-like respiratory illness and has a combination of symptoms, including malaise (a general ill feeling), fever, chest pain, dry or non-productive cough, headache, loss of appetite, shortness of breath, joint and muscle pains, chills, and hoarseness. Chronic lung disease due to histoplasmosis resembles tuberculosis and can worsen over months or years. Special antifungal medications are needed to arrest the disease.

H. capsulatum grows in soil throughout the world. In the United States, the fungus is endemic (more prevalent) and the proportion of people infected by *H. capsulatum* is higher in central and eastern states, especially along the valleys of the Ohio, Mississippi, and St. Lawrence Rivers and the Rio Grande. The fungus seems to grow best in soil having a high nitrogen content, especially that enriched with bat droppings or bird manure. Disturbances of contaminated material cause small H. capsulatum spores to become airborne or aerosolized.

The following actions must be taken to minimize the potential for infection:

- Workers who will disturb collections of bird or bat droppings must be trained in the potential hazard and control measures.
- Avoid disturbing collections of bird or bat droppings in any way that causes airborne dust.
- If collections of bird or bat droppings will be disturbed, wet droppings with water and surfactant before disturbing and continuously during disturbance.
- Stop work and take additional corrective action if visible airborne dust is observed.
- Use particulate respirators and disposable coveralls for work that may involve potentially significant or uncontrolled exposure to collections of droppings.

10.10 LYME DISEASE

Lyme disease is an infection caused by the corkscrew-shaped bacteria Borrelia burgdorferi that is transmitted by the bite of deer *(Ixodes scapularis)* and western black-legged *(Ixodes pacificus)* ticks. The deer tick, which normally feeds on the white-footed mouse, the white-tailed deer, other mammals, and birds, is responsible for transmitting Lyme disease bacteria to humans in the northeastern and north-central United States. On the Pacific Coast, the bacteria are transmitted to humans by the western black-legged tick. Ixodes ticks are much smaller than common dog and cattle ticks. In their larval and nymphal stages, they are no bigger than a pinhead. Adult ticks are slightly larger.

Ticks search for host animals from the tips of grasses and shrubs (not from trees) and transfer to animals or persons that brush against vegetation. Ticks only crawl; they do not fly or jump. Ticks found on the scalp usually have crawled there from lower parts of the body. Ticks can attach to any part of the human body but often attach to the more hidden and hairy areas such as the groin, armpits, and scalp. Research in the eastern United States has indicated that, for the most part, ticks transmit Lyme disease to humans during the nymph stage, probably because nymphs are more likely to feed on a person and are rarely noticed because of their small size. Thus, the nymphs typically have ample time to feed and transmit the infection (ticks are most likely to transmit infection after approximately 2 or more days of feeding). Adult ticks can transmit the disease, but since they are larger and more likely to be removed from a person's body within a few hours, they are less likely than the nymphs to have sufficient time to transmit the infection.

The following control measures must be followed:

- Whenever possible, avoid entering areas that are likely to be infested with ticks, particularly in spring and summer when nymphal ticks feed. Ticks favor a moist, shaded environment, especially which provided by leaf litter and low-lying vegetation in wooded, brushy, or overgrown grassy habitat.
- Wear light-colored clothing so that ticks can be spotted more easily and removed before becoming attached.
- Wear long pants and tuck pant legs into socks or boot tops or close the pant legs with tape or other means.
- Apply insect repellents containing n,n-diethyl-m-toluamide (DEET) to clothes and exposed skin.
- If personnel must enter areas with known heavy infestation, consider applying permethrin (which kills ticks on contact) to clothes.
- Conduct daily checks for ticks. Embedded ticks should be removed using fine-tipped tweezers.
- DO NOT use petroleum jelly, a hot match, nail polish, or other products. Grasp the tick firmly and as closely to the skin as possible. With a steady motion, pull the tick's body away from the skin. The tick's mouthparts may remain in the skin, but do not be alarmed. The bacteria that cause Lyme disease are contained in the tick's midgut. Cleanse the area with an antiseptic.
- Note the date of removal of any imbedded tick and seek medical attention if any signs and symptoms of early Lyme disease, Ehrlichiosis, or Babesiosis develop over the ensuing days or weeks.

10.11 ROCKY MOUNTAIN SPOTTED FEVER

Rocky Mountain Spotted Fever is a rickettsial disease caused by the organism *Rickettsia rickettsii*. It is transmitted by the bite of an infected tick and results in a systemic, febrile illness. Several ticks are responsible for the spread of this disease, and these vary by geographic region. The dog tick, *Dermacentor variabilis*, is probably the most common vector. According to the Ohio Department of Health, the incidence of Rocky Mountain Spotted Fever has increased in recent years.

The organism becomes infectious after the tick has been attached to the skin for at least 4 to 6 hr. It can also be transmitted in the process of tick removal if the tick is crushed, which allows infectious material to escape.

Symptoms of Rocky Mountain Spotted Fever include the sudden onset of a moderate to high fever (which can last 2 to 3 weeks if untreated), muscle pain, severe headache, and chills. A rash occurs in about half of the cases. It starts with the extremities and soon spreads to the palms of the hands and soles of the feet, then quickly spreads to the trunk and rest of the body.

Control measures are the same as those for Lyme disease ticks.

10.12 MOSQUITO-BORNE VIRUSES

According the Center for Disease Control, West Nile Virus (WNV) is a potentially serious illness. Experts believe WNV is established as a seasonal epidemic in North America that flares up in the summer and continues into the fall. Most often, WNV is spread by the bite of an infected mosquito. Mosquitoes become infected when they feed on infected birds. Infected mosquitoes can then spread WNV to humans and other animals when they bite. The easiest and best way to avoid WNV is to prevent mosquito bites.

- When outdoors, use insect repellent containing an United States Environmental Protection Agency (USEPA)-registered active ingredient. Follow the directions on the package.
- Many mosquitoes are most active at dusk and dawn. Be sure to use insect repellent and wear long sleeves and pants at these times or consider staying indoors during these hours.

About 1 in 150 people infected with WNV will develop severe illness. The severe symptoms can include high fever, headache, neck stiffness, stupor, disorientation, coma, tremors, convulsions, muscle weakness, vision loss, numbness, and paralysis. These symptoms may last several weeks, and neurological effects may be permanent. Up to 20% of the people who become infected have symptoms such as fever, headache, body aches, nausea, vomiting, and sometimes swollen lymph glands or a skin rash on the chest, stomach, and back. Symptoms can last for as short as a few days; although, even healthy people have become sick for several weeks. Approximately 80% of people (about four out of five) who are infected with WNV will not show any symptoms at all. People typically develop symptoms between 3 and 14 days after they are bitten by the infected mosquito (CDC 2006).

10.13 FUELS

Camp Ravenna procedures and applicable portions of Section 9 of the *USACE Safety and Health Requirements Manual* for use and storage of fuels, such as gasoline and diesel fuel, must be followed. These include, but are not limited to:

- Secondary containment for containers with a capacity of 100 gal or more;
- All spills must be immediately reported to Camp Ravenna Range Control at (614) 336-6041 and the procedures on the Camp Ravenna First Responder Form (Appendix A) will be followed;
- Spill response must comply with the current Installation Spill Contingency Plan for Camp Ravenna;
- Fuel storage areas will be posted with signs stating "No Smoking, Matches, or Open Flame," and no ignition sources will be allowed within 50 ft.

Only labeled/listed (by a nationally recognized testing laboratory) containers and portable tanks will be used for the storage of flammable and combustible liquids.

10.14 POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

PAHs are a group of over 100 different chemicals that are formed during the incomplete burning of coal, oil and gas, garbage, or other organic substances. PAHs are usually found as a mixture containing two or more of these compounds, such as soot. Some PAHs are manufactured. These pure PAHs usually exist as colorless, white, or pale yellow-green solids. Some PAHs are suspected human carcinogens.

PAHs can occur in air attached to dust particles. Some PAH particles can readily evaporate into the air from soil or surface waters. Most PAHs do not dissolve easily in water. They stick to solid particles and settle to the bottoms of lakes or rivers. In soils, PAHs are most likely to stick tightly to particles; certain PAHs move through soil to contaminate underground water. PAH contents of plants and animals may be much higher than PAH contents of soil or water in which they live.

In work areas where the potential for exposure to PAHs exists, the following steps will be taken as a minimum.

- Staying upwind of any dust-generating activities
- Avoiding skin and eye contact and any ingestion or inhalation contact with PAH contaminated air, water, soil or tools and equipment.
- Hazard communication training
- HAZWOPER training and medical clearance for hazardous waste work
- Decontamination of potentially contaminated equipment prior to servicing
- Monitoring - photoionization detector or other sampling as appropriate
- PPE (Level D) plus nitrile or equivalent gloves for contact with contaminated material.
- Washing face and hands prior to taking anything by mouth.
- Appropriate respiratory protection may be required if air sampling, site history data or a reasonable index of suspicion, indicate the presence of PAHs in the immediate work area.
- Waste containers and waste containment areas containing PAH contaminated material will be labeled to indicate contents and hazard.

10.15 THERMAL TREATMENT OF SOILS

The goal of Endpoint's patented VEG ex-situ thermal desorption technology is to thermally desorb (from soils into vapor phase) and/or otherwise decompose PAHs to non-hazardous materials. The process involves a mobile vapor energy generator, which utilizes propane, air, and water to generate steam at temperatures as high as 1,300 °F.

Profiled soils sent to Endpoint's laboratory by Alliant will then be removed from the drum using a shovel and placed onto a conveyor, which will in turn feed the soils directly into the preheated treatment chamber. Temperatures to be tested will range from 600 to 800 °F, with soil residence times ranging from 15 minutes to 30 minutes

As organic compounds (including PAHs) transition from solid phase adsorbed to soils to vapor phase within the renewal chamber, a vacuum system internal to the enclosed renewal chamber captures the organic vapors generated.

To properly remove any NOx, SOx and HCl compounds prior to rerouting of vapors back to the vapor generator, the desorbed vapors are first passed through a series of patented filters and caustic scrubber inserted in series within the pipeline that recycles desorbed material from the enclosing truck body back through the steam generator. The filter/scrubber system encompass an engineered mixture of caustic soda, zero valent iron (ZVI), lime, water, and steam and align in a slender packed column.

As the acid-laden vapor is pulled by vacuum up through the filter/scrubber column, any acidic compounds are neutralized by the filters and trickling down caustic soda (sodium hydroxide) liquid solution. Hence, any acid vapors (e.g., HNO3 (nitric acid) from NOx, H2SO4 (sulfuric acid) from SOx, and HCl are removed before the organic vapors are routed further downstream. Neutralization of the acidic compounds results in a benign dilute liquid solution of sodium nitrate (NaNO3), sodium bisulfate (NaHSO4), and sodium chloride (NaCl) for ultimate profiling and disposal offsite.

The optimal treatment temperature and residence time reflect conditions which will reduce PAH concentrations to low (i.,e below residential RSLs) or to non-detect levels.

During the bench-scale testing at Endpoint's California laboratory, treated soils will be considered as investigation derived wastes (IDW) regardless of the levels of PAHs, if any, present in the treated soils. These soils will be placed back into the original drums and disposed of at an appropriate landfill in accordance to the post-treatment concentrations serving as the profile for disposal.

The onsite pilot test will include mobilization to the site of the same VEG unit used at Endpoint's laboratory for the bench-scale test, housed on a 40-foot trailer. In addition, one conveyor for loading of soils into the VEG unit will be mobilized to the site, together with one 5-CY backhoe and a bobcat loader to be used for excavation, stockpile management, and loading of stockpiled soils onto the conveyor. Lastly, a 500-gallon propane tank and a 4,000-gallon water tank will also be brought onto the site for use in support of steam generation and thermal treatment by the VEG system.

The following precautions will be taken as a minimum to protect personnel and property during the thermal treatment process;

- Bulk propane tanks will be sited and placed in an approved location and at a safe distance from heat, flame or ignition sources and away from vehicle traffic or pedestrian movement. The tanks will be located at a safe and approved distance from areas occupied by personnel, including personnel trailers, offices, portable toilets and other areas where large numbers of personnel may be present.
- All motor vehicle operation, including powered lift trucks (forklifts), backhoes, front-end loaders, Bobcat skid steer devices and similar will require trained and qualified operators with valid driver's license, seat belt use, routine vehicle inspections, and no cell phone use while driving. Compliance with applicable laws and regulations, and defensive driving are required.
- Trained spotter personnel shall be used to assist drivers when vehicles are maneuvering in congested areas or near personnel or fixed objects.
- High visibility clothing shall be worn by pedestrians working in the area of motor vehicles and approved back-up alarms shall be in use on all vehicles.
- Vehicle operators shall perform a visual inspection prior to use that includes the vehicle and any associated items such as trailers or external cargo carriers. The operator verifies that the following items are present and functional: seatbelt(s), lights, turn signals, operating brakes, speedometer, fuel gage, horn, windshield, windshield wiper, defrosting/defogging system, rear view mirror, cab, non-slip surfaces on steps, and tires.
- Conveyer belt operations shall be evaluated by the site safety officer prior to operation and only trained and qualified personnel shall work with and near conveyer systems.

- Personal protective equipment for protection from thermal burns and steam burns shall be used by workers with potential exposure to these hazards. These include thermal protective gloves, arm sleeves, face shields and similar devices as necessary.
- Steam valves, boilers, fittings and piping shall be plumbed, installed, operated and maintained by personnel with the required training and certifications to perform such work and authorized to work with pressure vessels.
- Exhaust vents discharging process vapor, smoke or steam from the thermal treatment process shall, as applicable, be directed away from occupied areas. Exhaust vents and stacks shall be installed with consideration of prevailing wind direction and at sufficient height to avoid discharge or re-entrainment of smoke, vapor or heat in occupied areas.
- Due to the relative newness of the thermal treatment process, the site safety officer shall periodically review existing safety precautions for adequacy and adjust them or implement new precautions to address changing conditions or emerging problems.

11.0 SITE CONTROL MEASURES

The field oversight representative will be responsible for establishing the site control zones, as necessary, around Contractor-controlled areas that present physical or chemical hazards. Implementation of the site control zones will help to minimize the number of employees potentially exposed and to minimize the potential for the spread of contamination. The field oversight representative/SSHO will monitor the implementation of the required site control work rules and will report any deviations from prescribed practice to the Project Manager or stop work, as appropriate.

The Atlas Scrap Yard AOC is in a remote location with limited activity. Therefore, an exclusion zone will likely be necessary. The SSHO will be responsible for determining the need for establishing site controls and exclusion zones. An exclusion zone will be established if the work site will be left intact and unattended for an extended period of time (e.g., leaving an open excavation or drill rig in place overnight). If the SSHO determines that a potential exists for unauthorized personnel to approach within 25 ft of a work zone or otherwise be at risk due to proximity, then exclusion zones will be established as described in the following sections.

11.1 EXCLUSION ZONE

The exclusion (contamination) zone is the area where the greatest potential exists for exposure to contamination or physical hazards. The periphery of the exclusion zone will be identified by barricade tape or rope suspended above the ground. An entry and exit checkpoint will be visually defined to regulate the flow of personnel and equipment. The entry and exit checkpoint will be delineated with barricade tape/rope and signs. Signs may state “Construction Area,” or “High Noise Area,” as deemed appropriate by the SSHO. The number of people and equipment in the exclusion zone will be minimized to control physical hazards and the spread of contamination.

The following standard rules will apply to all entry into the exclusion zone:

- The field oversight representative/SSHO must approve (and log) entry into the exclusion zone.
- All personnel entering the exclusion zone will wear the prescribed level of protective clothing.

- All items and related paraphernalia intended to be placed on the face or in the mouth (e.g., cigarettes, lighters, matches, chewing tobacco, food, cosmetics) are prohibited in the exclusion zone.
- All personnel in the exclusion zone will follow the buddy system.

11.2 CONTAMINATION REDUCTION ZONE

A contamination reduction (buffer) zone will be established, as necessary, outside the exclusion zone to provide a transition from and a buffer between the exclusion zone and the support zone. A formal contamination reduction zone for personnel will not be established unless Level D+ PPE or higher level (A, B, C) is used or significant surface contamination is present or suspected. An entry and exit checkpoint will be visually defined at the periphery of the zone to regulate the flow of personnel and equipment. The entry and exit checkpoint and the perimeter of the zone will be delineated with the use of ropes/barricade tape and signs. A contamination reduction zone will be established around the central equipment decontamination pad.

All personnel entering the contamination reduction zone will wear the prescribed level of protective clothing required for that zone. All items intended to be placed on the face or in the mouth (e.g., cigarettes, chewing tobacco, food, cosmetics) are prohibited in the contamination reduction zone. Doffing of protective clothing and personnel decontamination will occur in the contamination reduction zones.

11.3 SUPPORT ZONE

The support zone is the clean and relatively safe area surrounding the exclusion and contamination reduction zones. Entry requirements for the support zone consist of those required for entry into the general area of the facility. Primary functions of the support zone are

- Staging area for clean equipment and supplies; and
- Location for support services (e.g., office trailers, laboratory trailers, eating area[s], toilet facilities, parking, visitor area[s]).

11.4 SITE VISITORS

The field oversight representative will add all employees/visitors to the on-site access roster. Alliant and the subcontractor will send a completed access roster to Ms. Rebecca Haney who will coordinate access with camp Ravenna. Once approved by Camp Ravenna, Alliant and the subcontractor will present identification at the gate when entry is required. Visitors will not be allowed inside areas controlled by Alliant and the subcontractor without specific approval of the field oversight representative/SSHO. Visitors must meet all regulatory (specifically 29 CFR 1910.120) and site health and safety requirements (e.g., proof of training, medical surveillance) to be considered for Camp Ravenna entry. All visitors will receive a health and safety briefing appropriate to the nature of the visit and the potential hazards associated with the visit. All visitors must sign the daily tailgate and health and safety briefing form (Appendix A).

11.5 SITE COMMUNICATION

Field personnel will be capable of contacting other field personnel and outside agencies. Communication on-site will be assured by hand-held radio, cellular phone, portable air horns, or vehicle horns. Short blasts (less than 1/2 sec) of an air horn or car horn will be used to request assistance. Prolonged blasts (more than 2 sec) will be used to signal an evacuation. If phone service is not immediately available on the site, the crew will be equipped with a cellular phone.

12.0 PERSONNEL HYGIENE AND DECONTAMINATION

A system of procedures will be used to control the spread of contamination from the exclusion (contamination) zone and to ensure that workers are sufficiently free of contamination to preclude adverse health effects. PPE doffing and personnel decontamination are part of this system. The SSHO will ensure the construction of a decontamination station, as necessary; instruct personnel on its proper use; and verify that personnel follow the appropriate steps. This section presents examples of basic requirements for personnel decontamination keyed to the level of protective clothing in use. It is the SSHO's responsibility to verify that personnel hygiene and decontamination processes are adequate to protect personnel and meet the requirements of Sections 06.M and 28 of the *USACE Safety and Health Requirements Manual* (USACE 2008).

12.1 LEVEL D+ PROTECTION DECONTAMINATION

Station 1: Tape removal

- Remove all tape (if used) from outer clothing and place in appropriate waste container.

Station 2: Boot covers, outer disposable garment, and chemical-resistant gloves removal

- Carefully remove boot covers, outer contamination-resistant garment, and gloves.

Station 3: Field wash

- Wash hands and face prior to eating, drinking, or smoking. This step may be accomplished with soap and water or disposable disinfectant wipes.

12.2 LEVEL C PROTECTION DECONTAMINATION

Station 1: Segregated equipment drop

- Deposit equipment used on-site (e.g., tools, sampling devices, containers, monitoring instruments, clipboards) on plastic sheets or in different containers with plastic liners. Segregating the equipment at the drop site reduces the possibility of cross-contamination.

Station 2: Outer boot and glove removal

- Remove tape from outer boots and outer gloves.
- Remove outer boot covers and outer gloves. Deposit gloves and boot covers in plastic trash bags.

Station 3: Cartridge change

- If a worker has left the exclusion zone for the sole purpose of changing a canister/cartridge of the respirator, this is the last step of the decontamination procedure. Once the worker's canister/cartridge has been replaced, the outer boots and gloves will be replaced and re-taped so that all potential pathways to the skin are sealed.

Station 4: Disposable outer garment removal

- Remove the disposable outer garment, deposit in a plastic trash bag, and dispose of it in accordance with the FWSAP.

Station 5: Respiratory protection and disposable inner glove removal

- The respirator is the next-to-last item for removal. The cartridges/canisters are placed in a plastic trash bag and disposed of in accordance with the FWSAP. The respirator is placed in a plastic bag dedicated for used respirators only. Disposable inner gloves are the last item removed; deposit them in a plastic trash bag in accordance with the FWSAP.

Station 6: Field wash

- Wash hands and face prior to eating, drinking, or smoking. This step may be accomplished with soap and water or disposable disinfectant wipes.

13.0 EMERGENCY PROCEDURES AND EQUIPMENT

If an emergency occurs, the field oversight representative/SSHO and the field team will participate in a post-emergency briefing to discuss the event, identify the causes, identify corrective measures, and evaluate the responses.

In the event of an accident or incident, the field oversight representative must first notify Camp Ravenna Range Control (614-336-6041) who will coordinate the response. The field oversight representative should then notify the USACE Project Manager immediately according to the requirements of the *USACE Safety and Health Requirements Manual* (USACE 2008). The required Accident Report (ENG Form 3394) must be completed and submitted to the USACE Project Manager within 2 days.

All personnel working on-site will be trained in the applicable emergency response requirements. This includes recognizing emergencies, reporting emergencies to the field oversight representative/SSHO, and responding to emergencies. Employees will also be informed of any changes in potential emergencies or response plans.

13.1 POTENTIAL EMERGENCIES

Credible potential emergencies for this work include fires, minor chemical spills, and personnel injury.

13.1.1 Fires

Small quantities of flammable solvents [typically less than 18.9 L (5 gal)], gasoline, and diesel fuel may be present on-site. In the event of a fire, Camp Ravenna Range Control (614-336-6041) will be notified immediately. If it is safe to do so, on-site personnel may attempt to extinguish the fire with the available fire extinguishers and isolate any nearby flammable materials. If there is any doubt about the safety of extinguishing the fire, site personnel will evacuate the area. The supervisor or knowledgeable employee will provide Camp Ravenna Range Control with relevant information when they arrive.

13.1.2 Spills

Potential spills include releases of fuels, lubricants, hydraulic fluids, and decontamination solvents. In the event of a spill or leak, the employee making the discovery will immediately notify the field oversight representative/SSHO. Field oversight will determine whether the leak poses an environmental risk or will exceed the capacity of on-site personnel and equipment. In the unlikely event that there is a probability that the spill will extend beyond the immediate area, result in an environmental insult, or exceed the capabilities of the on-site personnel, the field oversight representative will inform Camp Ravenna Range Control (614-336-6041) and the procedures on the Camp Ravenna First Responder Form (Appendix A) will be followed. If this is not the case, the on-site spill kit will be utilized to clean up the spill.

13.1.3 Medical Emergencies

Field crews will use a variety of equipment that could cause injuries. In the event of a medical emergency, the field oversight representative will notify Camp Ravenna Range Control (614-336-6041). At least one first aid/ CPR- trained individual will be on-site at all times, and will provide first aid pending release of the injured person to emergency medical staff. Automated External Defibrillators are located at Building 1067 and Guard Post 1. Contaminated injured personnel will be decontaminated to the extent feasible. Personnel with minor injuries will follow normal decontamination procedures. Personnel with serious injuries will be decontaminated, if necessary, by disrobing and wrapping in a blanket. Decontamination may be bypassed in the event of life-threatening injuries or illnesses.

13.2 EMERGENCY PHONE NUMBERS

Table 13-1 lists the emergency groups and their telephone numbers. A telephone and two-way radio will be present in the field and available for use at all times. All emergencies on-site will be coordinated first through Camp Ravenna Range Control (614-336-6041) who will coordinate the response.

Each team must have a telephone for communication with the Project Manager or field oversight representative. For the purposes of this requirement, a team is any individual(s) not having a line of sight or within normal voice range of another individual(s) having means of communication with the field oversight representative.

Robinson Memorial Hospital (also known as UH Portage Medical Center) is located approximately 32 km (20 miles) from the site at 6847 N. Chestnut Street in Ravenna, Ohio. It can be reached by taking Highway 5 E approximately 11 km (7 miles), Highway 5 approximately 3.2 km (2 miles), Highway 59, then right onto Highway 44 (Chestnut Street). Figure 13-1 contains a map and directions to Robinson Memorial Hospital.

13.3 EMERGENCY ALERTING

In the event of an emergency, contact Camp Ravenna Range Control at (614) 336-6041.If these attempts fail, additional emergency alerting procedures are as follows. Each team will have a means for generating an audible alarm, which will consist of a compressed gas horn or vehicle horn. These devices will be used to signal to other project personnel in the event of accidents or emergencies. Short blasts (less than 1/2 sec) of the horn will be used to request assistance, while extended blasts (more than 2 sec) will signal an evacuation.

Table 13-1. Emergency Contact Phone Numbers

Position	Phone
Camp Ravenna Range Control (Police, Fire, Emergency Medical)	(614)-336-6041
Hospital (Robinson Memorial, Ravenna)	(330) 297-2449/0811
USACE COR and Technical Manager Eric Cheng	(502)315-7443
Ohio EPA Spill Hotline	(800) 282-9378
Contractor Project Manager Belinda Price	(865) 934-5143
Field Oversight Representative/SSHO Richard Stout	(865) 255-5540
Restoration Cleanup Program Manager Mark Leeper	(703) 607-8955
Restoration Project Manager Kevin Sedlak	(614) 336-6000, ext. 2053
Environmental Specialist Katie Tait	(614) 336-6136

COR = Contracting Officer's Representative.
USACE = United States Army Corps of Engineers.
Ohio EPA = Ohio Environmental Protection Agency.
RVAAP = Ravenna Army Ammunition Plant.

13.3 EMERGENCY ALERTING

In the event of an emergency, contact Camp Ravenna Range Control at (614) 336-6041. If these attempts fail, additional emergency alerting procedures are as follows. Each team will have a means for generating an audible alarm, which will consist of a compressed gas horn or vehicle horn. These devices will be used to signal to other project personnel in the event of accidents or emergencies. Short blasts (less than 1/2 sec) of the horn will be used to request assistance, while extended blasts (more than 2 sec) will signal an evacuation.

13.4 EVACUATION

The SSHP project-specific addenda must contain a map that illustrates assembly points and egress routes from each AOC included in the investigation. The field oversight representative/SSHO will inform all employees of the designated evacuation routes and assembly area. The facility-wide assembly point is Guard Post 1 as indicated on Figure 13-2.

13.5 EMERGENCY EQUIPMENT

Several items of emergency equipment will be maintained at the work site. Any incident that is not clearly controllable by personnel wearing standard site clothing plus protective gloves and using the listed equipment will require re-evaluation by the SSHO. If the SSHO does not feel that on-site personnel can safely control the emergency with the available equipment, the crew will use an alternate approach such as allowing a small fire to burn out or evacuating the site. The required emergency equipment includes the following:

Robinson Memorial Hospital
847 N. Chestnut Street
Ravenna, Ohio
(330) 297-0811

Directions: West on State Route 5. Stay straight onto OH-59 West. Turn Right onto OH-14/OH-44. Turn Left onto North Chestnut St.

Figure 13-1. Route Map and Directions to Pre-Notified Medical Facility

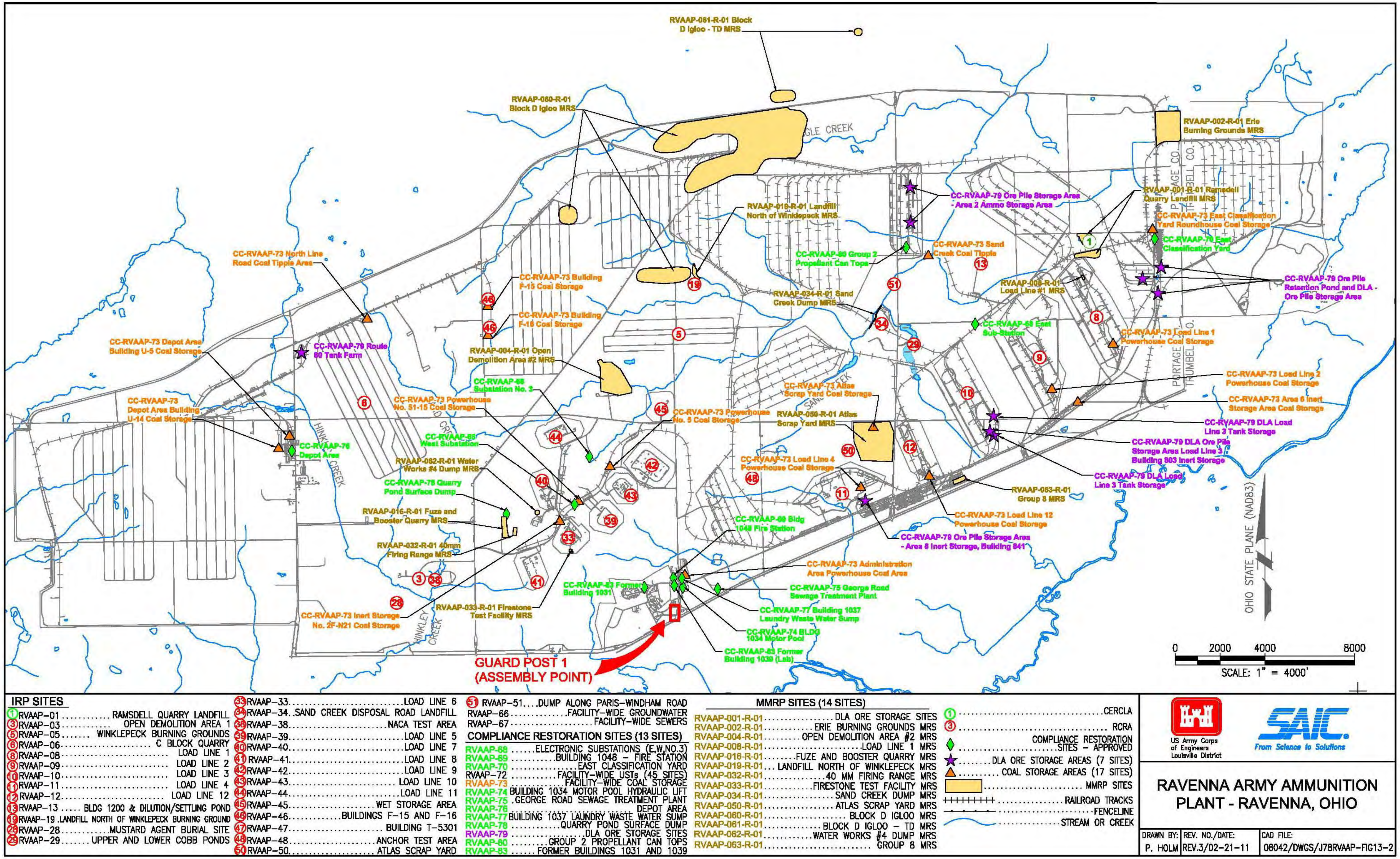

Figure 13-2. RVAAP Facility-Wide Assembly Area

- Fully stocked first aid kit indoors or in a weather-proof container, inspected weekly;
- Emergency eye wash to meet American National Standards Institute standard if corrosives (water sample preservatives) are being poured;
- Fire extinguisher(s) (at least 20-B) 7.6-22.9 m (25-75 ft) from outside the flammables storage (or use) area;
- Basic spill kit suitable to handle small spills of decontamination fluids, hydraulic fluid, or fuels and containing sorbent pads, tubes, and nitrile or similar gloves; and
- Cellular telephones.

14.0 LOGS, REPORTS, AND RECORD KEEPING

A system of reports and logs will be used to document activities related to site health and safety. The field oversight representative/SSHO will generate a brief weekly summary of health and safety issues and resolutions. These reports will include injuries, accidents, near accidents, interpretations of this SSHP or regulations, interactions with auditors/regulators/USACE personnel, and any off-normal events. These reports will be limited to one page or less.

In addition to the weekly reports, the following documents will be generated and submitted to the USACE Project Manager:

- Training logs will contain information covered and the signatures of the trainer and those attending. These logs will contain documentation of pre-entry (project start) training, routine ("tailgate") safety briefings, and visitor training.
- Daily safety inspection logs will contain the dates of inspections, identity of the person doing the inspection, the examined areas/activities/equipment, any deficiencies, and any corrective actions taken.
- Equipment maintenance logs will contain the dates and types of routine maintenance performed on-site equipment.
- The field oversight representative will add all employees/visitors to the on-site access roster. The roster includes the names of all personnel who will perform on-site work or visit the site and certification of required training. It will not contain the names of delivery or similar personnel.
- Environmental and personal exposure monitoring/sampling results will be maintained in a log that will contain monitoring data, location and time of monitoring, types of work being done, calibration records, and the identities of personnel performing monitoring.

Samples of reporting forms are included in Appendix A but any similar or equivalent forms may be used. If IDW is stored onsite, weekly inspections are required.

15.0 REFERENCES

ACGIH (American Conference of Governmental Industrial Hygienists) 2010. *2010 (Threshold Limit Values) TLVs® and Biological Exposure Indices (BEIs) and Guide to Occupational Exposure Values.*

CDC (Center for Disease Control) 2006. West Nile Virus: What You Need To Know. http://www.cdc.gov/ncidod/dvbid/westnile/wnv_factsheet.htm. September 2006.

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International Occupational Heath and Safety Information Center 2008. International Chemical Safety Cards. December 2007.

Leidos Engineering of Ohio, Inc. 2015. *Final Remedial Investigation Report for Soil, Sediment, and Surface Water at RVAAP-50 Atlas Scrap Yard, Ravenna Army Ammunition Plant, Ravenna, Ohio*, dated 18 June.

NIOSH (National Institute of Occupational Safety and Health)/OSHA/United States Coast Guard/United States Environmental Protection Agency 1985. *Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities.* October 1985.

NIOSH 2005. *NIOSH Pocket Guide to Chemical Hazards*. September 2005.

Ohio EPA (Ohio Environmental Protection Agency) 2004. *Director's Final Findings and Orders for the Ravenna Army Ammunition Plant*. June 2004.

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USACE 2004b. *Munitions and Explosives of Concern (MEC) Support During Hazardous, Toxic, and Radioactive Waste (HTRW) and Construction Activities* USACE Engineering Pamphlet EP 75-1-2. August 2004.

USACE 2007. *Safety and Occupational Health Requirements for Hazardous, Toxic, and Radioactive Waste and Ordnance and Explosive Waste Activities*. ER-385-1-92. May 2007.

USACE 2008. *USACE Safety and Health Requirements Manual*. EM 385-1-1. September 2008.

APPENDIX A
REPORTING FORMS

DAILY SAFETY INSPECTION

PROJECT:____ Page 1 of 2

N	Y	NA	Item
			Daily safety briefing conducted
			Emergency numbers and route to hospital posted
			FWSHP and project-specific Addenda on-site, available to employees, and complete
			Required exposure monitoring conducted and documented
			Monitoring instruments (PID, OVA, CGI) calibrated daily against known standard and documented
			First aid kit available and inspected weekly
			Personnel wearing PPE required by SSHP for fieldwork (at least safety shoes or boots, safety glasses with side shields, and nitrile or similar gloves to handle potentially contaminated material)
			Personnel using buddy system (maintain visual or verbal contact and able to render aid)
			If temperature >70°F: heat stress training conducted, cool fluids available, pulse rates of personnel wearing Tyvek® are being monitored, work/rest cycle in SSHP being followed
			If temperature <40°F: cold stress training conducted, controls in SSHP implemented
			Personnel using appropriate biological hazard controls (See SSHP)
			Drill rig operating manual on-site
			Drill rigs/backhoe inspected weekly and documented
			Personnel near drill rig/backhoe or other overhead hazards wearing hardhats
			Each of two drill rig emergency shutdown devices tested daily
			Employees excluded from under lifted loads
			Unnecessary personnel excluded from hazardous areas, specifically near heavy equipment
			Radius of exclusion zone around drill rig at least equal to mast height
			Personnel wearing hearing protection when within 25 ft of drill rigs,/backhoe, generators, or other noisy equipment
			Containers of flammable liquids closed and labeled properly
			Fully charged fire extinguisher available 25 to 50 ft from flammables storage area and inspected monthly
			Personnel exiting potentially contaminated areas washing hands before eating
			Personnel using steam washer wearing faceshield, hearing protection, heavy duty waterproof gloves, Saranax or rainsuit

DAILY SAFETY INSPECTION

PROJECT:____ Page 2 of 2

N	Y	NA	Item
			Portable electrical equipment plugged to a GFCI
			Electrical wiring covered by insulation or enclosure
			Three wire, UL approved, extension cords used
			Housekeeping adequate (walkways clear of loose, sharp or dangerous objects and trip hazards, work areas clear of objects that might fall on employees)
			Walking/working surfaces safe (not slippery, no unguarded holes, no trip hazards)
			Excavations deeper than 5 ft shored or sloped (if personnel will enter) and in compliance with SSHP
			Moving (rotating) machinery guarded to prevent employee contact
			Fall protection provided for work at elevations greater than 4 ft
			All containers of hazardous material labeled to indicate contents and hazards
			MSDSs for hazardous materials on-site
			All vehicles equipped with two-way radios and cellular phones
			15-min eyewash (accessible and full) within 100 ft of areas where corrosive sample preservatives are poured
			Potable and non-potable water labeled
			Chainsaws have anti kick-back protection, personnel wearing cut resistant gloves, protective chaps
			Visitor access controlled
			Site hazards and controls consistent with SSHP
			Site hazard controls appropriate and sufficient

Actions taken to correct or control any “N” responses

____

Name Signature Date

DAILY HEALTH AND SAFETY SUMMARY

PROJECT NAME: **PROJECT NO:**

NAME: DATE: M Tu W Th F Sa Su TIME:

TASKS PERFORMED:

OFF-NORMAL EVENTS:

TAILGATE SAFETY MEETING LOG

PROJECT NAME: PROJECT NO:

DATE: M Tu W Th F Sa Su TIME:

WEATHER:

WORKING CONDITIONS:

PPE:

ITEMS DISCUSSED:

THE FOLLOWING INDIVIDUALS ATTENDED THE DAILY TAILGATE SAFETY MEETING (SIGNATURES)

SITE SAFETY AND HEALTH OFFICER

HEALTH AND SAFETY MONITORING LOG

PROJECT NAME: **PROJECT NO:**

DATE	INSTRUMENT/NO.	RESULTS	TIME	REMARKS	NAME

(For Safety Staff only)	REPORT NO.	EROC CODE	**UNITED STATES ARMY CORPS OF ENGINEERS** **ACCIDENT INVESTIGATION REPORT** *(For Use of this Form See Help Menu and USACE Suppl to AR 385-40)*	**REQUIREMENT CONTROL SYMBOL: CEEC-S-8(R2)**

1. **ACCIDENT CLASSIFICATION**

PERSONNEL CLASSIFICATION	INJURY/ILLNESS/FATAL	PROPERTY DAMAGE	MOTOR VEHICLE INVOLVED	DIVING
GOVERNMENT ☐ CIVILIAN ☐ MILITARY	☐	☐ FIRE INVOLVED ☐ OTHER	☐	☐
☐ CONTRACTOR	☐	☐ FIRE INVOLVED ☐ OTHER	☐	☐
☐ PUBLIC	☐ FATAL ☐ OTHER		☐	

2. **PERSONAL DATA**

a. Name *(Last, First, MI)*	b. AGE	c. SEX ☐ MALE ☐ FEMALE	d. SOCIAL SECURITY NUMBER	e. GRADE

f. JOB SERIES/TITLE	g. DUTY STATUS AT TIME OF ACCIDENT ☐ ON DUTY ☐ TDY ☐ OFF DUTY	h. EMPLOYMENT STATUS AT TIME OF ACCIDENT ☐ ARMY ACTIVE ☐ ARMY RESERVE ☐ VOLUNTEER ☐ PERMANENT ☐ FOREIGN NATIONAL ☐ SEASONAL ☐ TEMPORARY ☐ STUDENT ☐ OTHER *(Specify)* ______

3. **GENERAL INFORMATION**

a. DATE OF ACCIDENT *(month/day/year)*	b. TIME OF ACCIDENT *(Military time)* hrs	c. EXACT LOCATION OF ACCIDENT	d. CONTRACTOR'S NAME (1) PRIME:
e. CONTRACT NUMBER ______ ☐ CIVIL WORKS ☐ MILITARY ☐ OTHER *(Specify)* ______	f. TYPE OF CONTRACT ☐ CONSTRUCTION ☐ SERVICE ☐ A/E ☐ DREDGE ☐ OTHER *(Specify)* ______	g. HAZARDOUS/TOXIC WASTE ACTIVITY ☐ SUPERFUND ☐ DERP ☐ IRP ☐ OTHER *(Specify)* ______	(2) SUBCONTRACTOR:

4. **CONSTRUCTION ACTIVITIES ONLY** *(Fill in line and corresponding code number in box from list - see help menu)*

a. CONSTRUCTION ACTIVITY	(CODE) #	b. TYPE OF CONSTRUCTION EQUIPMENT	(CODE) #

5. **INJURY/ILLNESS INFORMATION** *(Include name on line and corresponding code number in box for items e, f & g - see help menu)*

a. SEVERITY OF ILLNESS/INJURY	(CODE) #	b. ESTIMATED DAYS LOST	c. ESTIMATED DAYS HOSPITALIZED	d. ESTIMATED DAYS RESTRICTED DUTY

e. BODY PART AFFECTED PRIMARY ______	(CODE) #	g. TYPE AND SOURCE OF INJURY/ILLNESS	
SECONDARY ______	(CODE) #	TYPE ______	(CODE) #
f. NATURE OF ILLNESS/INJURY ______	(CODE) #	SOURCE ______	(CODE) #

6. PUBLIC FATALITY *(Fill in line and correspondence code number in box - see help menu)*

a. ACTIVITY AT TIME OF ACCIDENT ______	(CODE) #	b. PERSONAL FLOATATION DEVICE USED? ☐ YES ☐ NO ☐ N/A

7. MOTOR VEHICLE ACCIDENT

a. TYPE OF VEHICLE	b. TYPE OF COLLISION	c. SEAT BELTS	USED	NOT USED	NOT AVAILABLE
☐ PICKUP/VAN ☐ AUTOMOBILE ☐ TRUCK ☐ OTHER *(Specify)* ______	☐ SIDE SWIPE ☐ HEAD ON ☐ REAR END ☐ BROADSIDE ☐ ROLL OVER ☐ BACKING ☐ OTHER *(Specify)* ______	(1) FRONT SEAT			
		(2) REAR SEAT			

8. PROPERTY/MATERIAL INVOLVED

a. NAME OF ITEM	b. OWNERSHIP	c. $ AMOUNT OF DAMAGE
(1)		
(2)		
(3)		

9. VESSEL/FLOATING PLANT ACCIDENT *(Fill in line and correspondence code number in box from list - see help menu)*

a. TYPE OF VESSEL/FLOATING PLANT ______	(CODE) #	b. TYPE OF COLLISION/MISHAP ______	(CODE) #

10. ACCIDENT DESCRIPTION *(Use additional paper, if necessary)*

11. **CAUSAL FACTOR(S)** *(Read Instruction Before Completing)*

a. (Explain YES answers in item 13)	YES	NO
DESIGN: Was design of facility, workplace or equipment a factor?	☐	☐
INSPECTION/MAINTENANCE: Were inspection & maintenance procedures a factor?	☐	☐
PERSON'S PHYSICAL CONDITION: In your opinion, was the physical condition of the person a factor?	☐	☐
OPERATING PROCEDURES: Were operating procedures a factor?	☐	☐
JOB PRACTICES: Were any job safety/health practices not followed when the accident occurred?	☐	☐
HUMAN FACTORS: Did any human factors such as, size or strength of person, etc., contribute to accident?	☐	☐
ENVIRONMENTAL FACTORS: Did heat, cold, dust, sun, glare, etc., contribute to the accident?	☐	☐

a. *(CONTINUED)*	YES	NO
CHEMICAL AND PHYSICAL AGENT FACTORS: Did exposure to chemical agents, such as dust, fumes, mists, vapors or physical agents, such as, noise, radiation, etc., contribute to accident?	☐	☐
OFFICE FACTORS: Did office setting such as, lifting office furniture, carrying, stooping, etc., contribute to the accident?	☐	☐
SUPPORT FACTORS: Were inappropriate tools/resources provided to properly perform the activity/task?	☐	☐
PERSONAL PROTECTIVE EQUIPMENT: Did the improper selection, use or maintenance of personal protective equipment contribute to the accident?	☐	☐
DRUGS/ALCOHOL: In your opinion, was drugs or alcohol a factor to the accident	☐	☐

b. WAS A WRITTEN JOB/ACTIVITY HAZARD ANALYSIS COMPLETED FOR TASK BEING PERFORMED AT TIME OF ACCIDENT?

☐ YES *(If yes, attach a copy.)* ☐ NO

12. **TRAINING**

a. WAS PERSON TRAINED TO PERFORM ACTIVITY/TASK? ☐ YES ☐ NO	b. TYPE OF TRAINING. ☐ CLASSROOM ☐ ON JOB	c. DATE OF MOST RECENT FORMAL TRAINING. (Month) (Day) (Year)

13. **FULLY EXPLAIN WHAT ALLOWED OR CAUSED THE ACCIDENT; INCLUDE DIRECT AND INDIRECT CAUSES** *(See instruction for definition of direct and indirect causes.) (Use additional paper, if necessary)*

a. DIRECT CAUSE

b. INDIRECT CAUSE(S)

14. **ACTION(S) TAKEN, ANTICIPATED OR RECOMMENDED TO ELIMINATE CAUSE(S).**

DESCRIBE FULLY:

15. **DATES FOR ACTIONS IDENTIFIED IN BLOCK 14.**

a. BEGINNING (Month/Day/Year)	b. ANTICIPATED COMPLETION (Month/Day/Year)

c. SIGNATURE AND TITLE OF SUPERVISOR COMPLETING REPORT CORPS __________ CONTRACTOR __________	d. DATE *(Mo/Da/Yr)*	e. ORGANIZATION IDENTIFIER *(Div, Br, Sect)*	f. OFFICE SYMBOL

16. **MANAGEMENT REVIEW** *(1st)*

a. ☐ CONCUR b. ☐ NON CONCUR c. COMMENTS

SIGNATURE	TITLE	DATE

17. **MANAGEMENT REVIEW** *(2nd - Chief Operations, Construction, Engineering, etc.)*

a. ☐ CONCUR b. ☐ NON CONCUR c. COMMENTS

SIGNATURE	TITLE	DATE

18. **SAFETY AND OCCUPATIONAL HEALTH OFFICE REVIEW**

a. ☐ CONCUR b. ☐ NON CONCUR c. ADDITIONAL ACTIONS/COMMENTS

SIGNATURE	TITLE	DATE

19. **COMMAND APPROVAL**

COMMENTS

COMMANDER SIGNATURE	DATE

*U.S. GOVERNMENT PRINTING OFFICE: 1993-0-791-757

10. ACCIDENT DESCRIPTION *(Continuation)*

13a. DIRECT CAUSE *(Continuation)*

APPENDIX B
PROJECT-SPECIFIC QUALITY ASSURANCE PROJECT PLAN

Project-Specific Uniform Federal Policy - Quality Assurance Project Plan for a Pilot Study and Feasibility Study at RVAAP-50 Atlas Scrap Yard

Camp Ravenna
Ravenna, Ohio

19 February 2016

Contract No. W912QR-14-D-0001
Delivery Order No. 0004

Prepared for:

US Army Corps of Engineers
Louisville District
600 Martin Luther King Jr. Place
Louisville, Kentucky 40202

TABLE OF CONTENTS

1.0 INTRODUCTION

This Final Project-Specific Uniform Federal Policy - Quality Assurance Project Plan (UFP-QAPP) presents or references the organization, objectives, functional activities, and specific quality assurance (QA) and quality control (QC) activities associated with the Work Plan for a Pilot Study and Feasibility Study at former Ravenna Army Ammunition Plant (RVAAP)-50 Atlas Scrap Yard in Ravenna, Ohio. This UFP-QAPP was prepared in accordance with U. S. Environmental Protection Agency (USEPA) UFP guidance, and the Facility-Wide Quality Assurance Project Plan (FWQAPP) (SAIC 2011a). All QA/QC procedures are in accordance with applicable professional technical standards, USEPA requirements, government regulations and guidelines, and specific project goals and requirements.

Alliant Corporation (Alliant) was tasked by the U. S. Army Corps of Engineers (USACE) to prepare and submit this Project Specific UFP-QAPP to the U.S. Army in accordance with the Performance Work Statement (PWS), Contract No. W912QR-14-D-0001, Delivery Order (DO) No. 0004. The DO was issued by the United States Corps of Engineers, Louisville District on September 17, 2015. The following subsections present descriptions for the installation and the Atlas Scrap Yard area of concern (AOC).

1.1 PROJECT OVERVIEW

A brief project overview is provided in the following paragraphs. Additional information concerning the site history and background may be found in the Project-Specific Work Plan.

A Remedial Investigation (RI) was conducted previously conducted at the Atlas Scrap Yard AOC (Leidos, 2014). The RI identified five (5) PAHs as chemicals of concern (COCs) at the site. The identified PAHs are benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and dibenz(a,h)anthracene. The PAH COCs were primarily identified in the 0-1 foot (ft) below ground surface (bgs) interval near the stockpiled railroad ties as shown in Figure ES-2 of the Final RI Report (Leidos, 2015a), and Figure 3-1 of the project Work Plan. Additionally, a small area in the southern part of the site in the vicinity of a former incinerator has been characterized by elevated lead concentrations, and constitutes a lead “hot spot.”

Alliant has been tasked to 1) conduct a pilot study of the Vapor Energy Generator© (VEG©) technology for treatment of polycyclic aromatic hydrocarbon (PAH)-impacted soil, and conduct bench-scale studies for steel slag for treatment of lead-impacted soil, 2) and to obtain the data necessary to update a Feasibility Study (FS) Report for the Atlas Scrap Yard AOC.

Contaminated soils at the Atlas Scrap Yard AOC will be tested for the suitability of using VEG© technology to treat PAH-impacted soil, and steel slag to treat lead-impacted soil. The actual tests will be conducted by Alliant’s subcontractor, Endpoint Consulting, Inc. (Endpoint), a California-based environmental company. VEG© technology is a sustainable, green remediation technology that involves ex-situ thermal treatment of impacted soils in an enclosed treatment chamber using steam. A Preliminary Draft FS Report was previously prepared for the Atlas Scrap Yard AOC [Leidos Engineering of Ohio, Inc. (Leidos), 2015b]. Since completion of the FS Report, an additional technology has been identified as a potential remedial alternative. Therefore, the results from the pilot- and bench-scale studies will be used to complete the FS Report.

QAPP Worksheet #1
(UFP-QAPP Manual Section 2.1) -- Title and Approval Page

Project-Specific Quality Assurance Project Plan
Document Title

U.S. Army Corps of Engineers – Louisville District
Lead Organization

Richard Stout, Alliant Corporation
Preparer's Name and Organizational Affiliation

320 N Cedar Bluff Rd, Suite 200, Knoxville, TN 37923, 865-934-2222, rstout@alliantcorp.com
Preparer's Address, Telephone Number, and E-mail Address

19 February 2016
Preparation Date (Day/Month/Year)

Investigative Organization's Project Manager: On File
Signature
Belinda Price / Alliant Corporation / 19 February 2016
Printed Name/Organization/Date

Investigative Organization's Project QA Officer: On File
Signature
Paul Shipp / Alliant Corporation / 19 February 2016
Printed Name/Organization/Date

Lead Organization's Project Manager: On File
Signature
Eric Cheng / USACE COR / 19 February 2016
Printed Name/Organization/Date

Approval Signatures: See Ohio EPA Approval Letter
Signature

N/A
Printed Name/Title/Date

Approval Authority: Ohio EPA

Other Approval Signatures: N/A
Signature

N/A
Printed Name/Title/Date

Document Control Number: N/A

QAPP Worksheet #2
(UFP-QAPP Manual Section 2.2.4) -- QAPP Identifying Information

Site Number/Code: **1667000109 (Facility ID No.)**
Operable Unit: **N/A**
Contractor Name: **Alliant Corporation**
Contractor Number: **N/A**
Contract Title: **Pilot Study and Feasibility Study at RVAAP-50 Atlas Scrap Yard**
Work Assignment Number: **Task 0004**

1. Identify guidance used to prepare QAPP: Facility Wide Quality Assurance Project for Camp Ravenna and workbook for Uniform Federal Policy for Quality Assurance Project Plans
2. Identify regulatory program: CERCLA
3. Identify approval entity: CERCLA
4. Indicate whether the QAPP is a generic or a [✓ project-specific] QAPP. (circle one)
5. List dates of scoping sessions that were held:
6. List dates and titles of QAPP documents written for previous site work, if applicable:

Title	Approval Date
Not Applicable	

7. List organizational partners (stakeholders) and connection with lead organization: USACE, Ohio EPA, Army National Guard and Camp Ravenna
8. List data users: All of the above listed stakeholders
9. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusion below: # 3, 4, 5, 6, 7, 8, 9, 10, 13, 15, 18, 29, 31, 32 or 33 Explanations are included on individual forms.

Circle QAPP elements and required information that are not applicable to the project. Provide an explanation in the QAPP.

Required QAPP Element(s) and Corresponding QAPP Section(s)	Crosswalk to Required Documents	Optional QAPP Worksheet # in QAPP Workbook	Required Information
Project Management and Objectives			
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Required QAPP Element(s) and Corresponding QAPP Section(s)	Crosswalk to Required Documents	Optional QAPP Worksheet # in QAPP Workbook	Required Information
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QAPP Worksheet #3
(UFP-QAPP Manual Section 2.3.1) -- Distribution List

List those entities to whom copies of the approved QAPP, subsequent QAPP revisions, addenda, and amendments.

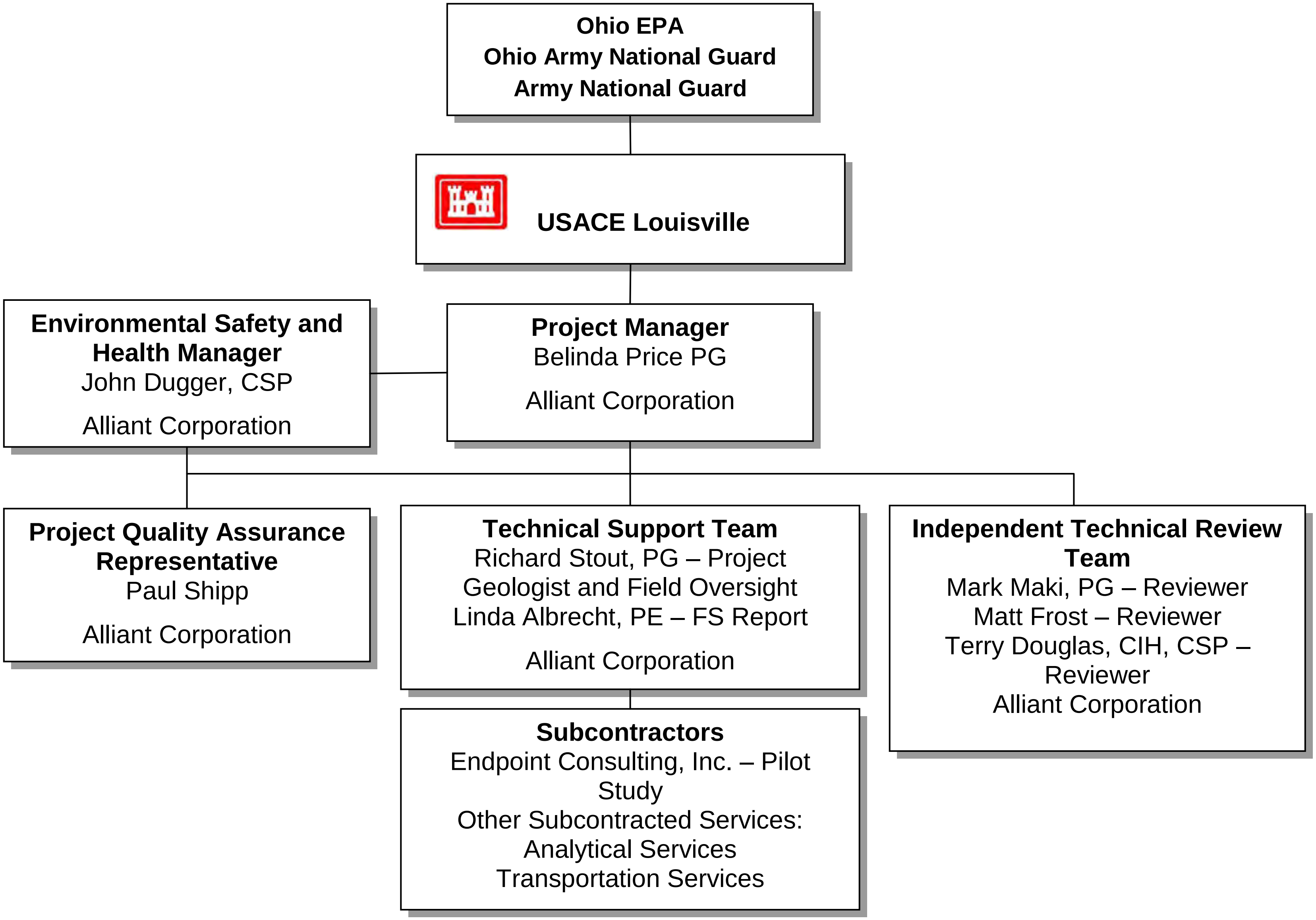
Name/Organization	Title	Address	Phone Number and Email
Justin Burke, Ohio EPA CO	Environmental Specialist III	50 West Town Street Suite 700 Columbus, OH 43216	T: (614) 644-2902 E: Justin.burke@epa.state.og.us
Bob Princic, Ohio EPA DERR		2110 East Aurora Road Twinsburg, OH 44087	T: (330) 963-1230 F: (330) 487-0769 E: bob.princic@epa.ohio.gov
Rod Beals, Ohio EPA DERR	Environmental Manager	2110 East Aurora Road Twinsburg, OH 44087	T: (330) 963-1218 E: rod.beals@epa.state.oh.us
Mark Leeper, ARNG	ARNG Directorate	111 S. George Mason Drive Arlington, VA 22204	T: (703) 607-7955 E: mark.s.leeper.civ@mail.mil
Kevin Sedlak, ARNG	Restoration Project Manager Camp Ravenna	1438 State Route 534 SW Newton Falls, OH 44444	T: (614) 336-6000 ext. 2053 E: kevin.m.sedlak.ctr@mail.mil
Katie Tait, OHARNG	Environmental Specialist	1438 State Route 534 SW Newton Falls, OH 44444	T : (614) 336-6136 F : (614) 336-6135 E : kathryn.s.tait.nfg@mail.mil
Greg Moore, USACE – Louisville District	Project Manager	600 Martin Luther King Jr. Place Louisville, KY 40201	T: (502) 315-6902 E: gregory.f.moore@usace.army.mil
Nathaniel Peters II, USACE – Louisville District	Contracting Officer	600 Martin Luther King Jr. Place Louisville, KY 40201	T: (502) 315-2624 E: nathaniel.peters.ii@usace.army.mil
Gail Harris, Vista Sciences Corporation, RVAAP Administrative Record	Archivist / Technical Librarian	1438 State Route 534 SW Newton Falls, OH 44444	T: (330) 872-8003 E: gail.harris@vistasciences.com
Pat Ryan, Leidos-REIMS	Senior Environmental Scientist	301 Laboratory Road Oak Ridge, TN 37830	T: (865) 481-4664 E: patrick.f.ryan@leidos.com
Eric Cheng, USACE – Louisville District	COR Technical Manager	600 Martin Luther King Jr. Place Louisville, KY 40201	T : (502) 315-7443 F : (502) 315-6309 E : eric.s.cheng@usace.army.mil
Belinda Price, Alliant	Project Manager	320 N Cedar Bluff Road, Suite 200 Knoxville, TN 37923	T: (865) 934-5143 F: (865) 769-0946 E: bprice@alliantcorp.com

QAPP Worksheet #4
(UFP-QAPP Manual Section 2.3.2) -- Project Personnel Sign-Off Sheet

Have copies of this form signed by key project personnel from each organization to indicate that they have read the applicable QAPP sections and will perform the tasks as described. Ask each organization to forward signed sheets to the central project file.

Name	Organization	Signature	Date

QAPP Worksheet #5
(UFP-QAPP Manual Section 2.4.1) -- Project Organizational Chart



Ohio EPA
Ohio Army National Guard
Army National Guard

USACE Louisville

Environmental Safety and Health Manager
John Dugger, CSP

Alliant Corporation

Project Manager
Belinda Price PG

Alliant Corporation

Project Quality Assurance Representative
Paul Shipp

Alliant Corporation

Technical Support Team
Richard Stout, PG – Project Geologist and Field Oversight
Linda Albrecht, PE – FS Report

Alliant Corporation

Independent Technical Review Team
Mark Maki, PG – Reviewer
Matt Frost – Reviewer
Terry Douglas, CIH, CSP – Reviewer
Alliant Corporation

Subcontractors
Endpoint Consulting, Inc. – Pilot Study
Other Subcontracted Services:
Analytical Services
Transportation Services

QAPP Worksheet #6
(UFP-QAPP Manual Section 2.4.2) -- Communication Pathways

Describe the communication pathways and modes of communication that will be used during the project, after the QAPP has been approved. Describe the procedures for soliciting and/or obtaining approval between project personnel, between different contractors, and between samplers and laboratory staff. Describe the procedure that will be followed when any project activity originally documented in an approved QAPP requires real-time modification to achieve project goals or a QAPP amendment is required. Describe the procedures for stopping work and identify who is responsible.

Communication Drivers	**Responsible Entity**	**Name**	**Phone Number**	**Procedure** (timing, pathways, etc.)

This information is provided in the Project Management Plan Section 3.2 Coordination and Communication.

QAPP Worksheet #7
(UFP-QAPP Manual Section 2.4.3) -- Personnel Responsibilities and Qualifications Table

Identify project personnel associated with each organization, contractor, and subcontractor participating in responsible roles.

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Belinda Price, P.G.	Project Manager	Alliant	Management of Project	MS, PG
Mehrdad Javaherian	Engineer	Endpoint Consulting, Inc.	Conduct Bench and Pilot Tests	PhD, PE, LEED-GA

See Worksheet #5 for additional personnel.

QAPP Worksheet #8
(UFP-QAPP Manual Section 2.4.4) -- Special Personnel Training Requirements Table

Provide the following information for those projects requiring personnel with specialized training. Attach training records and/or certificates to the QAPP or note their location.

Project Function	Specialized Training By Title or Description of Course	Training Provider	Training Date	Personnel / Groups Receiving Training	Personnel Titles / Organizational Affiliation	Location of Training Records / Certificates[1]

There are no special personnel training requirements for this project.

[1] If training records and/or certificates are on file elsewhere, document their location in this column. If training records and/or certificates do not exist or are not available, then this should be noted.

QAPP Worksheet #9
(UFP-QAPP Manual Section 2.5.1) -- Project Scoping Session Participants Sheet

Complete this worksheet for each project scoping session held. Identify project team members who are responsible for planning the project. The following is the generic form used for scoping meetings.

Project Name:
Projected Date(s) of Sampling:
____

Project Manager:

Site Name:

Site Location:

Date of Session:
Scoping Session Purpose:

Name	**Title**	**Affiliation**	**Phone #**	**E-mail Address**	**Project Role**

This project involves conducting Bench and Pilot Studies as well as preparation of a Feasibility Study and there were no formal project scoping sessions.

Comments/Decisions:

Action Items:

Consensus Decisions:

QAPP Worksheet #10
(UFP-QAPP Manual Section 2.5.2) -- Problem Definition

The problem to be addressed by the project:

- This project will address the efficacy of the treatment of PAH impacted soils at the site with ex-situ thermal treatment and lead impacted soil treatment by mixing the soil with steel slag

The environmental questions being asked:

- No questions are being asked other than whether or not the treatment options will effectively treat site soils. The information from the Pilot Study will be used in preparation of the Atlas Scrap Yard FS Report.

Observations from any site reconnaissance reports:

- There are no relevant observations other than the site description.

A synopsis of secondary data or information from site reports:

- There are no relevant secondary data.

The possible classes of contaminants and the affected matrices:

- Past practices at the site were the likely cause of the impacted soils. The Atlas Scrap Yard site soil is impacted with PAH and lead.

The rationale for inclusion of chemical and nonchemical analyses:

- Chemical analyses will be conducted to determine the effectiveness of the soil treatment pilot study.

QAPP Worksheet #10
(UFP-QAPP Manual Section 2.5.2) -- Problem Definition (continued)

Information concerning various environmental indicators:

A Preliminary Draft FS Report was previously prepared for the Atlas Scrap Yard AOC (RVAAP-50) (Leidos, 2015). Since completion of the FS Report, additional technologies as discussed above have been identified as potential remedial alternatives. Therefore, the results from the pilot- and bench-scale studies will be used to complete the FS Report.

Project decision conditions (If..., then...@ statements): [complete during in-class exercise]

Contaminated soils at the site will be tested for the suitability of using Vapor Energy Generation© (VEG©) technology to treat PAH-impacted soil in a sequence of a bench and pilot tests. Additionally a bench test only using steel slag will be conducted to test treatment of lead-impacted soil.

Samples will be collected from the soils prior to shipment to characterize PAH, lead, and leachable lead in the soils prior to treatment.

Bench-scale ex-situ thermal treatment of PAHs in site soils will be conducted by testing a series of treatment temperatures and treatment residence times within the VEG$^{©}$ Technology remediation system as described in the subcontractor Work Plan (Appendix C). The objective of the bench-scale tests is to determine the optimal system treatment temperatures and residence times for effective treatment of the PAH-impacted soils.
The specifics of the pilot-scale study at the Atlas Scrap Yard AOC (RVVAAP-50) will be based on the results of the VEG© bench-scale study. The objective of the pilot-scale test is to demonstrate the effectiveness of the VEG© technology for effective treatment of PAH-impacted site soils.

Upon completion of the tests, Endpoint will conduct post-treatment sampling of the soils.
The testing information will be used to prepare and submit to the Army a Draft Technical Memorandum outlining all procedures, results, and conclusions relative to bench-scale and pilot-scale tests performed.
The Army will prepare and submit a Revised Preliminary Draft, Draft, and Final FS Reports for RVAAP-50, Atlas Scrap Yard.

QAPP Worksheet #11
(UFP-QAPP Manual Section 2.6.1) -- Project Quality Objectives/Systematic Planning Process Statements

Use this worksheet to develop project quality objectives (PQOs) in terms of type, quantity, and quality of data determined using a systematic planning process. Provide a detailed discussion of PQOs in the QAPP. List the PQOs in the form of qualitative and quantitative statements. These statements should answer questions such as those listed below. These questions are examples only, however; they are neither inclusive nor appropriate for all projects.

Who will use the data?

Alliant's Subcontractor (Endpoint), Alliant and Stakeholders

What will the data be used for?

To determine the efficiency of the VEG® System and steel slag mixing for remediation of polycyclic aromatic hydrocarbons and metals in soils.

What type of data are needed (matrix, target analytes, analytical groups, field screening, on-site analytical or off-site laboratory techniques, sampling techniques)?

Off-site laboratory data and 7-point composite soil sampling thereafter.

How "good" do the data need to be in order to support the environmental decision?

The data quality will be sufficient to support the decision to evaluate the tested remedial actions and support preparation of the FS Report.

How much data are needed (number of samples for each analytical group, matrix, and concentration)?

Soil: (10) SVOC (PAHs) samples; (2) Lead samples; (1) TCLP sample; (16) SPLP samples; (1) pH sample.

Where, when, and how should the data be collected/generated?

The data will be collected during the bench-scale and pilot-scale testing

QAPP Worksheet #11
(UFP-QAPP Manual Section 2.6.1) -- Project Quality Objectives/Systematic Planning Process Statements (continued)

Who will collect and generate the data?

Alliant’s Subcontractor (Endpoint).

How will the data be reported?

The data will be reported in Technical Memoranda and also included in the Atlas Scrap Yard FS Report.

How will the data be archived?

The data will be archived in ERIS.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2) -- Measurement Performance Criteria Table

Complete this worksheet for each matrix, analytical group, and concentration level. Identify the data quality indicators (DQIs), measurement performance criteria (MPC), and QC sample and/or activity used to assess the measurement performance for both the sampling and analytical measurement systems. Use additional worksheets if necessary. If MPC for a specific DQI vary within an analytical parameter, i.e., MPC are analyte-specific, then provide analyte-specific MPC on an additional worksheet.

Matrix	Soil
Analytical Group[1]	
Concentration Level	

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and / or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
7-pt Composite	6020A/6010C	N/A	Laboratory QC	N/A	Analytical
7 pt Composite	8270D SIM	N/A	Laboratory QC	N/A	Analytical
7-pt Composite	1311	N/A	Laboratory QC	N/A	Analytical
7-pt Composite	1312	Field Duplicates	Laboratory QC	Reproducibility	Sampling and Analytical
7-pt Composite	9045	N/A	Laboratory QC	N/A	Analytical

[1] If information varies within an analytical group, separate by individual analyte.

[2] Reference number from QAPP Worksheet #21 (see Section 3.1.2).

[3] Reference number from QAPP Worksheet #23 (see Section 3.2).

QAPP Worksheet #13

(UFP-QAPP Manual Section 2.7) -- Secondary Data Criteria and Limitations Table

Identify all secondary data and information that will be used for the project and their originating sources. Specify how the secondary data will be used and the limitations on their use. Each project specific area must include any limitations on use of the data in the final report. Data from each project specific area is accumulated in the final site report and the limits on data use must be presented.

Secondary Data	Data Source (originating organization, report title and date)	Data Generator(s) (originating organization, data types, data generation / collection dates)	How Data Will Be Used	Limitations on Data Use

There are no secondary data relevant to this project.

QAPP Worksheet #14
(UFP-QAPP Manual Section 2.8.1) -- Summary of Project Tasks

Provide a brief overview of the listed project activities. The following table must be completed for each project area.

Sampling Tasks:

Collect 7-aliquot samples of soil Pre-Treatment. Collect 7-point composite samples for post-treatment analysis after the bench scale tests. Collect 7-point composite for both pre and post treatment analysis after pilot testing.

Analysis Tasks:

See Table 3-1 in Work Plan

Quality Control Tasks:

Collect ten (10) duplicate samples for analysis of Long-term Leachable Lead using USEPA Method SPLP 1312.

Secondary Data:

Not Applicable.

Data Management Tasks:

Data will be filed electronically on the Alliant server until submission to USACE. Otherwise, there are no data management tasks.

Documentation and Records:

Data will be submitted to USACE in Electronic Data Deliverable (EDD) format compatible with the Environmental Restoration Information System (ERIS).

Assessment / Audit Tasks

No Audits or Assessments are formally planned. The Alliant Project Manager will ensure compliance with the Work Plan, QAPP and Project Management Plan.

Data Review Tasks:

Data will be reviewed by the laboratory prior to submission. Additionally, data will be validated/reviewed by Alliant’s subcontractor in accordance with EPA 540-R-08-005.

QAPP Worksheet #15
(UFP-QAPP Manual Section 2.8.1) -- Reference Limits and Evaluation Table

Compound	CAS Number	Project Reporting Levels
		Soil (µg/kg)
Acenaphthene	83-32-9	6.50
Acenaphthylene	208-96-8	6.60
Anthracene	120-12-7	6.60
Benz(*a*)anthracene	56-55-3	6.60
Benzo(*a*)pyrene	50-32-8	6.60
Benzo(*b*)fluoranthene	205-99-2	6.60
Benzo(*ghi*)perylene	191-24-2	6.60
Benzo(*k*)fluoranthene	207-08-9	6.60
Chrysene	218-01-9	6.60
Dibenz(*a*,*h*)anthrancene	53-70-3	6.60
Fluoranthene	206-44-0	6.60
Fluorene	86-73-7	6.60
Indeno(1,2,3-*cd*)pyrene	193-39-5	6.60
Phenanthrene	85-01-8	6.60
Pyrene	129-00-0	6.60
Compound	**CAS Number**	**Project Reporting Levels**
		Soil (mg/kg)
Lead	7439-92-1	0.300

QAPP Worksheet #16
(UFP-QAPP Manual Section 2.8.2) -- Project Schedule / Timeline Table

List all project activities as well as the QA assessments that will be performed during the course of the project. Include the anticipated start and completion dates.

Activities	Organization	Dates (MM/DD/YY)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		

The project Schedule is presented in the Project Management Plan in Appendix A.

QAPP Worksheet #17
(UFP-QAPP Manual Section 3.1.1) -- Sampling Design and Rationale

Describe the project sampling approach. Provide the rationale for selecting sample locations and matrices for each analytical group and concentration level.

Describe and provide a rationale for choosing the sampling approach (e.g., grid system, biased statistical approach):

Samples will be collected during the bench-scale and pilot-scale tests as necessary to establish pre-treatment conditions.

Samples will also be collected to establish post-treatment conditions. Samples will be collected as 7-point composites from stockpiles to effectively allow for representative samples.

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will and at what concentration levels, the sampling locations (including QC, critical, and background samples), the number of samples to be taken, and the sampling frequency (including seasonal considerations) [May refer to map or Worksheet #18 for details]:

All of the samples will consist of soils in two 5-gallon buckets, a 55-gallon drum, or stockpiled soils. There will be ten (10) PAH samples (8270D SIM), one (1) TCLP sample for leachable lead (1311) and sixteen (16) SPLP samples for long-term leachable lead (1312). Additionally, two (2) samples will be analyzed for lead (6020A and 6010C), and one (1) sample will be analyzed for pH using Method 9045. The field activities will be conducted during the dry weather periods. Since these samples will help determine the efficiency of remedial alternatives, no background sampling will be necessary. Pretreatment profiles and sampling will establish baseline conditions.

QAPP Worksheet #18
(UFP-QAPP Manual Section 3.1.1) -- Sampling Locations and Methods/SOP Requirements Table

List all site locations that will be sampled and include sample/ID number, if available. (Provide a range of sampling locations of ID numbers if a site has a large number.) Specify matrix and, if applicable, depth at which samples will be taken. Only a short reference for the sampling location rationale is necessary for the table. The text of the QAPP should clearly identify the detailed rationale associated with each reference. Complete all required information, using additional worksheets if necessary

Sampling Location / ID Number	**Matrix**	**Depth** (units)	**Analytical Group**	**Concentration Level**	**Number of Samples** (identify field duplicates)	**Sampling SOP Reference**[1]	**Rationale for Sampling Location**

This information is provided in the Project-Specific Work Plan in Table 3-1.

[1] Specify the appropriate letter or number from the Project Sampling SOP References table (Worksheet #21).

QAPP Worksheet #19
(UFP-QAPP Manual Section 3.1.1) -- Analytical SOP Requirements Table

For each matrix, analytical group, and concentration level, list the analytical and preparation method/SOP and associated sample volume, container specifications, preservation requirements, and maximum holding time.

Matrix	**Analytical Group**	**Concentration Level**	**Analytical and Preparation Method / SOP Reference**[1]	**Sample Volume**	**Containers** (number, size, and type)	**Preservation Requirements** (chemical, temperature, light protected)	**Maximum Holding Time** (preparation / analysis)
Soil	PAHs	Low	8270D SIM/3550 (Ref 1)	Fill container full	250-ml glass w/PTFE Liner	Cool to 4°C	Extraction: 14 d Analysis: 40 d
Soil	Lead TCLP	N/A	1311/6010C (Ref 2/4)	200g	1-Liter glass, plastic or PTFE	Cool to 4°C	6 months
Soil	Lead SPLP	N/A	1312/6010C (Ref 3/4)	200g	250-ml glass, plastic or PTFE	Cool to 4°C	12 months
Soil	Inorganics	N/A	6020A (Ref 5)	200g	250-ml glass, plastic or PTFE	Cool to 4°C	6 months
Soil	General Chemistry	N/A	9045 (Ref 6)	100g	250-ml glass, plastic or PTFE	Cool to 4°C	As soon as possible

[1] Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).

These holding times are the maximum holding times as required by this worksheet. Turnaround times requested for each particular analysis are provided in Table 3-1 of the Project-Specific Work Plan.

QAPP Worksheet #20
(UFP-QAPP Manual Section 3.1.1) -- Field Quality Control Sample Summary Table

Summarize by matrix, analytical group, and concentration level the number of field QC samples that will be collected and sent to the laboratory.

Matrix	Analytical Group	Conc. Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations[2]	No. of Field Duplicate Pairs	No. of MS	No. of Field Blanks	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab
Soil	Inorganics–Long-term Leachable Lead	Low	1312 (ref 3)	(16) Post-Treatment Soil Samples	10	0	0	0	0	26

[1] Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).

[2] If samples will be collected at different depths at the same location, count each discrete sampling depth as a separate sampling location or station.

QAPP Worksheet #21
(UFP-QAPP Manual Section 3.1.2) -- Project Sampling SOP References Table

List all SOPs associated with project sampling including, but not limited to, sample collection, sample preservation, equipment cleaning and decontamination, equipment testing, inspection and maintenance, supply inspection and acceptance, and sample handling and custody. Include copies of the SOPs as attachments or reference all in the QAPP. Sequentially number sampling SOP references in the Reference Number column. The reference number can be used throughout the QAPP to refer to a specific SOP.

Reference Number	**Title, Revision Date and / or Number**	**Originating Organization**	**Equipment Type**	**Modified for Project Work?** (Y/N)	**Comments**
1	Work Plan for Pilot Study and FS at RVAAP-50	Alliant	Spoon/Scoops/Bowls /Sample Containers	N	
2	Work Plan for Bench- and Pilot Scale Testing	Endpoint		N	
3	Project-Specific Quality Assurance Project Plan	Alliant		N	

QAPP Worksheet #22
(UFP-QAPP Manual Section 3.1.2.4) -- Field Equipment Calibration, Maintenance, Testing, and Inspection Table

Identify all field equipment and instruments (other than analytical instrumentation) that require calibration, maintenance, testing, or inspection and provide the SO reference number for each type of equipment. In addition, document the frequency of activity, acceptance criteria, and corrective action requirements on the worksheet.

Field Equipment	Calibration Activity	Maint. Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Resp. Person	SOP Reference[1]
PID	Calibration Check	Charge or Change Batteries	None	Check Operation Status	Daily	Pass or Fail	Re-Calibrate	Alliant	Manufacturer's Instructions

[1] Specify the appropriate reference letter or number from the Project Sampling SOP References table (Worksheet #21).

QAPP Worksheet #23
(UFP-QAPP Manual Section 3.2.1) -- Analytical SOP References Table

List all SOPs that will be used to perform on-site or off-site analysis. Indicate whether the procedure produces screening or definitive data. Sequentially number analytical SOP references in the Reference Number column. Include copies of the SOPs as attachments or reference in the QAPP. The reference number can be used throughout the QAPP to refer to a specific SOP.

Reference Number	Title, Revision Date, and / or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
1	SW 846\ 8270D SIM	Definitive	Organics	GC/MS	TestAmerica	N
2	SW 846 1311	Definitive	Inorganics	ICP	TestAmerica	N
3	SW 846 1312	Definitive	Inorganics	ICP	TestAmerica	N
4	SW 846 6010C	Definitive	Inorganics	ICP	TestAmerica	N
5	SW 846 6020A	Definitive	Inorganics	ICP	TestAmerica	N
6	SW 846 9045	Definitive	N/A	pH Meter	TestAmerica	N

QAPP Worksheet #24
(UFP-QAPP Manual Section 3.2.2) -- Analytical Instrument Calibration Table

Identify all analytical instrumentation that requires calibration and provide the SOP reference number for each. In addition, document the frequency, acceptance criteria, and corrective action requirements on the worksheet.

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]

TestAmerica, the laboratory selected for this project is DoD-approved. Laboratory analyses for this project will be conducted in accordance with Quality Services Manual (QSM) 5.0 or later.

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[1] Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23)~~.~~

QAPP Worksheet #25
(UFP-QAPP Manual Section 3.2.3) -- Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

Identify all analytical instrumentation that requires maintenance, testing, or inspection and provide the SOP reference number for each. In addition, document the frequency, acceptance criteria, and corrective action requirements on the worksheet.

Instrument / Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]

TestAmerica, the laboratory selected for this project is DoD-approved. Laboratory analyses for this project will be conducted in accordance with Quality Services Manual (QSM) 5.0 or later.

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[1] Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).

QAPP Worksheet #26
(UFP-QAPP Manual Appendix A) -- Sample Handling System

Use this worksheet to identify components of the project-specific sample handling system. Record personnel, and their organizational affiliations, who are primarily responsible for ensuring proper handling, custody, and storage of field samples from the time of collection, to laboratory delivery, to final sample disposal. Indicate the number of days field samples and their extracts/digestates will be archived prior to disposal.

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT

Sample Collection (Personnel/Organization):

Sample Packaging (Personnel/Organization):

Coordination of Shipment (Personnel/Organization):

Type of Shipment/Carrier:

SAMPLE RECEIPT AND ANALYSIS

Sample Receipt (Personnel/Organization):

Sample Custody and Storage (Personnel/Organization):

Sample Preparation (Personnel/Organization):

Sample Determinative Analysis (Personnel/Organization):

SAMPLE ARCHIVING

Field Sample Storage (No. of days from sample collection):

Sample Extract/Digestate Storage (No. of days from extraction/digestion):

Biological Sample Storage (No. of days from sample collection):

SAMPLE DISPOSAL

Personnel/Organization:

Number of Days from Analysis:

TestAmerica, the laboratory selected for this project is DoD-approved. Laboratory analyses for this project will be conducted in accordance with Quality Services Manual (QSM) 5.0 or later.

QAPP Worksheet #27
(UFP-QAPP Manual Section 3.3.3) -- Sample Custody Requirements Table

Describe the procedures that will be used to maintain sample custody and integrity. Include examples of chain-of-custody forms, traffic reports, sample identification, custody seals, laboratory sample receipt forms, and laboratory sample transfer forms. Attach or reference applicable SOPs.

Field Sample Custody Procedures (sample collection, packaging, shipment, and delivery to laboratory):

Samples will be collected, packaged and shipped from Camp Ravenna or Endpoint Laboratories. Sample containers will be labeled and placed in a cooler with bagged ice to cool to 4°C. Bubble wrap or other types of packaging material will be placed in the cooler to prevent breakage. The Chain of Custody form will be taped under the cooler lid. Samples will be shipped by a commercial courier to the laboratory for next day delivery.

Laboratory Sample Custody Procedures (receipt of samples, archiving, disposal):

The analytical laboratory will be responsible for receipt of samples and for disposal of sample after analysis.

Soils used in the bench-scale studies, regardless of the levels of lead or PAHs detected, will be considered as IDW. The soils will be placed back into the original buckets or drums and disposed of at an appropriate landfill using the post-treatment sample results as the profile for disposal prior to offsite transport by Safety Kleen. The waste manifest confirming transport and disposal of the soil drums at the landfill will be included in the Technical Memoranda.

Sample Identification Procedures:

Samples will be identified with unique sample identification numbers which reference the location and type of sample.

Chain-of-custody Procedures:

Chain of custody will be maintained from the time of sample collection through analysis and documented on a Chain-of-Custody Form. The original form will accompany all samples from the time of collection through laboratory receipt. Each custody transfer by hand delivery shall be documented by signature of the relinquishing and receiving individuals and the date and time of transfer. Forms will be placed in a sealing plastic bag inside the cooler or shipping container. The airbill number will be entered on the Chain-of-Custody Form. Samples will be considered to be under custody if: (1)They are in the sampler's possession, or (2) They are in the sampler's line of sight after being in possession, or (3) They are in a designated controlled secure area. The person collecting the samples will have the overall responsibility for ensured the care and custody of the samples is maintained until they are transferred or properly dispatched to the laboratory.

QAPP Worksheet #28
(UFP-QAPP Manual Section 3.4) -- QC Samples Table

Complete a separate worksheet for each sampling technique, analytical method/SOP, matrix, analytical group, and concentration level. If method/SOP QC acceptance limits exceed the measurement performance criteria, the data obtained may be unusable for making project decisions.

Matrix	
Analytical Group	
Concentration Level	
Sampling SOP	
Analytical Method / SOP Reference	
Sampler's Name	
Field Sampling Organization	
Analytical Organization	
Number of Sample Locations	

QC samples are listed in the Project Work Plan in Table 3-1.

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Equip blank						
MS (Lab QC)						
Field Duplicate						
LFB (QL)						

QAPP Worksheet #29
(UFP-QAPP Manual Section 3.5.1) -- Project Documents and Records Table

Identify the documents and records that will be generated for all aspects of the project including, but not limited to, sample collection and field measurement, on-site and off-site analysis, and data assessment.

Sample Collection Documents and Records	On-Site Analysis Documents and Records	Off-Site Analysis Documents and Records	Data Assessment Documents and Records	Other
Sample Collection Logs, Chain-of-Custody	Field Log Book	Analytical Lab (TestAmerica) EDD ERIS Data Management	Technical Memorandum Feasibility Study Report	

QAPP Worksheet #30
(UFP-QAPP Manual Section 3.5.2.3) -- Analytical Services Table

Identify all laboratories or organizations that will provide analytical services for the project, including on-site screening, on-site definitive, and off-site laboratory analytical work. Group by matrix, analytical group, concentration, and sample location or ID number. If applicable, identify the subcontractor laboratories and backup laboratory or organization that will be used if the primary laboratory or organization cannot be used.

Matrix	**Analytical Group**	**Concentration Level**	**Sample Locations/ID Number**	**Analytical SOP**	**Data Package Turnaround Time**	**Laboratory / Organization** (name and address, contact person and telephone number)	**Backup Laboratory / Organization** (name and address, contact person and telephone number)
Soil	Organic	Low	10 Samples	EPA SW-846 8270D SIM	24-hr	TestAmerica	NA
Soil	Inorganic	Low	2 Samples	EPA SW-846 6020A/6010C	15-days	TestAmerica	NA
Soil	Inorganic	Low	1 Sample	SW 846 9045	15-days	TestAmerica	NA
Soil	Inorganic	Low	1 Sample	SW 846 1311	28-day	TestAmerica	NA
Soil	Inorganic	Low	16 Samples	SW 846 1312	90-days	TestAmerica	NA

A single laboratory (TestAmerica) will provide analytical services for this project. TestAmerica is DoD-approved and compliant with QSM version 5.0 or later. CH2M Applied Sciences Laboratory may also be used if necessary and is DoD-approved and compliant with QSM version 5.0 or later.

QAPP Worksheet #31
(UFP-QAPP Manual Section 4.1.1) -- Planned Project Assessments Table

Identify the type, frequency, and responsible parties of planned assessment activities that will be performed for the project.

Assessment Type	**Frequency**	**Internal or External**	**Organization Performing Assessment**	**Person(s) Responsible for Performing Assessment** (title and organizational affiliation)	**Person(s) Responsible for Responding to Assessment Findings** (title and organizational affiliation)	**Person(s) Responsible for Identifying and Implementing Corrective Actions (CA)** (title and organizational affiliation)	**Person(s) Responsible for Monitoring Effectiveness of CA** (title and organizational affiliation)
Technical Memorandum	D, DF, F	Internal	Alliant / Endpoint	Belinda Price / Alliant / PM	Belinda Price / Alliant / PM	Belinda Price / Alliant / PM	Belinda Price / Alliant / PM
FS Report	D, DF, F	Internal	Alliant / Endpoint	Belinda Price / Alliant / PM	Belinda Price / Alliant / PM	Belinda Price / Alliant / PM	Belinda Price / Alliant / PM

This is a project with a short time frame and limited scope. The assessments planned for this project are also limited.

QAPP Worksheet #32
(UFP-QAPP Manual Section 4.1.2) -- Assessment Findings and Corrective Action Responses

For each type of assessment describe procedures for handling QAPP and project deviations encountered during the planned project assessments.

Assessment Type	**Nature of Deficiencies Documentation**	**Individual(s) Notified of Findings** (name, title, organization)	**Timeframe of Notification**	**Nature of Corrective Action Response Documentation**	**Individual(s) Receiving Corrective Action Response** (name, title, organization)	**Timeframe for Response**
ITIR	Technical Memorandum and FS Report ITIR	Belinda Price / Alliant / PM	Immediate	Response to Comments	Mehrdad Javaherian / Endpoint / PM	10-days
Analytical Data Review	Data Load Report and Data Review	Belinda Price / Alliant / PM	Immediate	Analytical Review, re-test analytical results, reload data in EDD	Mehrdad Javaherian / PM / Endpoint & TestAmerica	10-days

This is a project with a short time frame and there are no planned assessments for this project. The assessments planned for this project are also limited.

QAPP Worksheet #33
(UFP QAPP Manual Section 4.2) -- QA Management Reports Table

Identify the frequency and type of planned QA Management Reports, the project delivery dates, the personnel responsible for report preparation, and the report recipients.

Type of Report	**Frequency** (daily, weekly monthly, quarterly, annually, etc.)	**Projected Delivery Date(s)**	**Person(s) Responsible for Report Preparation** (title and organizational affiliation)	**Report Recipient(s)** (title and organizational affiliation)

There are no QA reports planned for this project. However, Monthly Progress Reports will be prepared as discussed in Section 3.2.1 of the Project Management Plan.

QAPP Worksheet #34
(UFP-QAPP Manual Section 5.2.1) -- Verification (Step I) Process Table

Describe the processes that will be followed to verify project data. Describe how each item will be verified, when the activity will occur, and what documentation is necessary, and identify the person responsible. *Internal* or *external* is in relation to the data generator.

Verification Input	**Description**	**Internal / External**	**Responsible for Verification** (name, organization)
Data Review	The data will be checked for completeness, correctness, consistency, and conformance to the analytical procedures and contractual agreements, and to ensure that holding times for the analyses have been met upon receipt. Formal data validation will not be conducted for this project.	External	Belinda Price, Alliant Corporation Mehrdad Javaherian / PM / Endpoint & TestAmerica

QAPP Worksheet #35
(UFP-QAPP Manual Section 5.2.2) -- Validation (Steps IIa and IIb) Process Table

Describe the processes that will be followed to validate project data. Validation inputs include items such as those listed in Table 9 of the UFP-QAPP Manual (Section 5.1). Describe how each item will be validated, when the activity will occur, and what documentation is necessary and identify the person responsible. Differentiate between steps IIa and IIb of validation.

Step Iia / IIb	Validation Input	Description	Responsible for Validation (name, organization)

Formal data validation will not be conducted as part of the DQOs for this pilot study project.

QAPP Worksheet #36
(UFP-QAPP Manual Section 5.2.2) -- Validation (Steps IIa and IIb) Summary Table

Identify the matrices, analytical groups, and concentration levels that each entity performing validation will be responsible for, as well as criteria that will be used to validate those data.

Step IIa / IIb	Matrix	Analytical Group	Concentration Level	Validation Criteria	Data Validator (title and organizational affiliation)

Formal data validation will not be conducted as part of the DQOs for this pilot study project.

QAPP Worksheet #37
(UFP-QAPP Manual Section 5.2.3) -- Usability Assessment

Describe the procedures / methods / activities that will be used to determine whether data are of the right type, quality, and quantity to support environmental decision-making for the project. Describe how data quality issues will be addressed and how limitations on the use of the data will be handled.

Summarize the usability assessment process and all procedures, including interim steps and any statistics, equations, and computer algorithms that will be used:

Formal data validation will not be conducted for this project.

Describe the evaluative procedures used to assess overall measurement error associated with the project:

Identify the personnel responsible for performing the usability assessment:

Describe the documentation that will be generated during usability assessment and how usability assessment results will be presented so that they identify trends, relationships (correlations), and anomalies:

APPENDIX C
SUBCONTACTOR WORK PLAN

Endpoint.
Strategy. Science. Sustainability.

TECHNICAL MEMORANDUM

To: Eric Cheng, PE
US Army Corps of Engineers-Louisville District (USACE)

From: Mehrdad Javaherian, Ph.D., PE, LEED®GA
Endpoint Consulting, Inc. (Endpoint)

Cc: Belinda Price, PG
Alliant Corporation (Alliant)

Date: 10/07/15

Re: **Workplan for Bench- and Pilot-Scale Testing- Ex-Situ Thermal Desorption of Polycyclic Aromatic Hydrocarbons in Soils, and Bench-Scale Testing of Lead Stabilization in Soils,** RVAPP-50 Atlas Scrap Yard, Former Ravenna Army Ammunition Plant, Ravenna, OH

This Technical Memorandum (Memo) has been prepared by Endpoint as a subcontractor to Alliant Corporation. This Memo sets forth the approach for implementing bench- and pilot-scale studies for ex-situ thermal treatment of polycyclic aromatic hydrocarbons (PAHs) in soils at the above-referenced site. The Memo also includes the proposed approach for performing a focused bench-scale study on stabilization of lead in soil using steel slag.

1.0 Ex-Situ Thermal Desorption Bench-Scale Testing

This section summarizes the proposed approach to bench-scale testing of PAH-impacted soils using Endpoint's patented VEG ex-situ thermal desorption technology. Included are the purpose of the bench-scale testing, approach to pre- and post-treatment sampling of soils, and approach to thermal treatment of PAHs in soils. Much of the information presented for the bench-scale test is directly referenced later herein in support of summarizing the pilot-scale test activities.

1.1 Purpose and Objectives

The purpose and objectives of the bench-scale study are twofold:

1) To determine the potential for and magnitude of reductions in PAH soil concentrations resulting from ex-situ thermal treatment, particularly relative to industrial and residential regional screening levels (RSLs) protective of direct exposure pathways to soil as adopted by the US Environmental Protection Agency (USEPA). This finding, together with those of the pilot-scale test discussed later herein, will help assess the potential applicability of thermal treatment as a practical and effective remedial alternative for treatment of PAHs at the RVAAP-50 Atlas Scrap Yard (Scrap Yard) site, particularly for shallow, surficial soils where direct human exposure may remain a complete exposure

pathway and where significant reductions in PAH concentrations will be sought through the final soil remedy for the site. Treatment of PAHs to non-detect levels or below residential standards, followed by reuse of soils onsite may accordingly be evaluated as a potential remedial alternative for further consideration at the site.

2) To identify optimal treatment conditions, including treatment temperature and the residence time of soils within the VEG treatment chamber, deemed necessary to achieve the aforementioned numerical treatment objectives. The optimal treatment conditions will accordingly be implemented as part of pilot-scale testing activities referenced later herein.

The approach to the ex-situ thermal treatment bench-scale study, discussed in more detail in the following sections, has been developed to meet the objectives referenced above.

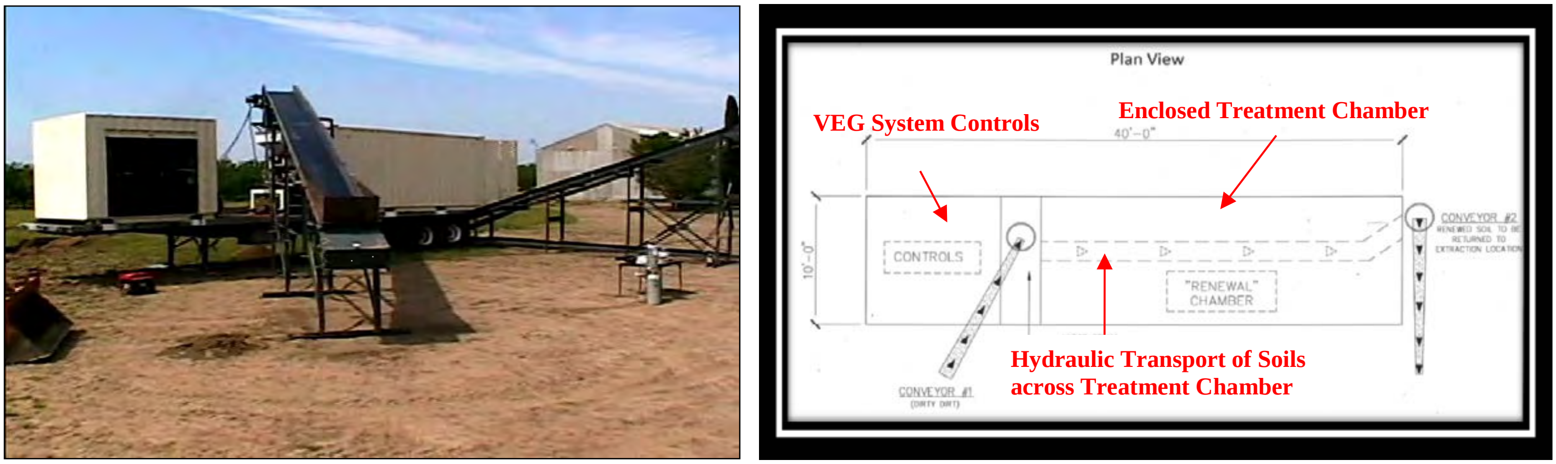
1.2 Approach to Thermal Treatment of Soils

Ex-situ thermal treatment of one pre-profiled drum of PAH-impacted soil will be performed using Endpoint's patented VEG technology at its laboratories in CA. This technology allows for application of steam for both in-situ and ex-situ thermal desorption. The goal of this treatment is to desorb (from soils into vapor phase) and/or otherwise decompose PAHs to non-hazardous materials. Thermal treatment of PAHs has been successfully used as a means of achieving this goal (e.g., see http://www.enviroklean.com/files/thermal_desorption_navy_report.pdf).

The thermal treatment process implemented by the VEG technology is summarized below.

1.2.1 VEG Thermal Treatment Process

At the core of the VEG treatment system is a highly efficient, patented mobile vapor energy generator, which utilizes propane, air, and water to generate steam at temperatures as high as 1,300 °F. For ex-situ thermal treatment applications, the vapor generator serves as an independent heat source to the enclosed thermal treatment chamber, through which soils are passed and subsequently treated (see graphics below).



VEG Soil Remediation System Layout and Internals Diagram

Target temperatures for ex-situ thermal treatment of PAHs have been defined in the range of 700 to 900 °F; however, due to the highly efficient nature of the patented vapor generator, and the fully enclosed system design inherent to the VEG system, Endpoint has successfully treated PAHs at lower temperatures. Properties of chemicals similar to those at the site and which have been successfully treatment via the VEG technology are summarized in the matrix below.

Properties of Key PAHs, PCBs, and Munitions Constituents

Chemical	Molecular Weight (g/mol)	Melting Point (°F)	Boiling Point (°F)	Vapor Pressure (Pa @ 20 °C)
TNT	227	178	563	1.60E-04
RDX	222	399	453	4.00E-07
DNT	182	156	527	9.90E-01
PETN	316	286	356	8.00E-04
Benzo(a)Pyrene	253	354	923	6.40E-07
Aroclor 1260	376	Not Available	759	3.08E-04

For the subject bench-scale test, the treatment chamber of the VEG system will be preheated by adding steam into the chamber until the initial target temperature range of 600 °F is reached within the treatment chamber. Profiled soils sent to Endpoint's laboratory by Alliant will then be removed from the drum using a shovel and placed onto a conveyor, which will in turn feed the soils directly into the preheated treatment chamber. Profile data used by Alliant in support of shipping the drums will be used as the pre-treatment concentration of PAHs in soils to be treated.

Target temperatures and the residence time of soils within the treatment chamber are adjustable and defined based on the properties of the soil, target organic chemicals to be treated, and target cleanup goals; both parameters will be adjusted during the bench-scale test to help determine the optimal temperature and residence time for maximum treatment of PAHs in soils. Temperatures to be tested will range from 600 to 800 °F, with soil residence times ranging from 15 minutes to 30 minutes based on successful applications of the technology to PAHs at other sites.

As organic compounds (including PAHs) transition from solid phase adsorbed to soils to vapor phase within the renewal chamber, a vacuum system internal to the enclosed renewal chamber captures the organic vapors generated. To the extent that there may be unknown organic compounds such as heavier-end petroleum hydrocarbons present in the soil subjected to treatment, it is also possible that desorbed acid compounds such as nitrous oxides (NOx) and sulfur oxides (SOx) may also be present within the renewal chamber in concert with the organic vapors. To properly remove the NOx, SOx and HCl compounds prior to rerouting of vapors back to the vapor generator, the desorbed vapors are first passed through a series of patented filters and caustic scrubber inserted in series within the pipeline that recycles desorbed material from the enclosing truck body back through the steam generator. The filter/scrubber system encompass an engineered mixture of caustic soda, zero valent iron (ZVI), lime, water, and steam and align in a slender packed column, which is six feet tall and six inches in diameter. As the acid-laden vapor is pulled by vacuum up through the filter/scrubber column, any acidic compounds are neutralized by the filters and trickling down caustic soda (sodium hydroxide) liquid solution. Hence, any acid vapors (e.g., HNO_3 (nitric acid) from NOx, H_2SO_4 (sulfuric acid) from SO_x, and HCl are removed before the organic vapors are routed further downstream. Neutralization of the acidic compounds results in a benign dilute liquid solution of sodium nitrate ($NaNO_3$), sodium bisulfate ($NaHSO_4$), and sodium chloride (NaCl) for ultimate profiling and disposal offsite.

Based on the patented design of the VEG system, following treatment through the patented filter/scrubber system, the treated vapors form a synthetic gas comprised largely of hydrogen and are routed back to the vapor generator to successfully replace the propane as fuel for ongoing treatment operations, with Endpoint's carbon dioxide (CO_2) filter serving to reduce CO_2 emissions by approximately 90% and to levels below ambient concentrations.

Treated soils emanating from this process will leave the treatment chamber and either fed directly into a loader bucket, or will be stockpiled on the lined (11 mil-thick tarp) ground surface via a second conveyor in support of post-treatment sampling, discussed in more detail below.

1.2.2 Treatment of PAHs in Soil

The bench-scale thermal treatment of the PAH-impacted soils will be initiated by evenly distributing the drum of soils into four equal stockpiles. The first batch of soil will be treated at a temperature of 600 F for 15 minutes. After this treatment run, these soils will be stockpiled and resampled and analyzed using EPA Method 8270SIM, with data to be validated to S2aVEM (EPA 540-R-08-005). Sampling of soils will occur in accordance to the SOPs included as Attachment A herein, including collection of one 3-point composite from each treated soil stockpile.

Depending on the post-treatment analytical results from the first treatment run, the temperature and residence time for treating the second batch of soils may be adjusted (likely increased temperature and/or residence times) to help define the optimal treatment conditions. It is expected that 50 to 100 F increases in temperature and potentially 5 to 10-minute increases in residence times will be tested using subsequent batches of soil to identify the optimal treatment conditions.

The optimal treatment temperature and residence time reflect conditions which will reduce PAH concentrations to low (i.e., below residential RSLs) or to non-detect levels. With the benefit of results from more than 10,000 soil treatment runs using the VEG system, it is evident that less thermal energy (i.e. lower temperatures and shorter residence times) is necessary to reduce chemical concentrations from high concentrations to relatively low concentrations, while it typically takes far greater thermal energy (i.e., higher temperatures and longer residence times) to reduce chemical concentrations from low levels to very low or non-detect levels. The same relationship has been observed in past treatment of PAHs using the VEG technology.

The hierarchy of the desired treatment results is defined as follows, with RSLs representing the PALs for this pilot study:

- Post-treatment levels are below detection limits (highest goal);
- Post-treatment levels are below residential RSLs (second highest goal);
- Post-treatment levels are below commercial RSLs (third-highest goal);
- Post-treatment results are below pre-treatment results, while still exceeding the commercial RSLs (fourth-highest goal).

Once the optimal temperature and residence time of soils have been defined, Endpoint will combine all soils together into one stockpile, and treat the entire soil stockpile under the optimal treatment conditions to ensure that all soils provided for this bench-scale study are treated to levels below detection limits and/or residential RSLs. Post-treatment sampling of the combined soil stockpile will be performed in accordance to the SOPs attached herein, including collection of one 3-point composite sample from the soil stockpile.

1.2.3 Disposal of Investigation Derived Wastes

Regardless of the levels of PAHs, if any, present in the treated soils, these soils will be considered as investigation derived wastes (IDW). These soils will be placed back into the original drums and disposed of at an appropriate landfill in accordance to the post-treatment concentrations serving as the profile for disposal. Soil profiles will be shared with Alliant and USACE to confirm disposal approach prior to offsite transport by Safety Kleen. In addition, the waste manifest confirming transport and disposal of the soil drums at the landfill will be provided to Alliant and USACE.

2.0 Ex-Situ Thermal Desorption Pilot-Scale Testing

Following completion of the bench-scale test, Endpoint will mobilize to the Scrap Yard site all necessary equipment to perform a pilot-test scale for thermal treatment of PAHs in soils. To summarize, the pilot-scale test will encompass onsite treatment of 100 cubic yards (CY) of soils, which will be placed back into the ground following completion of the pilot test. The pilot test will make use of the optimal treatment conditions (i.e, treatment temperature and residence time) identified through the bench-scale testing as capable of achieving the targeted goal of reducing PAHs to below residential RSLs, or below laboratory detection limits. The purpose of the pilot-scale test is to build on the bench-scale activities and further evaluate the potential for the feasibility of ex-situ thermal treatment as a viable remediation option for the site.

The onsite pilot test will include mobilization to the site of the same VEG unit used at Endpoint's laboratory for the bench-scale test, housed on a 40-foot trailer. In addition, one conveyor for loading of soils into the VEG unit will be mobilized to the site, together with one 5-CY backhoe and a bobcat loader to be used for excavation, stockpile management, and loading of stockpiled soils onto the conveyor. Lastly, a 500-gallon propane tank and a 4,000-gallon water tank will also be brought onto the site for use in support of steam generation and thermal treatment by the VEG system.

2.1 Soil Excavation

Excavation of soils will occur across an 18-yard by 18-yard square, extending to 1 foot below ground surface (bgs) where the majority of PAH impacts have been reported at the Scrap Yard site (Leidos, 2015)[1]. The excavation area will correspond to the approximate location of the former T-4703 Roads and Grounds Maintenance Building, formally recognized as a source area at the Scrap Yard site (see Figure 4-4 of Leidos, 2015, included herein as Attachment B); selection of this location was based on a field reconnaissance visit conducted by Endpoint, the Ohio Environmental Protection Agency, USACE, and personnel from the Ravenna AAP and the Army National Guard Bureau, recognizing that PAHs are ubiquitous in shallow soils across the entire Scrap Yard site. The selected location is readily accessible from existing roads, will be staked in support of excavation activities, and will be noted further with hand-held GPS coordinates for each of its four corners.

Soils will be excavated via a backhoe, targeting depths of no more than 1 foot bgs within the defined 18-foot by 18-foot area. Excavated soils from the target excavation location will be stockpiled immediately adjacent to the VEG system, which in turn will be placed no more than 25 feet from the target excavation area. The 100 CY of excavated soils will be stockpiled into two 50-CY stockpiles, each to be sampled prior to treatment via collection of one 3-point composite sample per stockpile and per the SOPs attached herein. As outlined in the SOP, the two soil samples (one from each 50-CY stockpile) will be submitted to the laboratory (Test America located in St. Louis, MO), with analyses (EPA Method 8270SIM) to be performed on a 24-hour turnaround time (TAT). During times of inactivity, stockpiles will be covered by plastic tarps, and the excavation area will be taped off to ensure safety.

2.2 Onsite Soil Treatment

Following completion of pre-treatment sampling, soils from each stockpile will be independently loaded into the VEG system pre-heated to the optimal treatment temperature identified from the bench-scale test. Soils will be treated using the same process outlined in Section 1.2.1 herein. Treated soils will be independently re-stockpiled (two 50-CY stockpiles) and subjected to post-treatment sampling. Post-treatment samples will also correspond to the SOPs attached herein, including one 3-point composite sample from each 50-CY stockpile to be overnighted to the laboratory for 24-hr TAT analyses for PAHs (8270SIM). This process will be duplicated for each of the two stockpiles, with soil treatment rates expected at 10 to 30 CY/hour depending on soil moisture and weather conditions.

The pilot-scale test will be targeted for a period of time where weather conditions are dry; however, should unexpected precipitation occur during testing, a decision will be made by Endpoint as to whether the pilot test should continue or whether the treatment should be stopped (and stockpiles covered) until dry conditions prevail. Although highly unexpected, it is possible

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[1] Leidos, 2015. Final Remediation Investigation Report, for Soil, Sediment, and Surface Water at RVAAP-50 Atlas Scrap Yard, Former Ravenna Army Ammunition Plant, Ravenna, OH.

that excess moisture introduced by precipitation events may cause the need to treat one or more stockpiles more than once. Under such conditions, Endpoint is prepared to treat each stockpile as much as 3 times, although this is highly unlikely nor necessary given the predetermination of optimal treatment conditions during bench-scale testing, and the ability to increase temperatures and residence times within the treatment chamber during pilot testing. Moreover, should unforeseen precipitation events occur during the pilot test, the stockpiles will be protected from erosion using necessary measures, including erection of silt fences as necessary, and any excess water potentially forming in the excavation pit will be pumped out prior to replacement of soils following completion of treatment.

The duration of the pilot test is estimated at 3 to 5 days, depending on weather conditions and associated rate of soil treatment (3 to 10 CY/hour). The estimated CO_2 emissions from the VEG system (with and without Endpoint's patented CO_2 filter) have been calculated in Attachment C.

2.3. Soil Backfilling and Demobilization

Upon completion of the soil treatment (marked by one round of treatment of each stockpile under dry conditions, or up to 3 rounds of treatment of each stockpile under wet conditions), soils will be placed back into the excavation hole using the backhoe, ensuring that the soils are compacted (using the backhoe bucket) such that the ground surface elevation of the backfilled area is even with the surrounding area.

Decontamination and demobilization activities will encompass removal of excess dirt and soils from all equipment used prior to removal from the site. This process will maximize the use of dry, clean vapors from the vapor energy generator system inherent to the VEG technology, thereby eliminating any rinsate or other IDW during decontamination procedures. All liquid IDW will be drummed, profiled, and shipped offsite, including fluid from the patented filtration system employed by Endpoint for the pilot test.

3.0 Lead Stabilization Bench-Scale Test

It is understood that a small focused area in the southern part of the Scrap Yard site has been characterized by elevated lead levels, constituting a lead "hot spot" in soils at the site. To assess the potential for onsite stabilization of lead in soils, a bench-scale study will be conducted to determine if steel slag fines (3/8-inch minus fraction) can effectively immobilize the lead-impacted soils from the Scrap Yard site.

The approach to bench-scale testing will be to evaluate mix designs using up to 30 % by weight maximum for potential onsite soil blending and encapsulation as a soil berm, as steel slag is far more cost effective than other proprietary reagents used for lead immobilization (e.g. phosphate compounds which must be overdosed and introduce water quality concerns). The steel slag fines will be used to create a compactable soil mixture that targets the immobilization of lead by a combination of pH control, long term soil pH buffering, and the creation of insoluble lead compounds that will be non-leachable under typical soil conditions. A series of five mix designs using two different sources of regionally available steel slag fines will be tested on soils (10-gallon bucket) provided to Endpoint by Alliant from the lead "hot spot" area at the Scrap Yard site, helping establish the upper dosing limit. Toxicity Characteristic Leaching Procedure (TCLP) and deionized (DI) water extractions will be performed in duplicate to assess lead immobilization potential on 28-day cured samples. Based on a combination of leaching performance, dose and expected cost, two leading candidate mix designs will be advanced to a final stage of testing. The final round of testing will involve one-dimensional semi-dynamic leach testing (EPA Method 1315) to assess the long-term leaching of the stabilized soil based on 28-day cured samples compacted to the equivalent of minimum 90% relative compaction by the modified Proctor test (ASTM D1557).

4.0 Reporting

The ex-situ bench-scale and pilot-scale tests referenced in prior sections will be documented in detail in an Implementation Memorandum (Implementation Memo), outlining all procedures implemented, and data collected, validated, and evaluated. Conclusions relative to the ability of ex-situ thermal desorption to treat PAHs in soils at the Scrap Yard site will be set forth, as will observed optimal temperatures and residence times relative to PAH treatment for the subject site. It is understood that the feasibility study (FS) for the site may be revised by Alliant under separate cover to potentially include ex-situ thermal treatment as one of the remedial alternatives for the Scrap Yard site, and the information in the Implementation Report may be used in support of those activities. Similarly, the potential for steel slag to immobilize lead in soils from the site will be documented in the Implementation Memo, including recommendations relative to full-scale application at the Scrap Yard site.

5.0 Schedule

A detailed scheduled for the bench and pilot-scale tests is included in the Uniform Federal Policy (UFP) Quality Assurance and Project Plan (QAPP) prepared under separate cover by Alliant. However, it is anticipated that the bench-scale test will be completed within 10 days of receipt of the soil drum, and the VEG pilot-sale test may be completed within 5 to 10 days following mobilization to the site. The steel slag bench-scale study will be completed within 60 days following receipt of the site soils.

ATTACHMENTS

Attachment A-	Standard Operating Procedures Soil Sample Collection, Handling, Custody, and Shipment
Attachment B-	Figure 4-4 (Leidos, 2015)
Attachment C-	Estimation of Carbon Dioxide Emissions from Pilot-Scale Thermal Treatment of Soils

STANDARD OPERATING PROCEDURES
SOIL SAMPLE COLLECTION, HANDLING, CUSTODY, AND SHIPMENT

The field technical lead (FTL) or designee will be responsible for completing the sample bottle label and chain-of-custody form, sample collection, sample packing, and coordination of sample shipment. The samples will be sent to the appropriate laboratory via FedEx overnight. The sample packing and shipping procedures are provided below.

Sample Collection:

Sample collection from stockpile soils will involve collection of one 3-point composite soil sample from each of the post-treated soil stockpiles. In the field, a 3-point composite sample will be collected from each stockpile by partially filling an 8-ounce glass jar with a large opening provided by the laboratory, with equal amounts of soil from each of the three locations within a given stockpile. The jar will be inserted approximately 6 inches into the surface of the stockpile when collecting soil from each of the three locations. The 4-ounce jars will be sent to the laboratory to be analyzed for PAHs (Method 8270SIM).

Sample Identification:

Each sample collected will be given a unique sample ID number that is stockpile-specific and also reflects pre- or post-treatment status. A record of sample ID numbers will be kept with the field records and recorded on chain-of-custody forms.

Sample Labels:

The sample labels will be affixed to sample containers.

The label will be completed with the following information written in indelible ink:

- Project name and location
- Sample ID number
- Date and time of sample collection
- Preservative used
- Sample collector’s initials
- Analysis required

Chain of Custody Form: Standard sample custody procedures will be used to maintain and document sample integrity during sample collection, transportation, storage, and analysis. A sample will be considered to be in custody if one of the statements below applies.

- It is in a person’s physical possession or view.

- It is in a secure area with restricted access.
- It is placed in a container and secured with an official seal such that the sample cannot be reached without breaking the seal.

Chain-of-custody procedures provide an accurate written record that traces the possession of individual samples from the time of collection in the field to the time of acceptance at the laboratory. The chain-of-custody record also will be used to document samples collected and the analyses requested. The field personnel will record the following information on the chain-of-custody record:

- Project name and number
- Sampling location
- Name and signature of sampler
- Destination of samples (laboratory name)
- Sample ID number
- Date and time of collection
- Number and type of containers filled
- Analysis requested
- Preservatives used (if applicable)
- Sample designation (grab or composite)
- Signatures of individuals involved in custody transfer, including the date and time of transfer

Sample Packaging and Shipping: After labeling, soil samples will be placed in a cooler that contains ice to maintain the sample temperature at 4 ± 2 ºC. A temperature blank will be provided in each cooler for the laboratory to confirm storage temperature upon sample receipt. Openings will be taped shut to prevent potential leakage during transport.

ID	Former Building Use and Description
T-2	Office Building
T-3	Office Building
T-4	Office Building
T-5	Field Hospital
T-6	Materials Testing Laboratory
T-7	Dormitory B
T-8	Dormitory A
T-9	Dormitory C
T-10	Dormitory D
T-11	Dormitory H
T-12	Commissary
T-13	Workmen's Sheds
T-14	Garage
T-15	Service Station #2
T-16	Blacksmith Shop
T-17	Dormitory Office Building
T-18	Office Building
T-19	Fire Station
T-20	Stock Room
T-21	Dormitory G
T-22	Service Station #1
T-23	Commissary
T-25	Tool Grease Rack
T-4703	Roads and Grounds Maintenance Building
T-4704	Roads and Grounds Maintenance Building
T-3901	Roads and Grounds Maintenance Building
T-4705	Roads and Grounds Maintenance Building

Figure 4–4. PBA08 RI – April 2010 Source Area Sampling Locations

Estimation of Carbon Dioxide Emissions from Pilot-Scale Thermal Treatment of Soils

Scrap Yard Site, Former Ravenna Army Ammunition Plant, Ravenna, OH

Polycyclic aromatic hydrocarbon (PAH) vapors induced from thermal treatment of the estimated 100 cubic yards of soil at the Scrap Yard site will be subject to treatment via a patented filter/scrubber system, which will target removal of desorbed acidic compounds such as nitrous oxides (NOx), sulfur oxides (SOx), and hydrogen chloride (HCl). The patented scrubber/filter system incorporates the use of an engineered mix of sodium hydroxide, lime, zero valent iron (ZVI), and water within a slender packed column which is approximately 6 feet in height and over six inches in diameter. Within the fully enclosed treatment chamber of the VEG thermal desorption system, as the acid-laden vapor is pulled by vacuum up through the filter/scrubber column, the acidic compounds are neutralized and any acid vapors (e.g., nitric acid from NOx, sulfuric acid from SOx, and hydrogen chloride) are removed before the VOC vapors are recycled to the VEG steam generator.

As the treated, hot vapor is then redirected back to the vapor generator and replaces the propane as the fuel to continue the thermal treatment process, nothing passes to the atmosphere in this continually looped system. Once the final component of soil treatment is completed and the system operations terminated, the sole emission to the atmosphere from the looped system is low levels of Carbon Dioxide (CO_2). The CO_2 emissions from operation of the thermal desorption operations may be estimated as the emissions from a stationary combustion source per the equation below:

Total GHG emissions [metric tons of CO_2) = emission factor [kg CO_2/MMBTU] x fuel consumed [MMBTU] x 0.001

where,

MMBTU = million British Thermal Units

Typical emission factors for propane approximate 61.46 kg CO_2/MMBTU, while that of landfill gases, which most closely resembles the expected fingerprint of the induced vapors from thermal treatment of PAH-impacted soils, approximates 52.07 kg CO_2/MMBTU (USEPA, 2014)[1].

Treatment rates during thermal treatment of the estimated 100 cubic yards of soils are expected to range between 5 to 30 cubic yards per hour, depending on soil types, soil moisture, and weather conditions. Assuming an average treatment rate of 5 cubic yards per hour and an average treatment time of 8 hours per day, the treatment operational period may be estimated at approximately 5 days. Over this period the patented vapor energy generator is expected to consume no more than 0.96 MMBTUs, nearly 75% of which will be met by the treated vapor stream from the thermal remediation activities.

Based on the above, the estimated CO_2 emissions from the treatment operations, 25% of which will be fueled by propane and 75% of will be fueled by the treated vapors, may be defined as follows:

GHG Emissions-(Propane) = 61.46 kg CO_2/MMBTU X 0.25(0.96 MMBTU) x 0.001 = 0.015 metric tons (MT)

GHG Emissions-(Treated Vapors) = 52.07 kg CO_2/MMBTU X 0.75(0.96 MMBTU) x 0.001 = 0.037 MT

The total estimated GHG emissions is therefore estimated as the sum of the above-referenced values, totaling an estimated 0.052 MT. It should be noted that as necessary, Endpoint's CO_2 emission-reducing

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[1] USEPA, 2014. Emission Factors for Greenhouse Gas Inventories, April 4th. Online at: http://www.epa.gov/climateleadership/documents/emission-factors.pdf

filter may also be used to further reduce the CO_2 emissions by an estimated 80 to 90%, further reducing the estimated CO_2 emissions to approximately 0.04 MT and to levels well below background.

APPENDIX D
RESPONSES TO WORK PLAN COMMENTS

NATIONAL GUARD BUREAU
111 SOUTH GEORGE MASON DRIVE
ARLINGTON VA 22204-1373

January 11, 2016

Ohio Environmental Protection Agency
DERR-NEDO
Attn: Ms. Vicki Deppisch
2110 East Aurora Road
Twinsburg, OH 44087-1924

Subject: Final Response to Ohio EPA Comments on the Work Plan for a Pilot Study and Feasibility Study at RVAAP-50 Atlas Scrap Yard at the Ravenna Army Ammunition Plant, Ravenna, Ohio, Dated, October 14, 2015 Ohio EPA ID # 267-000859-106

Dear Ms. Deppisch:

The Army National Guard Directorate is in receipt of comments on the above referenced Work Plan from Ohio Environmental Protection Agency (Ohio EPA) dated October 30, 2015. It was requested that we respond to comment #3 prior to beginning the pilot-test in order to obtain Ohio EPA conditional approval to begin the pilot-test, which was conducted the week of November 16, 2015. A separate letter addressing Comment #3 was submitted on November 4, 2015 and for completeness this response is also include herein. Therefore this letter addresses and finalizes the responses to all comments received in the October 30, 2015 letter. Please see the responses to your comments below:

1. General: The work plan states it was developed in accordance with many of the facility-wide documents, including the Facility-Wide Sampling and Analysis Plan/Quality Assurance Project Plan, and Safety and Health Plan. Where applicable, the bench- and pilot-tests must adhere to all relevant Facility-Wide documents, which would also include the Human Health Cleanup Goals, etc. Please review all Facility-Wide documents for applicability.

Response: Facility-wide documents will be reviewed and referenced to ensure that the bench- and pilot-scale tests adhere to the applicable requirements and guidance.

2. General: Facility-Wide Cleanup Goals (FWCUGs) have been developed for many constituents, specifically for the Ravenna Arsenal. The RSL cleanup level should not be used if a FWCUG exists.

Response: The FWCUGs will be used as cleanup levels for this project. RSL cleanup levels will be used only if a FWCUG does not exist. This will be specified in the document.

3. Ohio EPA noted that the PAH-excavated soil area will be in the approximate location of the former T-4703 Roads and Grounds Maintenance Building. According to multiple maps in the Final (RI) Report, dated June 26, 2015, there are many other source areas with much higher contaminant concentrations. Ohio EPA suggests the Army consider the area with the highest contamination for the tests.

Response: For the pilot test, the soils will not be excavated around building T-4703. The most highly contaminated area is located near the stock piled rail road ties. Please see attached Figure ES-2. The drum of soil that was collected for the VEG pre-calibration was collected from the yellow shaded area depicted on Figure ES-2 and the pilot test will be conducted in this area. The Work Plan will be revised accordingly.

4. The work plan did not specify, after the pilot test has been completed and the soils have been placed back in the excavation pit, if this area will be included in any future remediation using the VEG technology or if this area will be excluded due to previous treatment. The soils/area used in the pilot-test should not be excluded from the areas proposed in the FS for remediation. During the remediation process, sufficient confirmatory soil samples should be taken of the in-situ bottom soils, prior to backfilling the treated soils to demonstrate applicable standards have been met.

Response: The excavated area will be included in any future remediation at the site. This will be clarified in the Work Plan. It is noted that full remediation of the site will likely occur at a future date and sufficient confirmatory samples will be included at that time.

5. Lead: The work plan does not specify the composition of steel slag to be used with the lead, as various compositions exists. Please provide the composition and indicate if the same composition will be used throughout the pilot test. It is the understanding of Ohio EPA that the amount of lead-contaminated soil to be treated has not yet been determined. Steel slag in general, can have negative consequences to surrounding surface water and aquatic life by the generation of high pH waters, leaching of potentially problematic trace metals, and rapid rates of calcite precipitation. Although the purpose is to bind the lead, Ohio EPA wants to make sure another problem is not created. Please discuss.

Response: Treatment of lead-contaminated soils will only be conducted during bench-scale testing at the subcontractor's laboratory in California. We will be using Basic oxygen furnace (BOF) slag, electric arc furnace (EAF) slag, or stainless steel slag in the bench-scale test. The final choice will depend on the treatability study metrics. Our selection of the slag will also depend on the blending results during the bench-scale study (especially relative to the buffer capacity of the soil). Steel slag composition and the potential negative consequences of treatment of site soils with steel slag will be thoroughly discussed in the FS. Clarification of this path forward will be provided in the Work Plan. Additionally, technical articles regarding the addition of slag to immobilize lead will be included in an appendix of the Final Work Plan.

We will use the slag in a mode more consistent with soil blending and stabilization/solidification (S/S), where the slag is leveraged for its residual lime content and soluble silica to immobilize lead by pH control and precipitation of a variety of insoluble carbonates and silicates. In short, steel slag relies on a combination of chemical precipitation, metals complexation, and hydraulic conductivity reduction to bond metals in place. The approach will be to blend the slag with the impacted soil and compact in an above ground soil berm that will be covered with a natural soil (6 inches min) and seeded with grass. The slag will not impact the surface waters of Ohio in this application.

6. Health and Safety Plans: Ohio EPA reviews and comments, but does not approve, Health and Safety Plans. Ticks and poison ivy, as referenced in the "Site Safety and Health Plan" section, are numerous throughout the site. In addition, cell phone coverage is spotty. Ohio EPA suggests evaluating cell phone coverage specifically at the Atlas Scrap Yard area and perhaps plan on working in pairs.

Response: Comment noted. The information is appreciated. Upon arrival at the site, the field oversight representative will test cell phone coverage. Additionally, personnel from both Alliant and its subcontractor should be on site during the pilot study.

7. 3.1.1 Pre-Treatment Sampling and Worksheets: The text is not clear about how the composite samples will be collected from the 55 gal. drum (PAH) or the 10 gal. bucket (lead) or the number of samples that will go into each composite. The work plan states "…one 2-aliquot (or more) composite sample will be collected from soil contaminated in the 10-gallon container." Ohio EPA recommends 7 or 8 per container, to get a good distribution of the contents. The same should also apply to post-treatment samples collected in 3.1.2 and 3.1.3. A larger sample group makes for a more representative composite. As the bench-test is already in progress, please provide the number of aliquots that were collected and if less than 7-8, provide rationale and support for the pre-treatment number. As stated above, Ohio EPA recommends 7-8 aliquots (or points) be collected for post-treatment sampling.

Response: The information is appreciated. The pilot study sampling requirements will be revised to state that 7-point composites will be collected in the field instead of 3-point composites. Additionally, the pre- and post-test bench-scale sampling (for lead and PAHs) will be revised to include 7-point composites. The Work Plan will be revised to include these new requirements.

8. Pilot-Test: The work plan indicates the pre-treatment and post-treatment sampling will consist of 3 point composites. As stated above in comment #7, Ohio EPA recommends 7-8 point composite samples be collected for a more representative composite.

Response: The pilot study sampling requirements will be revised to state that 7-point composites will be collected in the field instead of 3-point composites. Additionally, the pre- and post-test bench-scale sampling (for lead and PAHs) will be revised to include 7-point composites. The Work Plan will be revised to include these new requirements. See also response to Ohio EPA Comment #7.

9. 3.1.3 Bench-Scale Testing for Treatment of lead in Soils: Ohio EPA recommends adding the Synthetic Precipitation Leaching Procedure (SPLP), method 1312, to the Method 1315 procedure, to assess leaching from the treated samples. The Method 1315 procedure uses deionized water, while the SPLP process uses a simulate acid rain solution. In that way, the effects of a more realistic or natural precipitation on leaching. As stated in the work plan, the standard method 1311 (TCLP) should still be included and used for disposal purposes. As it is the understanding of Ohio EPA that the bench-scale lead test is currently underway and a pilot test is not planned for lead, this issue will need to be resolved prior to moving forward with remediation.

Response: The decision to employ either Mass Transfer Rates using a Semi-dynamic Tank Leaching Procedure (TLP) Method 1315 or SPLP Method 1312 is generally made on the basis of the final disposition of the impacted soils. There are several alternatives for final disposition of the lead-impacted soils at the Atlas Scrap Yard. The most likely alternatives include excavating and landfilling the lead-impacted soils, treating the impacted soils and then disposing of them at a landfill, or treating the impacted soils and leaving them in place at the site. If the goal is to treat the soils, and then dispose of them in a landfill, then Semi-dynamic TLP Method 1315 should be used. Semi-dynamic TLP Method 1315 is a mass transfer rate of leaching test that would more accurately indicate the leaching potential of lead-impacted soils in a landfill since it employs deionized water as the leaching agent. If the goal is to treat the soils and leave them in place, then the soil should be characterized for leaching potential using SPLP Method 1312. SPLP Method 1312 would more accurately indicate the leaching potential of lead-impacted soils left on site since it uses a simulated acid rain solution which is more realistic of natural precipitation on leaching. The most probable alternative for disposition of the lead-impacted soils at the Atlas Scrap Yard is to treat the impacted soils and leave them in place on site. Therefore, SPLP Method

1312 will be used to determine the leaching potential of the treated soils during the bench scale testing. If the final remediation includes disposal of the treated soil at a landfill then the treated soil would be analyzed using EPA method 1311 for disposal purposes

10. QAPP Worksheet #17: Please insert the analytical methods next to the descriptions for clarification. For example, “semi-dynamic TLP samples” should state “semi-dynamic TLP samples (method 1315).”

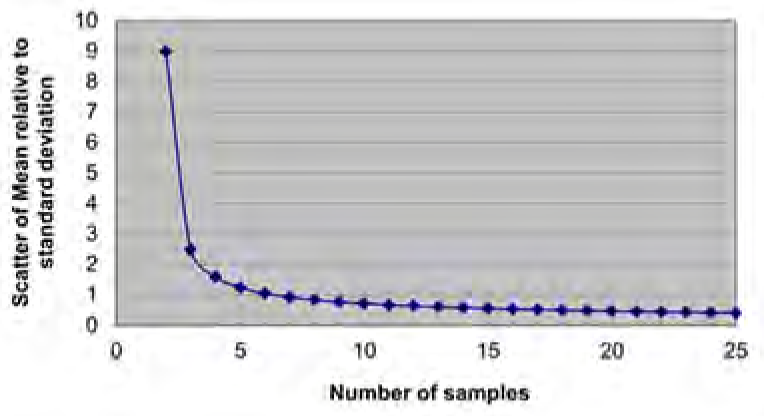
Response: Text in Worksheet #17 will be revised as follows: “All of the samples will consist of stockpiled soils. There will be eight (8) PAH samples (8270D SIM), and (1) PAH sample for pre-treatment (8270), five (5) TCLP samples (1311/6010C) and two (2) semi-dynamic TLP samples (TLP 1315). The field activities will be conducted during the dry weather periods. Since these samples will help determine the efficiency of remedial alternatives, no background sampling will be necessary. Pretreatment profiles and sampling will establish baseline conditions.” Note that the one PAH sample that is identified as being analyzed by 8270 rather than 8270 SIM was the sample collected in advance of sending the 55-gallon drum for bench-testing prior to the pilot test. Therefore the specific analytical test was assigned at the time of sampling and cannot be changed.

11. Method 1315: Please clarify the length of time it will take to turn around method 1315. U.S. EPA method 1315 indicates it will take 63 days; the work plan QAPP worksheet #30 indicates “data package turnaround time” is 28 days.

Response: According to the TestAmerica the turnaround time for USEPA Method 1315 ranges from 28 days to 63 days. Worksheet #30 will be revised accordingly.

12. 3.2.1 Soil Excavation and 3.2.2 Onsite Treatment: As with pre-treatment sampling, Ohio EPA recommends more than 3 points in the composite samples. Seven (7) or 8 points would result in a more representative composite. Refer to comment #3 above.

The following graph shows how the mean of a composite test sample can vary depending on the number of specimens that make up the sample.



The vertical axis is the 95% range of the scatter of the mean (relative to the true standard deviation of the population) as a function of the number of individual specimens in the composite. As the plot shows, when the number of specimens exceeds 7 or 8 the likely scatter of the sample mean gets smaller. Thus, the larger sample size means that the indicated value of the mean will probably be closer to the true value.

Response: The information is appreciated. The pilot study sampling requirements will be revised to state that 7-point composites will be collected in the field instead of 3-point composites. Additionally, the pre- and post-test bench-scale sampling (for lead and PAHs) will be revised to include 7-point composites. The Work Plan will be revised to include these new requirements. See also responses to Ohio EPA Comments #7, and #8.

13. QAPP Worksheet #28: This worksheet states that QC samples are listed in Table 3-1. Ohio EPA cannot locate any reference to QC samples in that table.

Response: Alliant's subcontractor will collect nine (9) polycyclic aromatic hydrocarbon (PAH) samples, and one (1) duplicate sample (field QC sample) as listed in Table 3-1. Other than the duplicate sample, no other field QC samples are planned. Laboratory QC samples will be analyzed in accordance with the USACE Quality Systems Manual (QSM) version 5. This will be clarified in a footnote for Table 3-1.

14. Please indicate the source of the water for the pilot test project.

Response: Water for the pilot test was obtained from Canton Water Works, and consisted of public water used by the city of Canton, Ohio.

15. Figure 4-4, April 2010 Source Area Sampling Locations: This is the only figure included in the work plan and although it does identify some of the source sampling areas it does not identify all sampling locations at the Atlas Scrap Yard. Other maps in the Final RI report identify additional sampling locations and contaminant concentrations. Please refer to comment #3.

Response: The pilot test will be conducted in one of the most contaminated areas at the site, in the vicinity of the stockpiled railroad ties. The Work Plan will be revised accordingly. Additionally, a new figure will be included in the Work Plan that more clearly depicts the excavation location. See also response to Ohio EPA Comment #3 which has been previously responded to in a letter dated November 4, 2015.

16. Air: The local air agency has reviewed the work plan and indicated to Ohio EPA that they have spoken with the contractor and the Army. The Agency stated the Permit-By-Rule (PBR) for the soil vapor remediation equipment was submitted for review and the contractor and the Army are aware of the requirements to use best practices for controlling visible emissions of fugitive dust from the roadways, storage piles, and material handling equipment. It appears the scope and scale of the pilot-test is small enough to not require permits for the fugitive sources at this time, provided the use of best practices is employed.

Response: A PBR has been granted for this work. The facility ID number is 1667000109 and the Permit Number is PBR14548. The contractor and the Army will employ best practices to control visible emissions as noted. A new section (Section 4.1) will be added to the Work Plan which discusses air permitting and fugitive dust.

17. Section 3.1.1 titled, "Pretreatment Sampling" is located on page 6. The Table of Contents does not mention this section. Please correct this discrepancy.

Response: This comment will be incorporated as requested. The Table of Contents will be revised to include this Section.

18. Sections 3.1.2 and 3.1.3 are located on page 8. These sections are not labeled correctly in the Table of Contents. Please correct this discrepancy.

Response: This comment will be incorporated as requested. The Table of Contents will be updated so that these sections are labeled correctly and it shows the correct page references.

19. Page 1, Section 1.1, paragraph 2, last sentence states that the 1280 acres are being remediated and managed by the Base Realignment and Closure Division (BRACD). This has changed, the site is not currently being addressed by BRACD, please modify this section.

Response: Text in this paragraph will be revised to state that, "The facility was formerly used as a load, assemble, and pack facility for munitions production. As of September 2013, administrative accountability for the entire 21,683-acre facility has been transferred to the United States Property and Fiscal Officer (USP&FO) for Ohio and the property was subsequently licensed to the Ohio Army National Guard (OHARNG) for use as a military training site, Camp Ravenna."

20. Page 3, Section 1.2, paragraph 1. The historical use of the Atlas Scrap Yard area also included the presence of an incinerator, underground storage tanks and was a storage area for numerous "treated" railroad ties and other items. This information should be included in the site description of this area.

Response: Text will be added at the end of this paragraph stating, "The Atlas Scrap Yard also included an incinerator, underground storage tanks, and was a storage area for numerous treated railroad ties."

21. Page 5, Section 3.0, paragraph 1 implies that the Feasibility Study (FS) will be completed as part of a Technical Memorandum, which presents the results and conclusions of the bench- and pilot-tests. Please clarify this sentence, which appears to conflict with other text areas that state a Draft FS Study for this AOC is under internal review by the Army, and this work plan will be inserted as part of the FS. Please note, that Ohio EPA anticipates that the FS will follow CERCLA's RI/FS guidance documents.

Response: The FS will be prepared separately from the Technical Memorandum. A Preliminary Draft FS was previously prepared for the site. The FS will be updated based on the results of the Bench- and Pilot-scale studies. Section 3 will be revised to clarify that the Work Plan, updated FS and Technical Memorandum will each be prepared separately. The FS will be prepared in accordance with CERCLA guidelines.

22. This Work Plan does not include a Vapor Energy Generation (VEG) process diagram. A process diagram would be useful to improve Ohio EPA's understanding of this treatment technology. Please provide a general process diagram as a Figure in Section 2 or 3.

Response: A simple process diagram along with a photograph of the system is presented in page 2 of the subcontractor's Work Plan. The subcontractor's Work Plan is provided in Appendix C. The process diagram and system photograph will be referenced in Section 2.

Please contact the undersigned at (703) 607-7955 or mark.s.leeper.civ@mail.mil if there are issues or concerns with the submittal.

Sincerely,

Mark Leeper
RVAAP Restoration Program Manager
Army National Guard Directorate

cc: Rod Beals, Ohio EPA, DERR
Bob Princic, Ohio EPA, DERR
Justin Burke, Ohio EPA, DERR-CO
Katie Tait, OHARNG Camp Ravenna
Kevin Sedlak, ARNG, Camp Ravenna
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Nathaniel Peters II, USACE Louisville
Eric Cheng, USACE Louisville
Gail Harris, Vista Sciences Corp.
Pat Ryan, Leidos-REIMS
Belinda Price, Alliant Corporation

APPENDIX E
ARTICLES CONCERNING IMMOBILIZATION OF LEAD IN SOIL VIA MIXING WITH STEEL SLAG

Grubb D.G., Wazne, M., Jagupilla, S.C., and Malasavage, N.E., 2010. “Arsenic immobilization using slag fines,” *Protection & Restoration of the Environment X*, Corfu, Greece, July 5-9, pp.8 (CD-ROM).

ARSENIC IMMOBILIZATION USING SLAG FINES

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ABSTRACT

The arsenic (As) immobilization potential of blast furnace and steel slag fines (BFF and SSF, respectively) were evaluated, where both crushed slag materials resemble a USCS SP type soil (3/8-inch minus fraction). Due to their granular nature, mineralogy and residual lime content, the slags appear to be well suited to achieve simultaneous geotechnical and environmental stabilization of fine grained soils such as dredged material (DM) using a single media. As immobilization in DM-Slag fines blends under both TCLP and SPLP conditions with and without slag cement as a polishing amendment are presented. Also, the ability of slag fines to individually immobilize As(III) and As(V) at target doses up to 10,000 mg/kg As was evaluated for beneficial use purposes.

1.0 INTRODUCTION

The Maryland Port Administration (MPA; Baltimore, MD, USA) initiated a program in 2008 to develop large scale opportunities to recycle upwards of 500,000 cubic yards of dredged material (DM) per year by 2023 from the Cox Creek Dredged Material Containment Facility (DMCF), due to its limited capacity [6 million cubic yards (MCY)]. Under Maryland State law, DM from the Baltimore Harbor can only be placed in a confined disposal facility (CDF) such as the Cox Creek DMCF. Recycling on such a large scale speaks to the need to develop sustainable, high volume commercial outlets for DM, such as earthwork construction related to coal mine or quarry closure, landfill daily cover, general, highway embankment and/or structural fill applications in the greater Baltimore metropolitan area.

However, DM is often an undesirable geotechnical construction material due to its soft, fine grained nature. Secondly, DM is often contaminated, making it even less desirable. Grubb and coauthors [1-6] evaluated the geotechnical enhancement of DM from Philadelphia using crushed curbside collected glass (CG) as a blending agent and demonstrated significant improvements to the DM such that the CG-DM blends could satisfy local regulations for highway embankment construction. One obvious limitation with CG, even in a large coastal city, is that any soil amendment be available in comparable volumes to the DM. In Baltimore, two such media are the blast furnace and steel slags generated at the Sparrows Point Steel Mill complex. Slag cement is also produced at the steel mill.

Construction grade aggregates are produced from both slag sources but the fines (3/8-inch minus fraction) produced from the bulk slag crushing and screening operations have limited beneficial use options despite their excellent environmental quality [7]. One use for the blast furnace fines (BFF) is as a component to mortar block production, whereas the steel slag fines (SFF) are currently stockpiled at the steel mill. The SSF materials contain up to 10% residual lime and visually appear as a 3/8-inch minus material or AASHTO No. 9 aggregate, less than 5% passing the No. 200 (0.75 mm) sieve.

The primary reason for blending the slag fines with DM is that they are granular and the residual lime was hypothesized to simultaneously provide strength enhancements (and aging effects) and passive treatment of heavy metals (mainly arsenic) contained in the DM. A secondary reason for blending with slag fines was pH control, as DM has the ability to acidify over time potentially releasing cationic heavy metals. Thus, ultimately choosing one slag source for blending with DM requires multiple considerations, including environmental quality, metals immobilization, pH control, geotechnical performance and cost [7]. Here, the acid neutralization capacity (ANC) and As immobilization of the BFF and SSF media are presented.

Total arsenic concentrations in the Baltimore harbor sediments and navigation channels can be as high as 100 mg/kg depending on the location, but the limited historic data on the Cox Creek DMCF indicates an average As concentration on the order of 20 to 30 mg/kg, which likely reflects the effects of mixing, dilution and sediment depositional processes that occur during the hydraulic placement of DM in the CDF. From an operational perspective, concern also arises as to what maximum As concentration can be tolerated in the DM prior to blending with the slag fines to safely undertake large scale recycling. Accordingly, a detailed As thresholding analysis was also completed which involved totals, toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP) analyses. The main purpose of these leaching-based tests was to illustrate the ability of the slag fines to immobilize significant total concentrations of arsenic via direct spiking and as occurring in the DM and DM-slag fines blends. In this way, As leaching behavior can be used to reverse engineer an upper cap on the permissible total As concentration in the DM prior to SSF blending.

2.0 MATERIALS

The DM was obtained for testing purposes from the "Volvo area" within the North cell of the Cox Creek DMCF during January 2009. Sixty (60) sealed 5-gallon buckets of fresh DM from 5 locations were collected to account for material variability purposes. The slag fines were collected from the Sparrow Point Steel mill complex in Baltimore, Maryland, USA. After the molten slag air cools for a minimum of 24 hours, they are processed through a conventional aggregate crushing and screening process. The fines (3/8-inch minus fraction) from each slag source are stockpiled in dedicated locations. BFF and SSF samples were collected from 5 random locations to develop a representative sample for testing.

Slag cement (NewCem®; NC) was included in the testing program because it was not clear at the outset of the project if the DM or slag fines alone could immobilize the As in the DM to acceptable levels. Accordingly, small doses of NC (<2.0 wt%) were included in the As thresholding analysis (see below) for environmental polishing purposes.

3.0 ACID NETRALIZATION CAPACITY (ANC) TESTING

The purpose of ANC test is to measure the buffer capacity of soil and soil-like media in response to natural acidification, acid attack and/or to simulate an acid rain exposure condition, e.g., repeated additions (equivalents) of an acid of known strength. The goal here was to determine how many equivalents of acid it would take to bring the DM and slag fines materials to pH~3.

The two slag fines were evaluated in their as-is and pulverized forms, where milling was accomplished using a Fritsch Planetary Ball Mill (samples SSFM and BFFM). Approximately 80g of the air-dried sample was placed into the milling containers and was pulverized for 20 minutes at a rotation speed of 250 RPM. The entire pulverized sample was passed through 100 sieve (0.15 mm) to avoid any fractionation. None of the samples were As spiked.

The ANC test procedure was based on the Generalized Acid Neutralizing Capacity test [8]. The procedure consisted of equilibrating the soil samples to increasing equivalents of reagent per kilogram of dry soil. Specifically, 6.5 g dry weight of each sample was placed in a series of 130 mL bottles. For strongly alkaline media, incremental amounts of 15.8 N nitric acid (HNO_3) were added to the sample (total liquid volume 130 mL), using a liquid:solid ratio of 20:1, identical to the TCLP and SPLP procedures. For media with a naturally near neutral pH (i.e., DM), incremental amounts of 10N sodium hydroxide (NaOH) were added to the sample to illustrate the impacts of alkalinity on the sample.

Intermediate solutions were then prepared. The resultant slurries were tumbled in a standard TCLP tumbler for 48 hours. The supernatants were then filtrated through a 0.45 μm nylon membrane filter, and the pH of the leachate was recorded using an Accumet AR20 pH–meter.

4.0 As(III) AND As(V) THRESHOLDING EXPERIMENTS

The overall purpose of the As thresholding experiments was to evaluate the ability of the slag fines to immobilize significant concentrations of arsenite [As(III)] and arsenate [As(V)] in the DM-slag fines either on their own, and/or with up to 2% NC if additional environmental polishing was required.

In the first series of tests (*DM-Slag fines Suite*), to establish a maximum threshold on As contamination reflecting the variable conditions in the Baltimore (MD, USA) harbor channels, the DM was individually spiked with 100 mg/kg As(III) and As(V), so that the DM would serve as the source of contamination. In the second series of experiments (*Raw Materials Suite*), the ability of the SSF and BFF to independently immobilize arsenic was evaluated up to target doses of 5,000 mg/kg As. In the last series of experiments (*SSF Suite*), the ability of the SSF media to immobilize up to 10,000 mg/kg was evaluated in triplicate to verify the results of the raw materials suite. Sodium arsenite ($NaAsO_2$) and sodium arsenate heptahydrate ($Na_2HAsO_4•7H_2O$) were used as the As(III) and As(V) sources, respectively (ACS grade, Fisher Scientific, GA).

4.1 DM-Slag Fines Blend Suite

Aqueous solutions of each arsenic salt were prepared using DI water and were targeted to achieve a DM MC on the order of 130 to 135%. This allowed the raw DM to have a liquid consistency sufficient to enable its homogenization with the much drier, granular slag fines. Raw DM was placed in a Globe SP-30 mixer (Dayton, OH) and was homogenized as-is for approximately 10 minutes. Thereafter, during mixing, the arsenic solution was gradually introduced to the DM using a series of polyethylene squirt bottles. Mixing was paused every 10 minutes to manually scrape the excess DM from the bucket sidewalls using a spatula. This material was blended initially by hand, and then the automated mixing bucket was restarted until a total of 40 minutes elapsed. The DM was then removed and the device was cleaned prior to mixing the next batch. Individual batches of As-spiked DM were stored in sealable 5-gallon bucket for a mellowing period of 30 days to enable equilibration.

The 20/80, 50/50 and 80/20 DM-Slag fines blends were prepared after the DM mellowed. Each media was dosed with 0 to 2 wt% slag cement at 0.5% increments, except the slag controls (0%, as control), and were mixed until visually homogenous. Next, each replicate (blend, NC dose) was compacted to greater than 90% of the maximum dry density by standard Proctor compaction for the requisite blend (the influence of low NC dose on compaction curve was ignored). Compaction indices and other geotechnical parameters for the DM-BFF and DM-SSF blends is provided elsewhere [7]. Once compacted, the replicates were extruded from the molds and then cured in sealable bags for an additional 30 days. After subsequent air-drying (up to 3 days), all replicates were analyzed for total-As, TCLP-As and SPLP-As.

4.2 Raw Materials Suite

For the 100 As mg/kg dosing level, five replicates of each raw material (BFF and SSF) were used. For the 1,000 and 5,000 mg/kg spiking level, only one replicate was used. Aqueous solutions of each arsenic salt were prepared using deionized water and the slag fines in their air-dried state. The spiked media were then individually stored in 1 gallon sealable plastic bags and allowed to mellow for 30 days. After subsequent air-drying (up to 3 days), all replicates were analyzed for arsenic by totals, TCLP and SPLP.

4.3 SSF Suite

Given the high As immobilization capacity of the SSF media (i.e., Section 4.2), aqueous As(III) and As(V) solutions were individually prepared by dissolving the corresponding salt in de-ionized water to achieve target doses between 100 mg/kg and 10,000 mg/kg to the SSF media (see Table 1). The SSF material was first wetted with the metals-spiked DI water solution, and then was mixed using a stainless steel spoon to achieve a moisture content of 16%. The metals-spiked SSF media was then stored in sealable plastic bags and allowed to mellow for 30 days. After mellowing, all the samples were air-dried and used for analytical testing.

Table 1: Arsenic thresholding suite for SSF media.

	Target Dose (mg/kg)				
Metal	**100**	**500**	**1,000**	**5,000**	**10,000**
As(III)	x	x	x	x	x
As(V)	x	x	x	x	x

For this suite, the sample size for the TCLP and SPLP analyses was reduced to 25 g. Three replicates each were prepared for each target dose for totals, TCLP and SPLP testing followed by ICP-OES analysis. For the 100 mg/kg level (when As was below ICP detection limit of 0.05 mg/L), the As concentration in the TCLP and SPLP leachates was determined using a graphite furnace atomic absorption spectrometer (GFAAS, Varian Zeeman Spectra AA 220Z). Prior to AA analysis, the solutions were acidified using concentrated HNO_3 in an amount of 1%.

5.0 RESULTS

The bulk chemistry of the four materials are shown in Table 2, as determined using X-ray flouresence (XRF). Geotechnically, the DM classified as an organic silt, or OH soil by the Unified Soil Classification System (USCS) [7]. For the BFF media and NC, they contained substantially less iron (Fe) and free lime than the SSF media, but the difference is made up by reactive silica compounds.

Table 2: Bulk chemistry of dredged material (DM), slag fines and slag cement (NC).

Compound	**DM**	**SSF**	**BFF**	**NC**
Silicon Dioxide (SiO_2)	53.94	10.65	35.98	37.29
Aluminum Oxide (Al_2O_3)	17.17	4.09	10.79	10.02
Iron Oxide (Fe_2O_3)	9.79	26.84	2.20	0.36
Calcium Oxide (CaO)	0.45	37.21	35.62	37.44
Magnesium Oxide (MgO)	1.88	10.31	10.94	12.22
Sodium Oxide (Na_2O)	0.85	0.03	0.23	0.23
Potassium Oxide (K_2O)	2.74	0.02	0.24	0.25
Titanium Oxide (TiO_2)	0.89	0.46	0.44	0.46
Phosphorous Oxide (P_2O_5)	0.23	0.78	0.02	<0.01
Manganese Oxide (Mn_2O_3)	0.21	3.97	1.15	0.57
Sulfur Trioxide (SO_3)	0.09	0.16	2.33	1.85
pH	8.72	12.08	10.9	11.40
Loss on Ignition (950°C)	11.23	5.49	0.54	--
Free CaO [CaO+$Ca(OH)_2$]	--	7.86	1.55	0.08

5.1 ANC Results

The ANC test results demonstrated a significant difference in the buffering capacity among the three raw materials, including the effects of milling. Figure 1 presents the results of the ANC for the DM and raw and milled BFF and SSF media. For comparison purposes the strength of a TCLP solution on the BFF and SSF media is shown in Figure 1. The legend in the figure also shows the strength of an SPLP solution (1.12 meq/kg), which is approximately 1,765 times weaker than a TCLP solution. Hence, a SPLP leach essentially abuts the Y-axis. Two portions of DM curve are shown because of its moderate pH; an acidification curve (HNO_3) and an alkaline curve (NaOH).

The steep ANC curves and their short range illustrate the weak buffering capacity of the DM. The pH of DM dropped from approximately 7 to less than 3 using less than 2 eq/kg acid. The SSF media consumes approximately 7 eq/kg of acid to reach a neutral pH (7) and approximately 12 eq/kg to achieve pH~3. The response of the SSFM sample is much stronger, requiring approximately 10 eq/kg to reach neutral pH (7) and 18 eq/kg to attain pH~3. This suggests that milling destroys the morphology of the SSF media and liberates alkalinity, whether it be in the form of lime or other pH buffering minerals. Similar behavior was observed for the BFF media and BFFM samples. The BFF media consumed approximately 1.8 eq/kg of acid to reach neutral pH, whereas the BFFM consumed approximately 5 eq/kg. To attain pH~3, the BFF and BFFM consumed approximately 12 eq/kg and 20 eq/kg of acid, respectively.

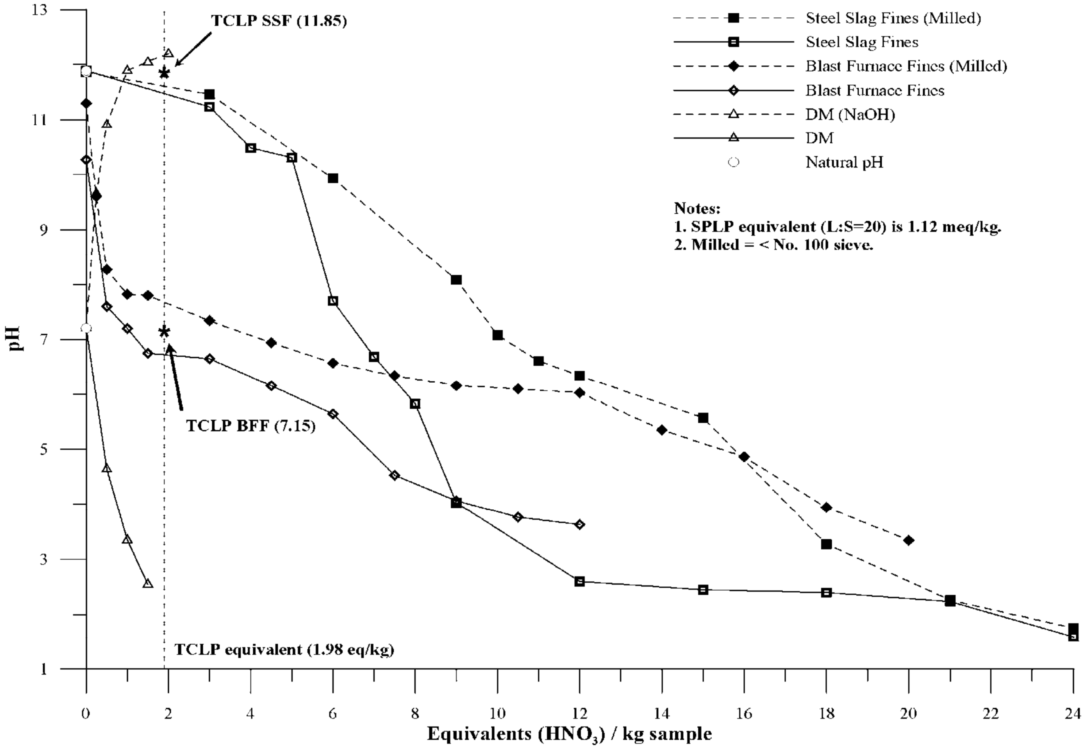

Figure 1: ANC Results for DM, and raw and milled BFF and SSF media.

For perspective, it takes approximately 20 eq/kg to lower the pH of Chromite Ore Processing Residue (COPR) to 3 [9]. This would be the equivalent of approximately 17,850 SPLP extractions. Worthy of note is that even though COPR remained in situ as a fill material for up to 50 to 70 years in the greater Baltimore and northern New Jersey area, the pH of COPR nevertheless remains above 11. While the BFF and SSF ultimately take essentially about the same amount of acid to reach pH~3, the SSF offers more buffering in the mid-range pH than does the BFF media. In this regard, the SSF media maintains an advantage. Extended DM-SSF blend aging tests are underway to evaluate the long (er) term buffering of the SSF media in DM.

5.2 As Thresholding results

5.2.1 DM-SSF Suite

In this series of tests, we distinguish between *raw* controls and *spiked* controls, where the raw controls reflect the natural As content of the individual media and their blending ratios. For the spiked controls, only the DM was spiked up with a total As concentration of 100 mg/kg and was mellowed for 30 days prior to blending with slag fines. Thus, the spiked DM control was expected to have approximately (25+100) or 125 mg/kg As. The As content of the blends therefore diminished proportionally to the blending ratios. Only in the case of the As-spiked controls were the slag fines spiked for quality assurance purposes, otherwise they contributed (essentially) no As to the DM-Slag fines blends.

In every case (DM-BFF, DM-SSF and NC dose) for both As oxidation states, the TCLP-As results were below the detection limit or DL (<0.25 mg/L), so the data is not shown. These results suggested that the DM alone and in combination with the slag fines were able to immobilize As, i.e., slag cement (NC) was not required as an additional stabilizing agent. This was an important cost saving outcome for synthetic fill production using DM and slag fines. For the SPLP results, all DM-BFF blends regardless of As oxidation state and slag cement dose produced As concentrations that were below the DL, except for the raw and spiked BFF controls.

For the DM-SSF blends, Table 3 shows that in every case for both oxidation states, the SPLP-As results were below the DL (<0.05 mg/L) except for the 80/20 DM-SSF blends for both As spikes and two As^{3+} spiked replicates with intermediate doses of slag cement (SPLP DL is lower than TCLP due to matrix interferences). It is not known why the 80/20 DM-SSF blend shows As values above the DL when the unamended DM itself does not in 8 out of 10 cases. Moreover, there was no clear trend with respect to pH, though the SPLP-pH of the samples above detection were in the range of 7.85 to 9.25 (data not shown). These occurrences are difficult to understand, but may involve a complex interaction between pH and other processes that control precipitation of As compounds.

Table 3: SPLP-As results for the *DM-Slag fines blends suite*.

Media	**Raw Control**	**Arsenite Spike [100 mg/kg As(III)]**				
		Control	**0.5% NC**	**1.0% NC**	**1.5% NC**	**2.0% NC**
DM	< 0.050	< 0.050	< 0.050	0.061	0.061	< 0.050
80/20	< 0.050	0.112	0.122	0.098	0.127	0.124
50/50	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
20/80	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
SSF	< 0.050	< 0.050	NA			
		Arsenate Spike [100 mg/kg As(V)]				
		Control	**0.5% NC**	**1.0% NC**	**1.5% NC**	**2.0% NC**
DM	above	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
80/20		0.054	0.079	0.056	0.053	0.071
50/50		< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
20/80		< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
SSF		< 0.050	NA			

Given the fact that several of the detected As concentrations for the DM-SSF blends were also very close to the DL and that the BFF controls produced As raw and spiked control concentrations that were almost 10x the DL [0.365 mg As(III)/L and 0.437 mg As(V)/L, respectively] while DM-BFF blends were all below the DL, it was determined that the performance of the BFF was slightly better, and a more detailed As thresholding evaluation of the BFF and SSF media alone was warranted.

5.2.2 Raw Materials Suite

Five additional replicates each of BFF and SSF were re-tested at the 100 mg/kg target level for each arsenic source. Single replicates of each media were individually dosed with 1,000 and 5,000 mg/kg of each As species in an attempt to establish an upper cap on As immobilization as a pure media. Table 4 presents the dosing targets (mg/kg), equivalent aqueous concentrations (as conservative tracer), and the measured As concentrations by totals, TCLP and SPLP analyses.

From a totals perspective, it appears that the slag fines were under -and over-spiked spiked with As, respectively. This really an artifact of the difference between test methods in that the TCLP/SPLP sample size (25.0g) is large enough to capture the full grain size distribution of a sample whereas the total sample size is much smaller (0.5g). When taken from the same batch, the totals sample is less representative of the full particle size distribution because the sample quantity really only allows the collection of the finest fractions. Note that grinding of the sample before/after spiking changes its ANC (see Figure 1), so this was avoided. Also, in the case of coarser grained media such as the SSF media (unless ground), spiking dry samples usually results in the preferential uptake of the metals by the finer fractions of the sample due to surface area effects and the wicking (capillarity) of the aqueous solution. This would give the appearance of over-spiking a sample even though the aqueous solutions were carefully measured and applied. For these reasons, emphasis is placed on the aqueous concentrations, not the measured totals.

Table 4: Arsenic thresholding for the *Raw Materials Suite*.

	Target Dose		**BFF-As(III)**		**SSF-As(III)**		**BFF-As(V)**		**SSF-As(V)**	
	Totals mg/kg	**Equiv. mg/L**	**Totals mg/kg**	**Conc. mg/L**	**Totals mg/kg**	**Conc. mg/L**	**Totals mg/kg**	**Conc. mg/L**	**Totals mg/kg**	**Conc. mg/L**
TCLP	**100**	**5**	86.6	0.098	142	<0.010	99	0.256	140	<0.010
	1,000	**50**	720	26	2,000	<0.010	860	18	1,900	<0.010
	5,000	**250**	5,400	160	7,900	0.029	5,800	300	8,800	<0.010
SPLP	**100**	**5**	same as above	0.25	same as above	<0.010	same as above	0.39	same as above	<0.010
	1,000	**50**		16		<0.010		15		<0.010
	5,000	**250**		190		<0.010		48		<0.010

The TCLP and SPLP DLs for As in Table 4 are lower than Table 3. On basis of Table 4, the SSF media immobilized greater amounts of As to lower concentrations than the BFF media, in some cases, by several orders of magnitude. In the case of the SPLP-As(III) and As(V) series, the upper As threshold prior to producing an As concentration that was above the TCLP or SPLP DL was not even established. In this way, the SSF media revealed greater As immobilization potential.

5.2.3 SSF Suite

The positive outcomes in Section 5.2.2 for the SSF media required verification as they were based on single replicates for the elevated As concentrations. Three additional replicates of the SSF media were re-tested (expanded) for their ability to immobilize up to 10,000 mg/kg As. Table 5 presents the pH and concentrations of As measured by totals, TCLP and SPLP analyses.

Table 5: Expanded As thresholding results for SSF media.

	Target Dose		**As(III)**				**As(V)**			
	Totals mg/kg	**Equiv. mg/L**	**Totals mg/kg**	**Aqueous mg/L**	**Removal %**	**pH**	**Totals mg/kg**	**Aqueous mg/L**	**Removal %**	**pH**
TCLP	**100**	5	218	0.02	99.00	11.20	245	0.01	99.00	11.43
	500	25	749	0.12	99.80	11.06	742	0.12	99.80	11.10
	1,000	50	1,582	0.26	99.90	11.35	1,409	0.35	99.90	11.32
	5,000	250	9,129	1.10	99.56	10.62	9,938	3.13	98.75	10.82
	10,000	500	14,222	7.07	98.59	9.89	19,226	5.46	98.91	10.12
SPLP	**100**	5	same as above	0.02	99.53	12.11	same as above	<0.001	99.98	12.09
	500	25		0.01	99.98	12.10		<0.01	99.99	12.11
	1,000	50		0.01	99.97	12.19		0.01	99.98	12.13
	5,000	250		0.41	99.84	12.14		0.73	99.71	12.13
	10,000	500		2.32	99.54	12.08		5.67	98.87	11.94

In the case of the totals, the target dosing maximums corresponded to measured totals concentrations exceeding 14,000 and 19,000 mg/kg for the As(III) and As(V) series, respectively, for the reasons described above. Under TCLP conditions and interpolating between the dosing targets, the SSF media immobilized approximately 8,250 mg/kg As (III) and 9,000 mg/kg As(V) before exceeding the TCLP-As criteria of 5.0 mg/L. Under SPLP conditions, very likely to due pH considerations, the federal drinking water were satisfied up to As(III) and As(V) total concentrations on the order of approximately 1,000 mg/kg. The performance of the SSF media in this series of experiments coupled with its superior ANC and comparable leaching performance when blended with DM, made the SSF media the preferred source of slag fines for additional study at the lab and field scales.

6.0 CONCLUSIONS

Thresholding experiments were used to gauge the ability of the various slag fines to immobilize significant concentrations of As for purposes of DM stabilization and water treatment. The SSF media demonstrated high pH buffering capacity which is believed to contribute to As immobilization. For any combination of DM-slag fines blending ratios, no As (III) or As(V) leaching occurred above the TCLP detection limit (0.250 mg/L). For SPLP conditions, only the 80/20 DM-SSF and DM-BFF blends leached minor amounts of As (0.05 to 0.124 mg/L) above the detection limit (0.050 mg/L). The SSF media immobilized approximately 8,250 mg/kg As (III) and 9,000 mg/kg As(V) before exceeding the TCLP-As criteria of 5.0 mg/L. Under SPLP conditions, very likely to due pH considerations, the federal drinking water were satisfied up to As(III) and As(V) total concentrations on the order of approximately 1,000 mg/kg.

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METALS IMMOBILIZATION USING SLAG FINES

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ABSTRACT

The metals immobilization potential of freshly crushed (blast furnace and steel) slag fines was evaluated, where each media resembled USCS SP type soil with <5% passing the No. 200 (0.075 mm) sieve. Because of their granular nature, hardness, mineralogy and residual lime content, these media are quite reactive. Accordingly, their metals (immobilization) potential was evaluated using aqueous metal solutions (Cd, Cu, Pb, Ni, W, Se(IV), Se(IV), Zn) having target doses equivalent to 100 mg/kg to 100,000 mg/kg to the slag fines. After 30 days of mellowing, all samples were tested for pH, totals, toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP) leaching behavior.

1.0 INTRODUCTION

The main environmental motivation for the thresholding experiments was to gauge the ability of various slag fines to immobilize significant concentrations of several target metals that are relevant to firing range, highway pavement runoff and industrial processes (Cd, Cu, Pb, Ni, W, Se(IV), Se(IV), Zn). This evaluation was driven by the unusual combination of the granular nature (<9.5 mm diameter) and particle reactivity of the slag fines, which is uncommon for soils. That is, reactivity is usually proportional to specific surface. Additionally, based on the significant arsenic immobilization potential of the steel slag fines (SSF) discussed in a companion paper to this conference [1], it was decided to explore the capability of the SSF media to immobilize other heavy metals.

The slag fines were collected from the Sparrow Point Steel mill complex in Baltimore, Maryland, USA (steel and blast furnace slag; SSF and BFF, respectively), and the Indiana Harbor East Steel Mill complex (steel slag; IND-SSF) in East Chicago, Indiana, USA. The bulk chemistry of the three slags is shown in Table 1.

The two steel slags are very similar, as expected, the two biggest differences being the aluminum and calcium oxide (in this case, free lime contents). For the BFF media, it contained substantially less iron (Fe) than the SSF media, but the difference is made up by silica compounds, namely reactive silicates. The exceptional environmental quality of the slags is shown in Table 2 versus the heavy metal soil chemistry of soil in the eastern US [2]. The data presented includes pH, totals (USEPA 6000/7000 Method series), toxicity characteristic leaching procedure (TCLP: USEPA Method 1311) and synthetic precipitation leaching procedure (SPLP; USEPA Methods 1312) results for the target analyte list (TAL) metals.

The SSF media exceed the typical soil ranges on only three metals: Fe, Mn and V. Like zero valent iron environmental remediation applications, the elevated iron content (typically 15 to 25 wt%) of the SSF media is considered to be an asset for its ability to precipitate and interact with other heavy metals, especially arsenic. The Mn and V contents, while from a totals perspective may be elevated above typical soils, the leaching of both metals are less than 0.005 mg/L, putting them on par with most drinking water criteria under SPLP conditions. The Fe concentrations of the BFF media are clearly less, but a main disadvantage of the BFF media is the arsenic concentrations, which exceed the SSF media by an order of magnitude and which may present challenges in certain states with respect to beneficial use and/or soil cleanup criteria (MD, but not PA or NJ).

Table 1: Bulk chemistry of select slags via X-ray Fluorescence (XRF).

Compound (wt%)	**SSF**	**BFF**	**SSF-IND**
Silicon Dioxide (SiO_2)	10.65	35.98	11.07
Aluminum Oxide (Al_2O_3)	4.09	10.79	8.33
Iron Oxide (Fe_2O_3)	26.84	2.20	27.25
Calcium Oxide (CaO)	37.21	35.62	33.24
Magnesium Oxide (MgO)	10.31	10.94	10.64
Sodium Oxide (Na_2O)	0.03	0.23	<0.01
Potassium Oxide (K_2O)	0.02	0.24	0.04
Titanium Oxide (TiO_2)	0.46	0.44	0.62
Phosphorous Oxide (P_2O_5)	0.78	0.02	0.65
Manganese Oxide (Mn_2O_3)	3.97	1.15	3.98
Sulfur Trioxide (SO_3)	0.16	2.33	0.24
Miscellaneous			
pH (-)	12.08	10.9	12.4
Loss on Ignition (950^{o}C)	5.49	---	3.44
Free CaO [CaO+Ca$(OH)_2$]	7.86	1.55	2.63

Given the prior research activities of Stevens in the area of the characterization of firing range soils and their remediation [3-11], the obvious question arose to the possible use of BFF and/or SSF media as possible firing range berm media based on the granular nature of the slags, as well as their inherent alkalinity and iron contents. Most firing ranges use soil impact berms behind the target line to stop bullets from leaving the firing range. These impact berms are usually constructed of mixtures of sand, silt, and clay soils. These soils have very little sorption and immobilization potential for heavy metals, and they must be routinely sieved to remove bullet fragments and/or be changed out [3,6]. Previous Pb leachability studies showed that if proper management was not implemented, the Pb leachability may not satisfy the TCLP regulatory limit of 5 mg/L [6,10].

The main opportunity evaluated was the potential to use BFF and/or SSF media as a substitute for the gravelly/sandy/clayey soils currently used as backstop media. Conceptually, three main applications were envisioned for using slag fines: 1) as an alternate impact berm media or the trapezoidal embankment material situated behind the targets and into which bullets ultimately penetrate and come to rest; 2) as a drainage layer directly underneath the impact berm media to treat infiltrating water passing through the bottom of the impact berm into the subsoils; and/or, 3) as a drainage trench material at the bottom slopes of the embankments to intercept and divert runoff.

Accordingly, preliminary experiments were conducted to evaluate the ability of the slag fines to immobilize high concentrations of Pb. Both materials contain less than 5% fines (silt/clay), classifying as a poorly graded sand or SP soil by the Unified Soil Classification System (USCS). A preliminary experiment was set up by spiking the slag fines with a lead salt $(PbNO_3)_2$ at concentrations of 500, 1,000, 5,000 and 10,000 mg Pb/kg. The lead salt and SPLP solution (20:1 liquid to solid ratio) were simultaneously applied to the SSF and BFF materials and then they were rotated in a tumbler for 18 hours prior to extraction. Tests were run in triplicate and average results are reported in Table 3.

Pb leaching from the BFF media was surprisingly low given the fact that there was no mellowing or curing time after Pb spiking to allow for pozzolanic reactions such as those occurring in cement systems which can take up to 28-days. Here, the results were essentially instantaneous, and even more impressive considering that the slag fines are a coarse, granular media and no optimization was attempted.

Based on Table 3, one would be tempted to pick the BFF media for immediate rollout and testing in the field. However, as the BFF media weather in the field, one can imagine that its buffer capacity

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Table 2: Environmental Chemistry Comparison of Eastern US soils versus BFF and SSF media.

Metal	**Eastern US Soils**[1]		**Sparrows Point -BFF**			**Sparrows Point-SSF**			**Indiana Harbor East-SSF**		
	Range (mg/kg)	**Average (mg/kg)**	**Totals (mg/kg)**	**TCLP (mg/L)**	**SPLP (mg/L)**	**Totals (mg/kg)**	**TCLP (mg/L)**	**SPLP (mg/L)**	**Totals (mg/kg)**	**TCLP (mg/L)**	**SPLP (mg/L)**
Aluminum (Al)	7,000 to 100,000	57,000	41,800	---	---	19,000	0.83	0.250	16,000	2.3	13
Antimony (Sb)	<1.0 to 8.8	0.76	<2.0	<0.100	<0.010	< 5.0	< 0.05	< 0.0005	< 5.0	< 0.050	< 0.0005
Arsenic (As)	<0.1 to 73	7.4	7.3	<0.500	<0.050	< 1.0	< 0.10	< 0.0005	< 1.0	< 0.10	< 0.0005
Barium (Ba)	10 to 1,500	420	526	---	---	78	0.32	0.260	100	0.23	0.200
Beryllium (Be)	<1.0 to 7.0	0.85	5.42	<0.100	<0.010	< 0.20	< 0.008	< 0.00028	< 0.20	< 0.008	< 0.00028
Boron (B)	---	---	---	---	---	39	<0.10	< 0.05	35	0.22	< 0.05
Cadmium (Cd)	ND to 4.0	---	0.029	<0.100	<0.010	24	< 0.008	< 0.00022	16	< 0.008	< 0.00022
Calcium (Ca)	---	---	---	---	---	330,000	1,880	715	220,000	698	285
Chromium (Cr)	1.0 to 1,000	52	48	<0.500	<0.050	1,100	< 0.10	0.0024	980	< 0.10	0.0047
Cobalt (Co)	---	---	---	---	---	1.6	0.04	0.00050	< 1.0	< 0.040	0.00018
Copper (Cu)	<1.0 to 700	22	8.42	<0.100	<0.010	4.6	< 0.10	0.00057	3.7	< 0.10	0.0013
Iron (Fe)	100 to 100,000	25,000	19,320	<0.500	<0.500	220,000	< 0.20	< 0.100	170,000	< 0.20	< 0.100
Lead (Pb)	<10 to 300	17	4.9	<0.500	<0.050	< 2.0	< 0.20	0.0091	43	< 0.20	0.0049
Magnesium (Mg)	---	---	---	---	---	78,000	<1.0	< 0.500	70,000	< 1.0	< 0.500
Manganese (Mn)	<2.0 to 7,000	640	16,860	---	---	36,000	< 0.10	< 0.005	27,000	< 0.10	< 0.005
Mercury (Hg)	<0.01 to 3.4	0.12	<0.025	0.0018	<0.0008	< 0.100	< 0.001	< 0.001	< 0.100	< 0.001	< 0.001
Nickel (Ni)	<5.0 to 700	18	27.7	<0.100	<0.010	7.1	< 0.10	0.0038	7.3	< 0.10	0.0017
Potassium (K)	---	---	---	---	---	< 500	< 20	< 10	< 500	< 20	< 10.0
Selenium (Se)	<0.1 to 3.9	0.45	2.44	<0.500	0.018	< 4.0	< 0.20	0.0019	< 4.0	< 0.20	0.0056
Silver (Ag)	---	---	<2.0	<0.100	<0.10	< 1.0	< 0.040	< 0.0002	< 1.0	< 0.040	< 0.0002
Sodium (Na)	---	---	---	---	---	170	---	---		1,300	8.82
Thallium (Tl)	---	---	<1.0	<0.100	<0.010	2.2	< 0.50	< 0.0002	2.5	< 0.50	0.00046
Vanadium (V)	<7.0 to 300	66	33.6	---	---	730	< 0.050	0.00068	670	0.072	0.0047
Zinc (Zn)	<50 to 2,900	52	22.4	<0.200	0.039	76	< 0.10	< 0.010	200	< 0.10	< 0.010
pH			11	7.15	10.33	11.8	11	11.37	11.6	11	11.27

1: Dragun and Chekiri (2005)

Table 3: SPLP results for the Pb-spiked BFF and SSF media

Sample Description	**Pb (mg/L)**	**SPLP pH**
Blast Furnace Fines (BFF) Control	ND	10.30
Pb 500 mg/kg spike	0.03	10.19
Pb 1,000 mg/kg spike	0.04	10.16
Pb 5,000 mg/kg spike	0.11	9.25
Pb 10,000 mg/kg spike	0.16	8.10
Steel Slag Fines (SSF) Control	0.23	11.85
Pb 500 mg/kg spike	2.39	11.81
Pb 1,000 mg/kg spike	6.07	11.76
Pb 5,000 mg/kg spike	51.41	11.80
Pb 10,000 mg/kg spike	154.87	11.88

will be more rapidly diminished than the SSF media, allowing the system pH to drift into the acidic zone where the Pb concentrations begin increasing based on the Pb solubility curve. On the other hand, the SSF media steel slag is very strongly buffered, and initially, the Pb concentrations may be high as it goes into service, but with time, the pH will drop and immobilization similar to the BFF media can be expected for long-term operations. Since both slags are often generated at the same steel mix complexes, blends are possible to achieve specific performance.

With respect to firing range soils, the metals that are of traditional interest include copper (Cu), lead (Pb), nickel (Ni), and tungsten (W) [3, 9, 11]. The first three metals are cationic and amphoteric, meaning they are soluble at both low and high pH and between a typical pH of 7 to 11, they achieve their minimum solubilities. Tungsten persists as an oxyanion at pH>6.2. In expanding the range of metals that could be potentially immobilized by the SSF media in passive berm, drainage, trench and filter-like applications, focus was additionally placed on DOT pavement or highway runoff applications, and challenging industrial metals such as selenium [Se(IV), Se(VI)] which are difficult to immobilize from a remediation and mining perspective. A brief review of the environmental literature pertaining to pavement runoff [12, 13] suggested that As, Cd, Cr, Cu, Pb, Ni and Zn are the key metals of interest.

2.0 METALS THRESHOLDING EXPERIMENTS

A thresholding analysis is a leaching-based treatability study that establishes the corresponding leaching potential of a constituent of concern (COC) from a fixed quantity of sorbent or immobilizing media for increasing doses of the COC. The maximum threshold (concentration or mass) that is immobilized against a regulatory cirtierion or objective is determined for certain leaching conditions (TCLP, SPLP, DI water, etc.) based on the initial COC concentration and the L:S ratio of 20:1. The metals evaluated and the dosing schedule shown in Table 4.

Procedurally, aqueous metal solutions were individually prepared by dissolving the corresponding salt in de-ionized water to achieve target doses (see Table 4). The SSF material was first wetted with the metals-spiked DI water solution, and then was mixed using a stainless steel spoon to achieve a moisture content of 16%. The metals-spiked SSF material was then stored in sealable plastic bags and allowed to mellow for 30 days. After mellowing, all the samples were air-dried and subjected to analytical testing. The sample size for the TCLP and SPLP analyses was reduced to 25 g. Three replicates each were prepared for each target dose for totals, TCLP and SPLP testing followed by ICP-OES analysis for all metals except for the totals digestion of W. The Cd concentration in the TCLP and SPLP leachates was also determined using a graphite furnace atomic absorption spectrometer (GFAAS, Varian Zeeman Spectra AA 220Z). Prior to analysis, the solutions were acidified using concentrated HNO_3 in an amount of 1%.

Table 4: Metals Thresholding Suite to SSF and SSF-IND media.

			Target Dose (mg/kg)						
Metal	**Reagent**	**Purity (%)**	**100**	**500**	**1,000**	**5,000**	**10,000**	**50,000**	**100,000**
Cd	$CdCl_2$	99.4	x	x	x	x	x		
Cu	$Cu(NO_3)_2 \cdot 2.5H_2O$	99.9	x	x	x	x	x		
Ni	$Ni(NO_3)_2 \cdot 6H_2O$	99.9	x	x	x	x	x		
Pb	$Pb(NO_3)_2$	99+			x	x	x	x	x[1]
Se^{4+}	Na_2SeO_3	99	x	x	x	x	x		
Se^{6+}	Na_2SeO_4	98	x	x	x	x	x		
W	$Na_2WO_4 \cdot 2H_2O$	99.3	x	x	x	x	x		
Zn	$Zn(NO_3)_2 \cdot 6H_2O$	99.9	x	x	x	x	x		

Note 1: SSF-IND evaluated for these conditions only.

The total digestion procedure for the W-containing samples used a modified US Occupational Safety and Health Administration (OSHA) method, namely, Method ID-213 [14]. Acid digestion was performed using 0.5 gram soil aliquots in 125 mL beakers (Phillips) in a three step process. The first extraction used 2mL NH_4OH (certified ACS grade) for a minimum of 12 hours (overnight). To this soil-extract solution was added 2 mL each of DI water, 85% H_3PO_4, and concentrated HCl, HNO_3 and H_2O_2, and the resulting solution was left overnight. Afterwards, 5 mL of concentrated HNO_3 was added, and the soil-extractant mixture was then refluxed over a hotplate (190°C) using a ribbed watch glass cover until the mixture was reduced to approximately 2 mL (essentially H_3PO_4). After cooling, the digestate was filtered through No. 42 Whatman filter and remaining solution was diluted to 100 mL using DI water prior to ICP/OES analysis. For quality control purposes the analysis also included the digestion of tungsten powder (99.99% purity, Sigma Aldrich, MO) and matrix-spiked samples.

The controls and Pb-spiked SSF and SSF-IND media at the 50,000 and 100,000 mg/kg dosing levels were also evaluated for the potential phases responsible for immobilization by X-ray powder diffraction (XRPD). The XRPD sample preparation included first grinding of 20 g of an air-dried, bulk sample of the SSF media using a standard compaction hammer to break the larger particles (minus 9 mm to 2 mm). Afterwards, a 2g sub sample from the pulverized SSF sample (< 2 mm size) was then micronized in a McCrone micronizing mill for 10 min using 7 mL cyclohexane as the milling fluid. The resulting slurry was air dried and then mixed with corundum (α-Al_2O_3, Sawyer) on an 80:20 weight basis for XRPD analyses. Corundum was used to determine the amorphous content in the slag fine samples.

Step-scanned XRPD data was collected by the Rigaku Ultima 4 computer-automated diffractometer using Bragg-Brentano geometry. Diffractometry was conducted at 40 kV and 40 mA using a diffracted beam graphite-monochromator with Cu radiation. The data was collected in the 2θ range of 5° to 85° with a step size of 0.03° per 8 s. The qualitative and quantitative analyses of the XRPD patterns were performed using the Jade software version 7.5 [15] and the Whole Pattern Fitting function of Jade, which is based on the Rietveld method [16]. The reference databases for powder diffraction and crystal structure data were the International Center for Diffraction Data database [17] and the Inorganic Crystal Structure Database [18], respectively.

3.0 RESULTS

The results of the metals thresholding experiments are shown in Tables 5 to 7. Lead leaching complied with the TCLP standard (5.0 mg/L) for totals concentrations up to 100,000 mg/kg. The SPLP-Pb results were somewhat lower, due to high pH (11.5 to 12.5). Nickel was removed below the detection limit of 0.05 mg/L. Tungsten removal was also extremely high without any attempt at optimization (SPLP-W =2.6 mg/L for 10,000 mg/kg W soil spike). The highest concentrations of cadmium, copper and zinc were removed by both TCLP and SPLP to below USEPA drinking water criteria without any attempt at optimization. Selenium, which is extremely difficult to immobilize

[19], was removed at modest levels, but since selenium is usually encountered at trace to low concentrations (<10 mg/L), the SSF materials would likely perform well in natural systems or as a filtering medium [TCLP-Se(IV); SPLP- Se(IV) both <0.5 mg/L for 100 mg/kg Se(IV) soil spike].

Table 5: Pb thresholding results for SSF and SSF-IND media.

	Target Dose		**SSF**		**SSF-IND**	
	Totals	**Equiv.**	**Aqueous**	**Removal**	**Aqueous**	**Removal**
	mg/kg	**mg/L**	**mg/L**	**%**	**mg/L**	**%**
TCLP	**1,000**	50	0.18	99.63	<0.05	99.90
	5,000	250	0.13	99.95	<0.05	99.98
	10,000	500	0.31	99.94	<0.05	99.99
	50,000	2,500	1.34	99.95	0.39	99.98
	100,000	5,000	2.12	99.96	194.72	96.11
SPLP	**1,000**	50	1.66	96.68	0.06	99.98
	5,000	250	18.92	92.43	0.96	99.61
	10,000	500	55.76	88.85	2.91	99.42
	50,000	2,500	113.91	95.44	6.43	99.74
	100,000	5,000	138.72	97.23	11.62	99.77

Table 6: SFF thresholding results for additional firing range metals.

	Target Dose		**Cu**		**Ni**		**W**	
	Totals	**Equiv.**	**Aqueous**	**Removal**	**Aqueous**	**Removal**	**Aqueous**	**Removal**
	mg/kg	**mg/L**	**mg/L**	**%**	**mg/L**	**%**	**mg/L**	**%**
TCLP	**100**	**5**	0.03	99.41	<0.05	99.00	0.79	84.19
	500	**25**	0.03	99.88	<0.05	99.80	5.99	76.03
	1,000	**50**	0.03	99.94	<0.05	99.90	9.70	80.61
	5,000	**250**	0.04	99.99	<0.05	99.98	18.18	92.73
	10,000	**500**	0.04	99.99	<0.05	99.99	21.28	95.74
SPLP	**100**	**5**	0.01	99.75	<0.05	99.00	0.10	98.00
	500	**25**	0.08	99.68	<0.05	99.80	0.22	99.12
	1,000	**50**	0.11	99.78	<0.05	99.9	0.52	98.95
	5,000	**250**	0.18	99.93	<0.05	99.98	1.43	99.43
	10,000	**500**	0.16	99.97	<0.05	99.99	2.58	99.48

Table 7: SFF thresholding results for typical highway runoff and industrial process metals.

	Target Dose		**Cd**		**Se (IV)**		**Se (VI)**		**Zn**	
	Totals	**Equiv.**	**Conc.**	**Removal**	**Conc.**	**Removal**	**Conc.**	**Removal**	**Conc.**	**Removal**
	mg/kg	**mg/L**	**mg/L**	**%**	**mg/L**	**%**	**mg/L**	**%**	**mg/L**	**%**
TCLP	**100**	**5**	<0.0005	99.99	0.43	91.33	2.7	46.01	0.03	99.49
	500	**25**	<0.0005	99.99	2.43	90.28	13.69	45.22	0.04	99.85
	1,000	**50**	<0.0005	99.99	5.95	88.10	29.28	41.44	0.02	99.97
	5,000	**250**	0.001	99.99	52.79	78.88	185.30	25.88	0.06	99.98
	10,000	**500**	0.0021	99.99	60.11	87.98	426.87	14.63	0.02	100.00
SPLP	**100**	**5**	<0.0005	99.99	0.35	92.97	1.72	65.57	0.04	99.14
	500	**25**	<0.0005	99.99	2.49	90.05	8.80	64.81	0.12	99.52
	1,000	**50**	<0.0005	99.99	4.70	90.60	20.40	59.19	0.29	99.43
	5,000	**250**	<0.0005	99.99	9.94	96.02	130.19	47.93	1.55	99.38
	10,000	**500**	<0.0005	99.99	29.31	94.14	442.17	11.57	1.29	99.74

Due to the detection limits of the XRD device (~1 wt% or 10,000 mg/kg) for select elements and minerals, only the SSF media was evaluated for the two highest Pb spikes to determine if Pb containing minerals played a role in the immobilization of Pb. The annotated diffractogram for the Pb-spiked SSF media is shown in Figure 1. Almost 50% of the initial Pb mass form the 100,000 mg/kg spike was accounted for by the crystalline phases massicot (PbO), hydrocerrusite [$Pb_3(CO_3)_2(OH)_2$] and lead oxide (Pb_2O_3) in the respective weight percents of 0.96, 3.84 and 2.21 based on Rietveld quantification analyses. These minerals have frequently been identified in firing range soils [6] and Pb-contaminated soils that have been treated by stabilization/solidification processes [7, 8, 20], which illustrates that more than Pb sorption is operative in these systems. For the SSF-IND sample, no massicot was detected, and the hydrocerrusite and lead oxide contents were on the order of 3.62 and 3.53 wt%, respectively. For each media, the remaining Pb mass was distributed in either in minerals below the detection limit or the amorphous phase.

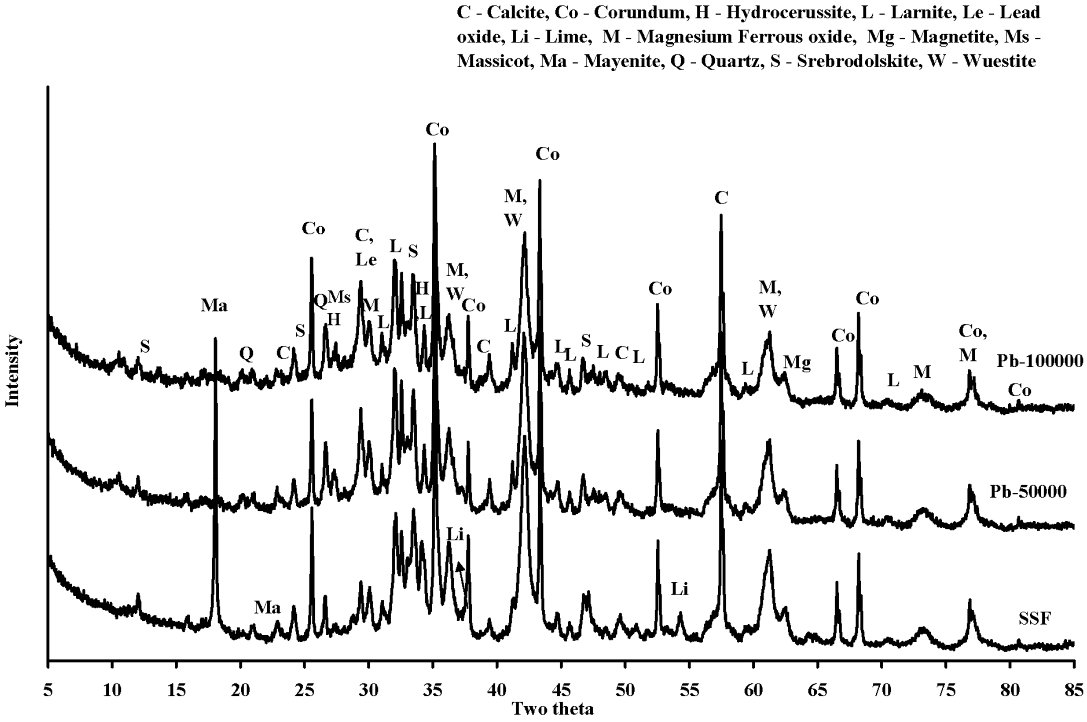

Figure 1: Annotated diffractograms for the raw and Pb-spiked SSF media at the 50,000 and 100,000 mg/kg dosing levels.

4.0 CONCLUSIONS

The main environmental motivation for the thresholding experiments was to gauge the ability of the various slag fines to immobilize significant concentrations of several target metals that are relevant to firing range, highway pavement runoff and industrial processes [Cd, Cu, Ni, Pb, Se(IV), Se(VI), W, Zn]. For doses up to 10,000 mg/kg, the Cd, Cu, Ni, Pb and Zn removal efficiency of the SSF media for both TCLP and SPLP conditions was almost always greater than 99%. Se(IV) and W removal efficiencies frequently exceeded 90% whereas Se(VI) removal averaged on the order of 41%, which for this metal is still a considerable removal rate in terms of actual mass.

At the 50,000 and 100,000 mg/kg levels, Pb removal exceeded 95% (frequently >99%) for both SSF media and leaching conditions. The corresponding XRPD results indicated that massicot, hydrocerrusite and lead oxide were the key crystalline phases associated with Pb removal.

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Beneficial Use of Steel Slag Fines to Immobilize Arsenite and Arsenate: Slag Characterization and Metal Thresholding Studies

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Abstract: This study presents the results of an extensive beneficial-use evaluation of 3/8-in. minus steel slag fines (SSF) to immobilize arsenic. Two primary sets of experiments were undertaken to assess (1) the ability of SSF to immobilize 100 mg/kg arsenite (As^{3+}) and arsenate (As^{5+}) in dredged material when blended with SSF, including slag cement doses (up to 2%) to determine if additional environmental polishing was necessary; and (2) the ability of SSF alone to immobilize each As species. Visually, the SSF materials resemble an AASHTO No. 9 (fine) aggregate, with a small fraction passing the No. 200 (0.075 mm) sieve. In order to establish the design parameters for deploying the slag media in geoenvironmental applications (soil blending, drainage, reactive trenches, and filters), the soil classification and grain-size distribution, specific gravity, loss on ignition (ash content), standard and modified Proctor compaction behavior, direct shear strength, and swell behavior of the SSF media were evaluated. Additionally, the following geochemical attributes of the SSF media were evaluated: bulk chemistry, mineralogy, pH, anion scan, total priority pollutant list (PPL) metals, toxicity characteristic leaching procedure (TCLP), and synthetic precipitation leaching procedure (SPLP) leaching behavior for PPL metals. Arsenic thresholding studies were performed, in which the uptake of each As source on the SSF materials was evaluated. The SSF materials immobilized approximately 7,900 mg/kg As^{3+} and 8,800 mg/kg As^{5+}, producing TCLP and SPLP concentrations less than 0.010 mg/L in three of four cases. X-ray diffraction (XRD) and scanning electron microscopy (SEM) studies were used in combination with MINTEQ modeling to isolate the mechanisms responsible for the As immobilization in the SSF materials. **DOI:** 10.1061/(ASCE)HZ.1944-8376.0000077.

CE Database subject headings: Arsenic; Dredging; Cement; Slag; Recycling.

Author keywords: Arsenic; Dredged spoil; Slag; Recycling.

Introduction

In December 2008, The Maryland Port Administration (MPA; Baltimore) issued its first award under its request for proposal No. 270025-S, "Innovative Reuse of Dredged Material." The program focuses on developing large-scale opportunities to recycle more than 382,000 m^3 (500,000 cu yd of dredged material (DM) per year by 2023 to support the limited capacity (3.5 million m^3 or 6 million cu yd) of the Cox Creek Dredged Material Containment Facility in Curtis Bay, Maryland. Under Maryland state law, DM from the Baltimore Harbor can only be placed in a confined disposal facility (CDF), such as the Cox Creek DMCF. Recycling on such a large scale illustrates the need to develop sustainable, high-volume commercial outlets for DM, such as earthwork construction related to coal mine or quarry closure, landfill daily cover, general, embankment, or structural fill applications, in the greater Baltimore metropolitan area to minimize transportation costs.

The primary challenge is that the soft, fine-grained compressible nature of DM, even dewatered (moisture content of 40–100%), makes DM generally undesirable for geotechnical applications other than liners, barriers, and caps/covers. However, when DM is blended with coarse(r) materials on the scale of sands or gravels, the mixes can be quite competent, if local inexpensive sources of coarse-grained materials can be found. The approach is not without precedent. Grubb et al. (2006a, b, 2007a, b, 2008a, b) reported on the geotechnical advantages and field performance of uncontaminated DM blended with Philadelphia curbside-collected crushed glass (CG) in three percentages (20, 50, and 80% CG by dry weight). A 100% DM embankment was also built. The CG was a very angular 9.5 mm (3/8 in.) minus material with less than 5% fines. The addition of the (low-valued) CG to the DM (an organic silt) significantly enhanced the geotechnical properties of the DM. The 20/80 CG-DM blend (dry CG content reported first) was borderline on local Department of Transportation (DOT) specifications, and the 50/50 and 80/20 CG-DM blends satisfied the DOT embankment and structural fill requirements, respectively. Over the course of one year, these embankments aged under their own self-weight [only 3.7 m (12 ft) high], doubling to tripling in strength, as measured by triaxial strength and cone-penetrometer resistance (Grubb et al. 2008b). Because these studies did not have

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an environmental treatment component, the question arose as to how to handle the dewatered, contaminated DM from the Cox Creek DMCF. Could another low-cost, coarse-grained material with pozzolanic attributes be blended with the DM to provide the geotechnical and environmental enhancements simultaneously?

Accordingly, a regional materials analysis was performed, and it revealed that steel slag fines (SSF) generated at the steel mill at Sparrows Point (Baltimore) were produced in volumes consistent with DM management needs. Specifically, the SSF media is produced during the bulk slag crushing and screening operations for the bulk iron recovery operations and the manufacture of construction grade aggregates. The SSF materials contain up to 10% residual lime and visually appear as a 9.5 mm (3/8 in.) minus material, or AASHTO No. 9 aggregate, with a small fraction passing the No. 200 (0.075 mm) sieve. The SSF materials do not have an identified beneficial use despite their excellent environmental quality, as illustrated subsequently in this paper. Also, there are currently no regulations governing the beneficial use of DM in Maryland, and the SSF materials are classified as a residual waste. A key reason for blending the SSF materials with DM is that they are granular, and the residual lime was hypothesized to simultaneously provide strength enhancements (aging effects) and passive treatment of U.S. EPA priority pollutant list (PPL) metals (primarily arsenic) contained in the DM.

Total arsenic concentrations in the Baltimore harbor sediments and navigation channels can be as high as 100 mg/kg depending on the location, but the limited historic data on the Cox Creek DMCF indicates an average As concentration of approximately 20–30 mg/kg, which likely reflects the effects of mixing, dilution, and sediment depositional processes that occur during the hydraulic placement of DM in the CDF. From an operational perspective, another concern is what maximum As concentration can be tolerated in the DM prior to blending with the SSF materials to safely undertake large scale recycling. Accordingly, a detailed As thresholding analysis was completed, in which totals, toxicity characteristic leaching procedure (TCLP), and synthetic precipitation leaching procedure (SPLP) were analyzed. The main purpose of these leaching-based tests was to illustrate the ability of the SSF materials to immobilize significant total concentrations of arsenic through direct spiking and as occurring in the DM and DM-SSF blends. In this way, As leaching behavior can be used to reverse engineer an upper cap on the permissible total As concentration in the DM prior to SSF blending.

Thus, to support large scale recycling of potential DM-SSF blends as geotechnical fill, a detailed geotechnical and geoenvironmental evaluation of the DM and SSF materials was completed. This paper presents the materials characterization and As-immobilization potential of the DM and SSF materials and their blends.

Materials and Methods

Raw Materials

The DM sampled for this field demonstration project was obtained for testing purposes from the Volvo area within the north cell of the Cox Creek DMCF in January 2009. The bulk of the DM was collected in the vicinity of the outfall area. Sampling also occurred at four other locations positioned almost equally along the remaining north-south transect of the isolated Volvo area. Sixty sealed 19-L (5-gal.) buckets of fresh DM from five locations were collected to account for material variability purposes.

The SSF materials were derived from the basic oxygen furnace (~1,700°C) at the Sparrows Point steel mill complex. After the molten slag from the kettles is dumped on the slag pile, it air cools for approximately 24 h. Then the slag is processed through a conventional aggregate crushing and screening process, and the coarse-sized aggregates go to commercial construction. The fines [9.5 mm (3/8 in.) minus fraction] are stockpiled in dedicated locations. Samples of SSF materials from five random locations were collected to develop a representative sample for testing.

Slag cement [NewCem (NC)] is also produced at the Sparrows Point steel mill complex. NC was included in the testing program because it was not clear at the outset of the project if the SSF materials alone could immobilize the As in the DM to acceptable levels. Accordingly, small doses of NC (up to 2%) were included in the As thresholding analysis (see following section) for environmental polishing purposes. However, the hope was to avoid the use of NC from a synthetic fill cost perspective.

Baseline Geotechnical Characterization

A series of laboratory tests was performed to evaluate the basic properties of the DM, SSF materials, and slag cement, including the bulk chemistry, natural moisture content (MC), specific gravity (G_s), and loss on ignition (LOI). The DM and SSF materials were further evaluated for their grain-size distribution, soil type according to the Unified Soil Classification System (USCS), compaction behavior in raw and blended forms, direct shear strength, and swell behavior.

The bulk chemistry was determined using X-ray fluorescence (XRF) spectroscopy. The natural MC and specific gravities of the three raw materials were determined using ASTM methods D2974 (ASTM 2000c) and D854 (ASTM 2002), respectively. The LOI was used to determine the organic matter content of all media. The tests were performed in two stages by using ASTM D2974 (Method D). First, the samples were oven-dried for 16 h at 105°C for the MC determination (Method A). The samples were then transferred to a muffle furnace (450°C) for 12 h for the LOI determination.

The grain-size distributions of the DM and SSF materials and their blends were determined in accordance with ASTM D421 (ASTM 1985) and ASTM D422 (ASTM 1998). Two oven-dried samples for each material were sieved under two conditions: (1) as received, and (2) water-washed over a No. 200 sieve. The latter was undertaken because the SSF materials have cementitious properties, and consequently, a potential for larger perceived grain diameters. Soil classification was determined in accordance with ASTM D2487 (ASTM 2006).

To determine how the geotechnical properties varied as a function of materials blending, the data presented in this paper will focus on the 20/80, 50/50, and 80/20 DM-SSF blends, in which the dry weight percentage of the DM is reported first. Briefly, the blending process involved preproportioning the raw materials on the basis of their initial moisture contents of 110% and 10% for the DM and SSF media, respectively. Molds with a diameter of 15.2 cm (6 in.) were used in all cases (except 100% DM) because of the maximum particle size of the SSF materials. The DM-SSF blends were hand mixed until they were visually homogeneous. In all cases, the DM-SSF blends were dried back to specific, targeted MC values prior to compaction by standard and modified Proctor effort [ASTMs D698 (ASTM 2000b) and D1557 (ASTM 2000a)]. This procedure was adopted to simulate anticipated field operations and to avoid the introduction of irreversible soil fabric effects in the DM by repeated drying/wetting cycles.

Direct shear (DS) testing was performed on the SSF samples in general accordance with ASTM D3080 (ASTM 2004). Two material fractions were evaluated: (1) the as-received SSF material, and (2) the SSF material filtered to remove the fraction larger than the No. 4 sieve. Shear testing on the latter material was performed to minimize the effects of interaction between the specimen and the shear box. The 6.4 cm (2.5 in.) diameter specimens were placed in the molds by using thin lifts and were compacted by using a rubber-tipped pestle. They were compacted to minimum 95% relative compaction (RC) and within +/-2% of w_{opt} on the basis of ASTM D698. The selected normal stresses corresponded to shallow-to-moderate depth overburden conditions ($\sigma_n = 70$, 207, and 345 kPa). Tests were performed under as-compacted (partially saturated), total stress conditions. Shear rates were selected as 1% per min.

An essential feature of geotechnical fills is their volume change behavior, and one concern about lime-containing media is their tendency to swell. To assess the swell behavior of the DM, SSF materials, and their blends, a series of long-term swell tests were conducted. One-dimensional swell testing was conducted in general accordance with ASTM D1883 (ASTM 2005) because these specimens were also used for California bearing ratio (CBR) testing after termination of the swell test. Raw DM, SSF, and three DM-SSF blends were compacted to 95% RC of their respective maximum dry densities by the modified Proctor test. Each material was inundated with tap water to mimic submerged field conditions and provide ample water for the potential hydration of free lime. Specimens were free to swell (or compress) under a 14.4 kPa (300 $\mathrm{lb/ft^2}$) seating load at room temperature (20°C) for more than 200 days (Table 3). Displacement data were collected continuously at 1–30 min intervals by using an automated data acquisition system. A 3:1 kaolinite/bentonite blend (model clay) was also tested for comparison purposes.

Baseline Environmental Characterization

When evaluating beneficial-use applications, the environmental quality of all source materials should be determined to gauge total composition versus leaching behavior against several criteria. Environmental testing of the DM and SSF materials included totals (U.S. EPA 6000/7000 method series), TCLP (U.S. EPA Method 1311), and SPLP (U.S. EPA Method 1312) analyses for PPL metals. Five replicates of each material were randomly collected during the field sampling event, and these replicates were used to gauge source material variability. A subsequent round of field testing was undertaken that involved the collection of three sets of random DM and SSF samples from the same general field locations for purposes of conducting anion scans. Chromium speciation work was also conducted on the same samples by using the alkaline digestion process (U.S. EPA Method 3060/7196 or 7199), speciated isotope dilution technique (U.S. EPA Method 6800), and X-ray absorption near-edge spectroscopy (XANES).

X-Ray Absorption Near-Edge Spectroscopy

X-ray absorption near-edge spectroscopy (XANES) was used to speciate chromium and iron in the SSF materials because of environmental concerns [chromium(VI)] and to assess the reactivity of the iron. The SSF materials were pulverized by using a Fritsch planetary ball mill. Approximately 10 g of the air-dried sample was placed into the milling containers and pulverized for 20 min at a rotation speed of 250 RPM. The entire pulverized sample was passed through a No. 100 sieve (0.15 mm) to avoid any fractionation.

Three standards each were used as reference for the quantification of Cr and Fe, respectively. For XANES-Cr analyses, the reference standards for chromium(VI) and chromium(III) were potassium chromate (K_2CrO_4; 99% purity, Fisher Scientific, Georgia) and chromium nitrate nonahydrate [$Cr(NO_3)_3 \bullet 9H_2O$; 99% purity, Fisher Scientific], respectively. A combination chromium standard was prepared by mixing 70% chromium(VI) and 30% chromium (III) on a dry weight basis. For XANES-Fe analyses, the reference standards for iron(0), iron(II), and iron(III) were nano zerovalent iron (synthesized in laboratory), ferrous sulfate heptahydrate ($FeSO_4 \bullet 7H_2O$, 99% purity, Fisher Scientific) and ferric chloride hexahydrate ($FeCl_3 \bullet 6H_2O$, 98% purity, Fisher Scientific), respectively. The pulverized SSF materials and six metal standards were shipped to the Pohang Accelerator Laboratory, South Korea, for XANES analyses.

XANES-Cr analyses were performed by using a BL7C1 (electrochemistry) beamline with a Si(111) monochromator and ring current of 130–185 mA at 2.5 GeV. The Cr K-edge XANES spectroscopic data were collected in the fluorescence mode by using pure N_2 gas-filled ionization chambers as gas detectors over the range from 200 eV below the Cr K-edge at 5,989 eV to as much as 900 eV above the edge. In order to remove the energy shift problem, energy calibration was carried out by measuring the XANES spectra of Cr foil (99.99% purity, Exafs Materials, Inc., California) and the samples simultaneously. Likewise, XANES-Fe analyses were performed by using a BL7C1 (electrochemistry) beamline with a Si(111) monochromator and ring current of 120–170 mA at 2.5 GeV. The Fe K-edge XANES spectra were collected in both transmission and fluorescence modes over the range from 100 eV below the Fe K-edge at 7,112 eV to as much as 900 eV above the edge. In order to remove the energy shift problem, energy calibration was carried out by measuring the XANES spectra of Fe foil (99.99% purity, Exafs Materials, Inc.) and the samples simultaneously.

For both chromium and iron, quantitative XANES analyses were conducted by using the ATHENA program in the IFEFFIT computer package (Newville 2001).

Acid Neutralization Capacity

One of the key aspects of controlling As speciation and leaching is pH control. In this regard, the residual lime content (Table 1) of the SSF media is an advantage, and for civil and environmental engineering applications, it is important to assess the long-term weathering of the SSF media and the impact of its buffering capacity on the DM when blended. Accordingly, acid neutralizing capacity (ANC) tests (Isenburg and Moore 1992) were performed on the raw DM and SSF materials, three DM-SSF blends, and a milled SSF sample. The milled SSF sample (SSFM) was prepared by using a Fritsch planetary ball mill. Approximately 40 g of air-dried SSF was placed into the milling container and pulverized for 15 min at a rotation speed of 250 RPM. The entire sample was pulverized to pass through a No. 100 sieve (0.15 mm). The raw DM and SSF materials (including the milled sample) were evaluated without a curing time. The DM-SSF blends were homogenized and mellowed for seven days prior to ANC testing.

The ANC procedure consisted of equilibrating the DM, SSF, and their blends to increasing equivalents of reagent per kilogram of dry soil. Specifically, 6.5 g of each dry sample were placed in a series of 130 mL bottles. For strongly alkaline media, incremental amounts of 15.8 N nitric acid (HNO_3) were added to the sample (total liquid volume 130 mL), with a liquid/solid ratio of 20:1, identical to the TCLP and SPLP procedures. For media with a naturally near-neutral pH (i.e., DM), incremental amounts of 10 N sodium hydroxide (NaOH) were also added to the sample to illustrate the impacts of alkalinity on the sample.

The resultant slurries were tumbled in a standard TCLP rotating extractor for 48 h. The supernatants were then filtrated through a 0.45 μm nylon membrane filter, and the pH of the leachate was recorded using an Accumet AR20 pH meter. All samples were stored in the refrigerator at a temperature of 4°C before they were analyzed for pH and total dissolved As, Cr, and Fe concentrations.

Table 1. Bulk Chemistry through X-Ray Fluorescence (XRF)

Compound (percent by weight)	DM	NC	SSF	BOF[a]	BOF[b]	BOF-EMg[c]	BOF-C[d]	BOF-US[e]
Silicon dioxide (SiO_2)	53.94	37.29	10.65	14.55	12.5	12–18	9–15	10–15
Aluminum oxide (Al_2O_3)	17.17	10.02	4.09	5	2.4	< 3	0.9–2.8	2
Iron oxide (Fe_2O_3)	9.79	0.36	26.84	26.8	31.2	21–29	24–39	21–43
Calcium oxide (CaO)	0.45	37.44	37.21	41.0	41.3	42–50	34–48	40–50
Magnesium oxide (MgO)	1.88	12.22	10.31	7.5	4.3	5–8	2.5–10	5–10
Sodium oxide (Na_2O)	0.85	0.23	0.03	—	—	—	—	—
Potassium oxide (K_2O)	2.74	0.25	0.02	—	—	—	—	—
Titanium oxide (TiO_2)	0.89	0.46	0.46	—	0.8	—	—	—
Phosphorous oxide (P_2O_5)	0.23	< 0.01	0.78	0.8	1.1	< 2	0.9	1–3
Manganese oxide (Mn_2O_3)	0.21	0.57	3.97	5.56	6.79	< 6	2–6.5	5.6–11
Sulfur trioxide (SO_3)	0.09	1.85	0.16	—	—	—	—	—
Miscellaneous								
pH (-)	8.72	11.40	12.08	—	—	—	—	—
Loss on ignition (950°C)	11.23	—	5.49	—	—	—	—	—
Free CaO $[CaO + Ca(OH)_2]$	—	0.08	7.86	—	—	< 10	—	—
Specific gravity (G_s)	2.58	3.00	3.27	—	—	3.3	—	—
Cl (mg/kg)	2,970	—	33	—	—	—	—	—
NO_3-N (mg/kg)	0.91	—	1.07	—	—	—	—	—
NO_2-N (mg/kg)	1.65 (2)	—	< 0.034	—	—	—	—	—
P-ortho (mg/kg)	< 0.42	—	< 0.42	—	—	—	—	—
SO_4 (mg/kg)	4,423	—	23.1	—	—	—	—	—

Note: Anion data based on average of 3 replicates.
[a] National Slag Association (1988), renormalized.
[b] French BOF slag data; Chaurand et al. (2007).
[c] European Mg-rich BOF slag data; Motz and Geiseler (2001).
[d] Chinese BOF slag data; Shen and Forssberg (2003).
[e] U.S. BOF slag data; Proctor et al. (2000).

Arsenic Thresholding

The purpose of the As thresholding experiments was to evaluate the ability of the SSF materials to immobilize significant concentrations of arsenite (As^{3+}) and arsenate (As^{5+}) in the DM-SSF blends, either on its own or with up to 2% NC if additional environmental polishing was required. In the first series of tests (DM-SSF blend suite), DM naturally containing approximately 20–30 mg/kg As was individually spiked with 100 mg/kg As^{3+} or As^{5+} to act as the source of As contamination. After 30 days of mellowing, the DM was then blended with SSF materials, and the DM-SSF blends were compacted and cured for and additional 30 days prior to analytical testing. In the raw materials suite, the 100% DM and 100% SSF leaching results were reverified, and the SSF materials were additionally spiked with target concentrations of 1,000 and 5,000 mg/kg As^{3+} or As^{5+} to establish an upper limit on As immobilization prior to leaching detectable concentrations by both the TCLP and SPLP tests. For both testing suites, sodium arsenite ($NaAsO_2$) and sodium arsenate heptahydrate ($Na_2HAsO_4 \bullet 7H_2O$) were used as the As^{3+} and As^{5+} sources, respectively (ACS grade, Fisher Scientific).

DM-SSF Blend Suite

Aqueous solutions of each arsenic salt were prepared by using deionized water and were targeted to achieve a DM MC of approximately 130–135%. This allowed the raw DM to have a liquid consistency sufficient to enable its homogenization with the much drier, granular SSF materials. Raw DM was placed in a Globe SP-30 mixer (Dayton, Ohio) and was homogenized as-is for approximately 10 min. Thereafter, during mixing, the arsenic solution was gradually introduced to the DM by using a series of polyethylene squirt bottles. Mixing was paused every 10 min to manually scrape the excess DM off of the bucket sidewalls with a spatula. This material was blended initially by hand, and then the automated mixing bucket was restarted, until a total of 40 min elapsed. The DM was then removed, and the device was cleaned prior to mixing the next batch. Individual batches of As-spiked DM were stored in sealable 19-L (5-gal.) buckets for a mellowing period of 30 days to achieve equilibration.

The 20/80, 50/50, and 80/20 DM-SSF blends were prepared after the DM mellowed. Each media was dosed with 0–2% by weight slag cement at 0.5% increments, except the 100% SSF (0%, as control), and they were mixed until visually homogenous. Next, each replicate (blend, NC dose) was compacted to greater than 90% of the maximum dry density by standard Proctor compaction for the requisite blend (the influence of low NC dose on compaction curve was ignored). Once compacted, the replicates were extruded from the molds and then cured in sealable bags for an additional 30 days. After subsequent air-drying (up to three days), all replicates were subjected to total-As, TCLP-As, and SPLP-As analyses.

Raw Materials Suite

For the 100 As mg/kg dosing level, five replicates of each raw material (DM and SSF) were used in the procedure outlined previously. For the 1,000 and 5,000 mg/kg spiking level, only one replicate of SSF was used. Aqueous solutions of each arsenic salt were prepared by using deionized water and were targeted to achieve a DM and SSF MC of approximately 130–135% and 16%, respectively. The spiked media were then individually stored in 3.7 L (1 gal.) sealable plastic bags and allowed to mellow for 30 days. After subsequent air-drying (up to three days), all replicates were analyzed for totals, TCLP and SPLP for As, Cr, and Fe. Select air-dried samples were reserved to conduct X-ray powder diffraction and SEM-EDX analyses.

X-Ray Powder Diffraction

X-ray powder diffraction (XRPD) and Rietveld quantification analyses (RQA) were used to assess the mineralogical composition of the SSF media alone and spiked with As^{3+} and As^{5+} target concentrations of 5,000 mg/kg. XRPD sample preparation included first grinding of 20 g of an air-dried, bulk sample of the SSF media by using a standard compaction hammer to break the larger particles (minus 9 to 2 mm). Afterward, a 2 g subsample from the pulverized SSF sample (< 2 mm size) was then micronized in a McCrone micronizing mill for 10 min by using 7 mL cyclohexane as the milling fluid. The resulting slurry was air dried and mixed with corundum (α-Al_2O_3; Sawyer, Lot No. C04-AO-41) on an 80:20 weight basis and was subjected to XRPD. Corundum was used to determine the amorphous content in the SSF media.

Step-scanned XRPD data were collected by the Rigaku Ultima 4 computer-automated diffractometer using Bragg-Brentano geometry. Diffractometry was conducted at 40 kV and 40 mA using a diffracted beam graphite-monochromator with Cu radiation. The data were collected in the 2θ range of 5–85° with a step size of 0.03° per 8 s. The qualitative and quantitative analyses of the XRPD patterns were performed by using the software Jade Version 7.5 and the whole pattern fitting function of Jade, which is based on the Rietveld method (Rietveld 1969). The reference databases for powder diffraction and crystal structure data were the International Center for Diffraction Data database (PDF-2) and the Inorganic Crystal Structure Database (ICSD), respectively.

Scanning Electron Microscopy–Energy Dispersive X-Ray (SEM-EDX)

The SSF media spiked with 5,000 mg/kg As were also subjected to scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analyses by using a LEO-810 Zeiss microscope equipped with an EDX, ISIS-LINK system. The EDX device was calibrated by using known weights of calcium oxide (CaO) and sodium arsenate ($NaAsO_2$) and their blends at operating voltages of 5 keV and 16 keV. Desired quantities of the two compounds were mixed by using a mortar and pestle to achieve a homogenous mix. Air-dried subsamples of the calibration standards, raw SSF media, and As-spiked SSF media were prepared by using double-sided carbon tape.

Results

Baseline Geotechnical Characteristics

The bulk chemistry determined by using X-ray fluorescence is shown in Table 1. The DM bulk chemistry is consistent with other studies (Grubb et al. 2010) and the specific gravity of the SSF materials (3–3.5 depending on the sample) reflects its high iron content (18.77% by weight), whereas its strong alkalinity results from the free lime and MgO contents. The NC is comprised of almost equal parts of calcium and silica contents (37%), and 10–12% each of aluminum and magnesium oxides. The LOIs reported in Table 1 are referenced to 950°C.

Table 2 summarizes the physical properties of the DM and SSF materials and the applicable ASTM testing methods. The average MCs for the DM and SSF were 104% and 9%, respectively. The LOIs of the DM and SSF were 11.76% and 4.36%, respectively. As would be expected, the LOI value of the DM-SSF blends are linearly related to the raw materials, as with the specific gravities. The LOI of the DM reflects its soil organic matter content, whereas the LOI of the SSF materials is likely related to carbonaceous material, namely carbonates. The LOIs reported in Table 2 are the average of triplicate samples and are referenced to 450°C.

The grain-size distributions of the DM, SSF, and their blends are presented in Fig. 1 and summarized in Table 2. The DM had approximately 99% passing the No. 200 sieve (0.075 mm) and it was characterized by a liquid limit (LL) of 140 and a plasticity index of 95. The DM was a high-plasticity organic silt (OH) by USCS. The SSF media was dominated by the sand and gravel fraction with $< 5\%$ passing the No. 200 sieve (0.075 mm). Because of its granularity, the SSF was nonplastic and classified as a well-graded sand (SW) by USCS. The DM-SSF blends were classified either as an organic silt (OH) or silty sand (SM). Fig. 1 shows the average gradation curve for each media shown in Table 2 complete with error bars denoting one standard deviation based on triplicate tests. For the finest SSF sample, the sample was also washed to determine if the loss of fines and potential dissolution would significantly impact the grain-size distribution (very minor changes occurred).

Table 3 and Fig. 2 summarize the maximum dry densities ($\gamma_{d,\max}$) in both SI (kN/m^3) and Imperial (lb/ft^3) units and the optimum moisture content (w_{opt}) for both compactive efforts. Zero air voids (ZAV) curves for specific gravities from 2.5–3.5 are shown for comparative purposes to account for the DM (2.58) and SSF (3.45). The moisture-density curves for the SSF materials exhibit a convex shape typical of granular soils, and are slightly offset $\gamma_{d,\max}$ ($\sim 1\ kN/m^3$ or $\sim 6\ lb/ft^3$) and w_{opt} ($\sim 5\%$) from standard to modified effort. For the DM, the difference between $\gamma_{d,\max}$ and w_{opt} for standard to modified Proctor effort were on the order of 3 kN/m^3 (20 lb/ft^3) and 7%, respectively, and its modified value is among the larger unit weights for DM (Grubb et al.

Table 2. Physical Properties and Classification of DM and SSF

	Water content	Specific gravity	Loss on ignition	Particle size			USCS
	D2974	D854	D2974	D422			D2487
Media tested	Percent	(-)	Percent	Percent gravel	Percent sand	Percent fines	
100% DM	104	2.58	11.76	0.0	1.2	98.8	OH
80/20 DM-SSF	—	2.87	10.10	1.1	15.5	83.4	OH
50/50 DM-SSF	—	3.06	6.80	10.3	41.4	48.3	SM
20/80 DM-SSF	—	3.28	5.94	15.5	62.7	21.7	SM
100% SSF	9	3.45	4.36	35.6	61.1	3.4	SW
SSF (washed)	—	—	—	38.7	58.6	2.7	SW

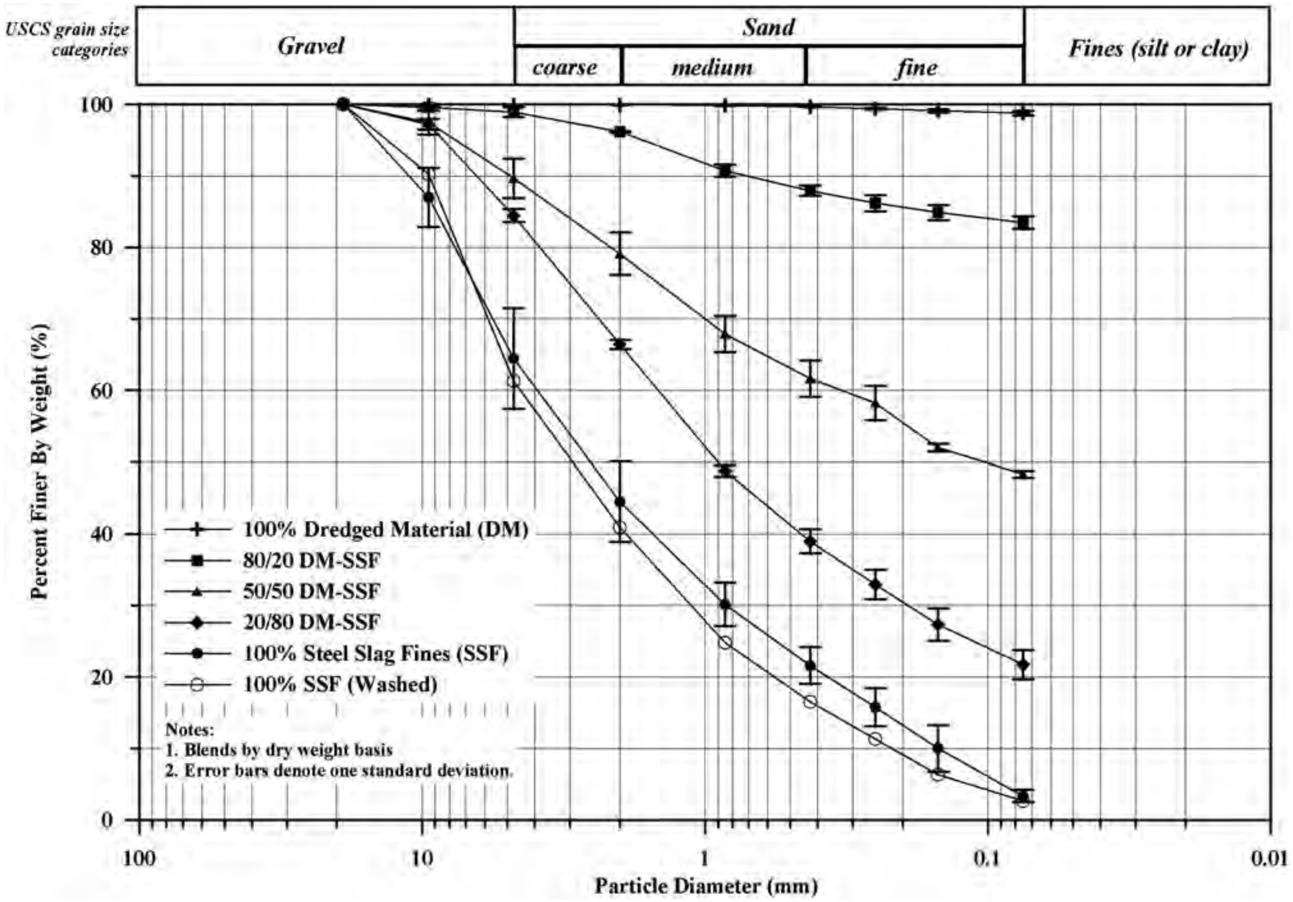


Fig. 1. Grain-size distribution for DM, SSF, and three DM-SSF blends

Table 3. Summary of Compaction and Direct Shear Strength Parameters

	Standard compaction		Modified compaction		Direct shear		One-dimensional swell	
	D698		D1557		D3080		D1883	
Media tested	$\gamma_{d,\max}$ kN/m^3 (lb/ft^3)	w_{opt} (percent)	$\gamma_{d,\max}$ kN/m^3 (lb/ft^3)	w_{opt} (percent)	c kPa (lb/ft^2)	ϕ (degrees)	Time (days)	Swell (percent)
100% DM	10.4 (66.0)	48.0	13.8 (87.5)	26.0	—	—	217	0.46
80/20 DM-SSF	12.0 (76.5)	37.0	14.7 (93.5)	17.0	—	—	242	2.7
50/50 DM-SSF	14.1 (89.5)	27.5	16.5 (105.0)	18.5	—	—	242	2.4
20/80 DM-SSF	18.0 (114.5)	18.1	20.0 (127.0)	12.0	—	—	246	−0.02
100% SSF	21.6 (137)	13.8	23.3 (148.5)	10.5	41 (850)	48.3	239	−0.38
SSF—Minus #4	—	—	—	—	99 (2,074)	40.4	—	—

2008a). The 80/20 DM-SSF blend curves mirrored the 100% DM trends. Adding 50% SSF to the DM before standard compaction achieves the same unit weight of the 100% DM compacted by modified Proctor without the necessity of drying back the DM by almost 25 moisture points. In terms of local applications, Maryland State Highway Administration (MDSHA) has a minimum acceptable maximum dry density of 15.7 kN/m^3 (100 lb/ft^3) by modified compactive effort for borrow (embankment) material without seeking a variance to the Section 916 specification (MDSHA 2008). This is achieved easily through the use of the 50/50 DM-SSF blend, although the 80/20 DM-SSF blend is only approximately 1 kN/m^3 (6.5 lb/ft^3) less and could potentially qualify for a special provision based on its other favorable geotechnical properties through a petition. Alternatively, the use of heavy compaction equipment may enable the 80/20 DM-SSF blends to qualify as borrow in Maryland.

The DS results for the 100% SSF media are summarized in Table 3. In most of the specimens tested, there was a defined peak stress that could be taken to denote failure. A less pronounced (or nonexistent) peak was observed at the lowest normal stress. Strain hardening behavior was not observed in any specimen. In general, the SSF materials exhibited significant shear strength friction angles. Testing of the fraction finer than the No. 4 sieve had a friction angle lower by almost eight degrees but a cohesion value more than doubled in value. Shear strength is impacted by several factors: (1) grain-size distribution; (2) compaction stresses; and (3) specimen-shear box interactions. Removing coarse material from a sample reduces particles interlocking, which results in lower friction angles. Compaction stresses generate perceived cohesion (i. e, soil fabric), and they are likely the cause of the measured cohesion values and the lack of defined peak shear stress at the lowest normal stress.

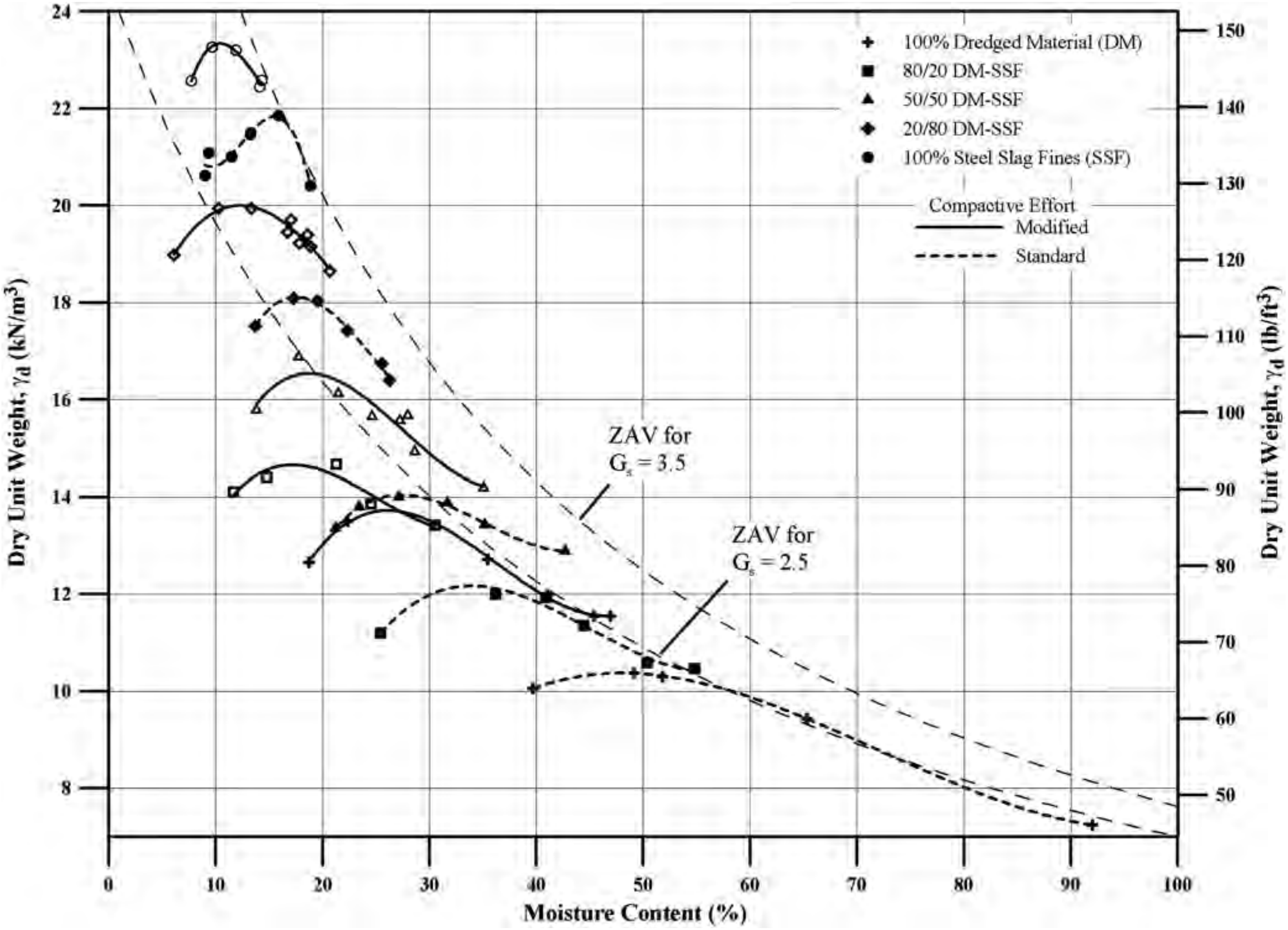


Fig. 2. Standard (ASTM D698) and modified (ASTM D1557) compaction curves for DM, SSF, and three DM-SSF blends

Swell of the various media measured over a minimum of 200 days under inundated conditions ranged from approximately −0.4% (compression) for raw SSF to 2.7% (expansion) for the 80/20 DM-SSF blend, as summarized in Table 3. By comparison, the 3/1 kaolinite/bentonite blend expanded by 18.6% in 210 days. Data loss due to power outages occurred twice during the testing period (Fig. 3); however, both events occurred significantly after expansion/compression had occurred. Generally, increasingly expansive behavior was observed for increasing DM content, with the exception of the raw DM. This discrepancy is likely attributable to the ability of SSF in blended materials to facilitate water uptake to DM in DM-SSF blends versus the lower permeability of compacted pure DM.

Expansion/compression for all materials generally plateaued within the first week of testing (Fig. 3) and often within 24 h, a timeline consistent with embankment construction. This suggests that increasingly expansive behavior may have been the result of short-term water uptake, rather than long-term formation of expansive minerals. Either way, the swell behavior of the DM-SSF blends is essentially constant and predictable and can be easily accommodated in large-scale fill construction.

Baseline Environmental Characteristics

A summary of the total concentration of metals (totals, mg/kg) based on five replicates of the randomly sampled DM and SSF materials is shown in Table 4 for comparison purposes with Maryland Soil Voluntary Cleanup Program (VCP) standards for residential and nonresidential site uses [Maryland Department of the Environment (MDE) 2008] and the neighboring Pennsylvania and New Jersey criteria for managing dredged material [Pennsylvania Department of Environmental Protection (PADEP) 2004; New Jersey Department of Environmental Protection (NJDEP) 2009]. Because Maryland does not currently have beneficial-use guidelines for DM, the VCP values are informally used for benchmarking until a framework can be developed. Ultimately, the DM-SSF blends are not intended for residential uses, which is generally the case for the long-term DM beneficial uses adopted in neighboring states, whose numerous permits include said numerical values plus a series of additional engineering controls, depending on the actual application. For several metals (arsenic, beryllium, copper, and iron), the values (particularly nonresidential) adopted by Maryland are significantly lower than surrounding states with mature beneficial-use frameworks for DM. The adopted values for arsenic are below the naturally occurring background values in Maryland, which range from 4–11 mg/kg (MDE 2008).

The total concentrations for PPL metals for DM and SSF, shown in Table 4, either reflect the method detection limit (DL) for all five replicates or the average concentration developed by using the detected values (number of replicates above DL shown in parentheses). The DM fails the residential criteria on four metals (antimony, arsenic, chromium, and iron) and nonresidential criteria on arsenic. Antimony concentrations are slightly above residential limits, whereas the average arsenic concentration is well above Maryland criteria and borderline on Pennsylvania and New Jersey.

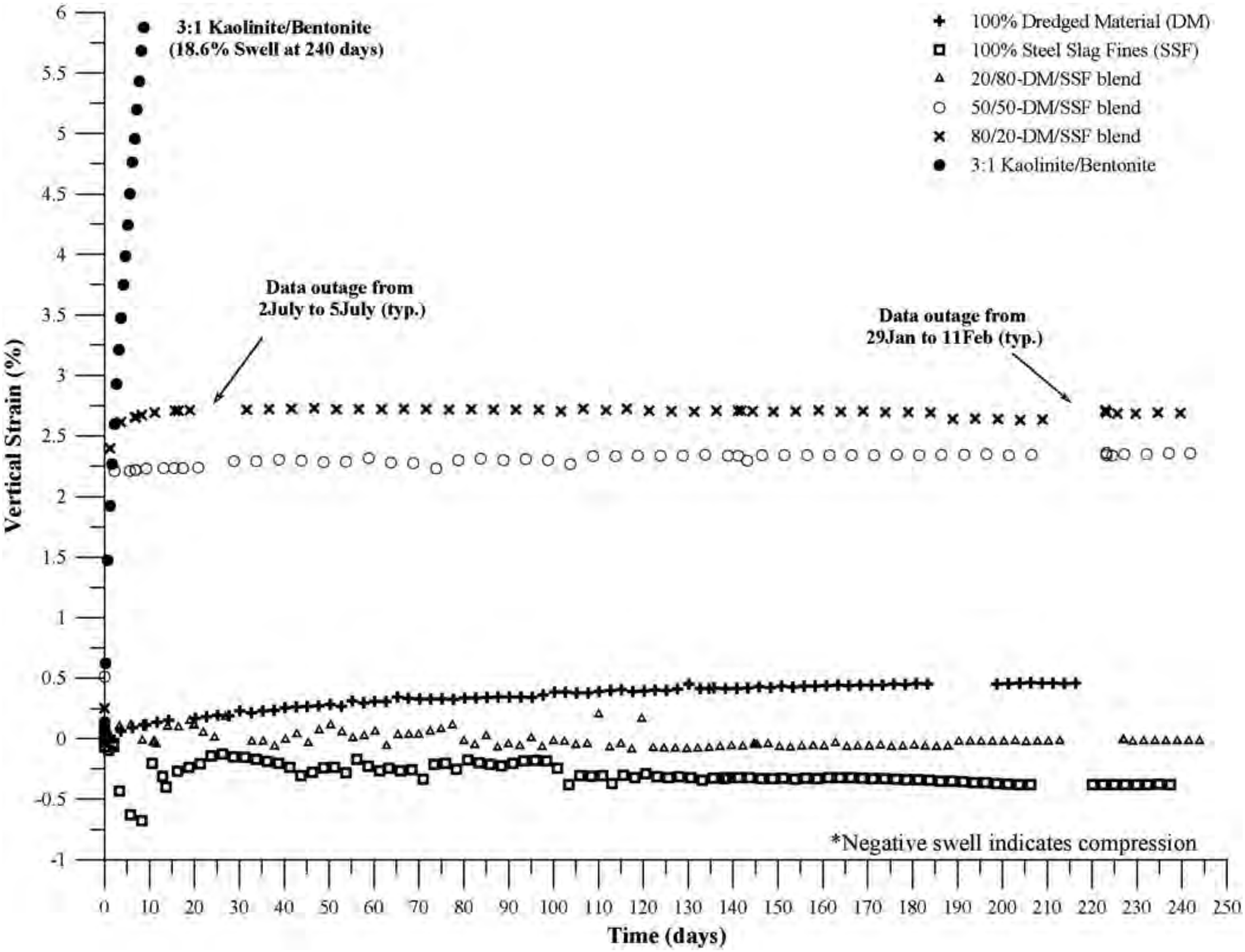


Fig. 3. One-dimensional swell (ASTM D1883) of DM, SSF, DM-SSF blends and model clay at 14.3 kPa (300 psf) seating pressure

The average total chrome and iron concentrations comply with Maryland nonresidential limits, although the individual concentrations of iron can exceed nonresidential limits. On a totals basis, the SSF quality exceeds that of the DM with respect to almost every metal except chromium and iron, the latter of which is viewed to be an asset when it comes to immobilizing arsenic.

Table 5 provides a direct comparison between regional groundwater quality standards, method DLs and the TCLP and SPLP leaching behavior of the DM and SSF materials. Only detections and their frequency are shown. Although TCLP and SPLP solutions cannot be directly compared to groundwater because of ideality and dilution issues, several of the SPLP DLs were less than the drinking water criteria. Excluding the individual hits on iron in both the DM and SSF, which are significantly above the DLs and appear to be outliers, only four metals (copper, mercury, nickel, and zinc) were detected above their respective TCLP limits, all of them in the DM. Three metals (copper, mercury, and zinc) were detected via SPLP in the DM, all below the Maryland aquifer criteria. Only zinc was detected in the SPLP extract of the SSF media, which was likewise below the Maryland aquifer media. Additionally, despite the iron content of the SSF materials of approximately 13.12% weight by volume (131,000 mg/kg), the SPLP leaching of iron was below the Maryland aquifer criteria. On the basis of TCLP and SPLP leaching behavior for PPL metals, the environmental quality of the SSF materials again exceeds that of the DM. The major anions in the DM and SSF media are shown in Table 1. The chloride and sulfate concentrations in the DM reflect the brackish water of the port. A comparison of the anion data also shows the high environmental quality of the SSF media.

Despite the favorable leaching behavior of total chromium (Table 5, all nondetects), the elevated total concentration of chromium in the SSF materials nevertheless triggered Cr speciation work for both media because the blends could potentially contain elevated chromium(VI) concentrations. In trial experiments, the alkaline digestion process (U.S. EPA 3060/7196A and 7199) was found to be unsuccessful in speciating the total chrome in the DM on the basis of poor chromium(VI) spike recoveries and/or reactions occurring during the analytical procedure. This was later confirmed by comparing the results of the alkaline digestion process (7196A) versus the Cr-isotope method (6800), as shown in Table 6. Method 7196A underpredicted the chromium(VI) content of the DM by two orders of magnitude, whereas it was within a factor of five for the slag. The isotope method provided an interesting result: the DM contained one-fifth of the total chromium but over three times greater chromium(VI) content than the SSF materials.

XANES

Because the Cr-isotope method is expensive and XANES allows for direct measurement performed on the solid media, the two

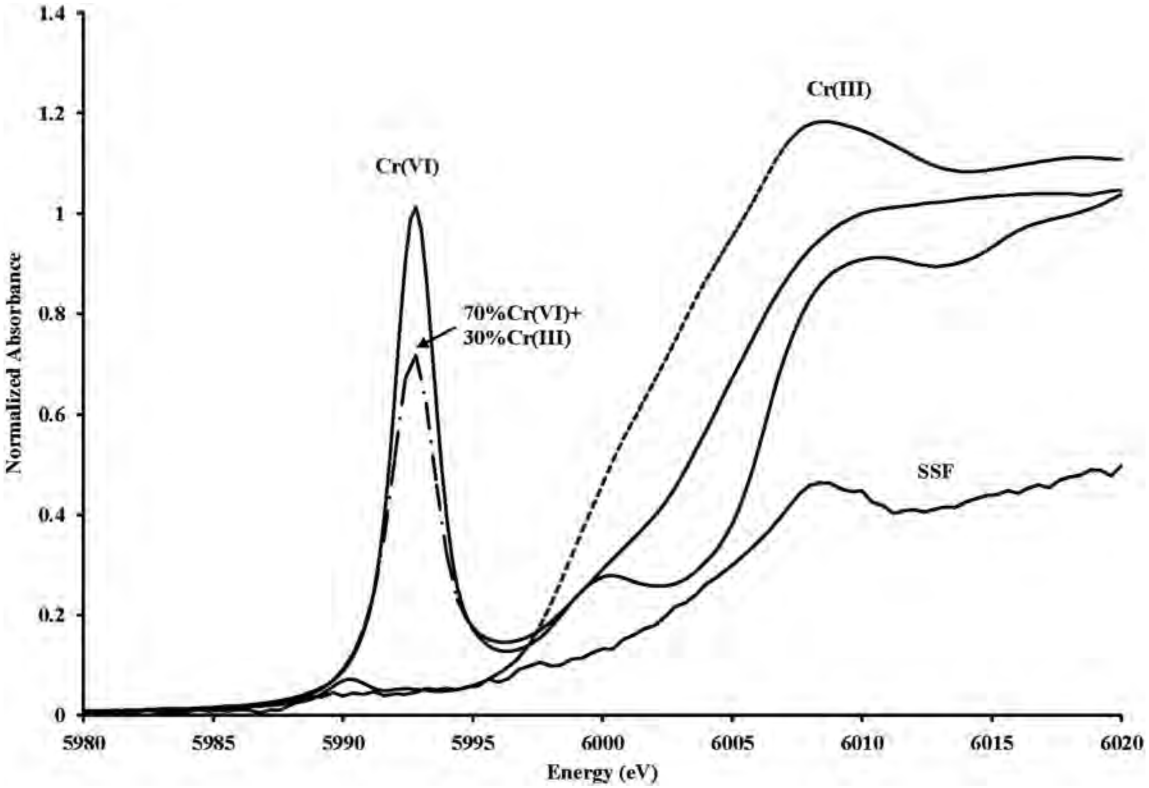


Fig. 4. Chromium K-edge XANES spectra for calibration standards and fresh SSF media

techniques were compared. The comparison was also done to speciate the iron in the SSF materials to assess its reactivity [iron(0) content], even though the Fe did not apparently interfere with the Cr readings in the SSF materials during the alkaline digestion process [unlike in chromite ore processing residue or COPR (Wazne et al. 2007)].

The XANES spectrum for the chromium(VI) standard showed a well-defined preedge peak starting at approximately 5,990 eV. The height and area of this preedge peak is quantitatively proportional to the chromium(VI) concentration (Paterson et al. 1997; Szulczewski et al. 1997). Fig. 4 presents the chromium *K*-edge spectrum for the three chromium standards and SSF materials, plotted using the processed XANES data from the ATHENA program. A well-defined preedge peak of the chromium(VI) standards was consistent with the XANES patterns observed in other steel slag and COPR samples (Chaurand et al. 2007; Wazne et al. 2007).

Table 4. Summary of Total PPL Metals (mg/kg) for DM and SSF Media Versus Regional Soil Cleanup and Beneficial-Use Criteria

	MDE soil cleanup		Pennsylvania		New Jersey			
Metal	Residential	Nonresidential	Clean	Regulated	Residential	Nonresidential	DM	SSF
Antimony (Sb)	3.1	41	27	27	31	450	< 4.0	< 1.5
Arsenic (As)	0.43	1.9	12	53	19	19	20.6 (5)	< 1.40
Barium (Ba)	1,600	20,000	8,200	8,200	700	47,000	—	—
Beryllium (Be)	16	20	320	320	16	140	1.74 (4)	0.40 (4)
Cadmium (Cd)	3.9	100	38	38	78	78	0.54 (3)	1.87 (5)
Chrome (total)	23	310	NR	NR	NR	NR	157.8 (5)	1,100 (5)
Chrome(III)	12,000	150,000	190,000	190,000	120,000	NR	—	—
Chrome(VI)	23	310	94	190	240	6,100	—	—
Copper (Cu)	310	4,100	8,200	36,000	3,100	45,000	121.7 (5)	30.44 (5)
Iron (Fe)	5,500	72,000	NR	190,000	NR	NR	71,020 (5)	131,200 (5)
Lead (Pb)	400	1,000	450	450	400	800	73.3 (5)	7.12 (4)
Mercury (Hg)	2.3	31	10	10	123	65	< 0.5	< 0.25
Nickel (Ni)	160	2,000	650	650	1,600	23,000	50.7 (5)	15.92 (5)
Selenium (Se)	39	510	26	26	390	5,700	< 3.5	< 1.10
Silver (Ag)	39	510	84	84	110	4,100	< 3.5	< 8.0
Thallium (Tl)	0.55	7.2	14	14	5	79	< 0.475	< 0.175
Zinc (Zn)	2,300	31,000	12,000	12,000	1,500	1,500	234 (5)	186.8 (5)
pH							8.6 (5)	12.41 (5)

Note: Totals by U.S. EPA 6000/7000 series.

Table 5. Leaching Behavior of DM and SSF Media (mg/L)

			Detection limits		DM		SSF	
Metal	Maryland Type I/II aquifer	U.S. EPA TCLP	TCLP	SPLP	TCLP	SPLP	TCLP	SPLP
Antimony (Sb)	0.006	NR	< 0.100	< 0.010				
Arsenic (As)	0.01	5.0	< 0.500	< 0.050				
Barium (Ba)	2.0	100.0	—	—				
Beryllium (Be)	0.004	NR	< 0.100	< 0.010				
Cadmium (Cd)	0.005	1.0	< 0.100	< 0.010				
Chrome (total)	0.100	5.0	< 0.500	< 0.050				
Chrome(III)	0.100	NR	—	—				
Chrome(VI)	0.100	NR	—	—				
Copper (Cu)	1.3[a]	NR	< 0.100	< 0.010	0.262 (1)	0.023 (3)		
Iron (Fe)	2.6[a]	NR	< 0.500	< 0.500	15.7 (1)	1.68 (5)	22.3 (1)	
Lead (Pb)	0.015	5.0	< 0.500	< 0.050				
Mercury (Hg)	0.002	0.2	< 0.0008	< 0.0008	0.0021 (4)	0.0009 (1)		
Nickel (Ni)	0.073[a]	NR	< 0.100	< 0.010	0.214 (5)			
Selenium (Se)	0.05	1.0	< 0.500	< 0.005				
Silver (Ag)	0.018[a]	5.0	< 0.100	< 0.010				
Thallium (Tl)	0.002	NR	< 0.100	< 0.010				
Zinc (Zn)	1.1[a]	NR	< 0.200	< 0.020	1.04 (5)	0.108 (5)		0.098 (5)
pH		—	—	—	5.08 (5)	7.83 (5)	11.85 (5)	12.37 (5)

Note: NR = not regulated. Only hits above the detection limit and (number) are shown for DM and SSF.
[a]Equivalent with U.S. EPA drinking water standards.

Table 6. Chromium Speciation Testing of DM and SSF Media

Media	Totals[a] EPA 6020 (mg/kg)	Chromium(VI)[a] EPA 7196A (mg/kg)	Chromium(VI)[a] EPA 6800 (mg/kg)	Chromium(VI) XANES (mg/kg)
DM1	174	0.24 (2)	27.1	—
DM2	288	< 0.69 (2)	31.7	—
DM3	308	0.21; < 0.66	48	—
DM4	120	< 0.61 (2)	34.2	—
DM (average)	222.50	< 0.69	35.25	—
SSF1	1,020	2.9 (2)	12.7	—
SSF2	960	3.2 (2)	11.2	—
SSF3	912	2.35 (2)	6.1	—
SSF4	981	2.75 (2)	11.1	—
SSF (average)	968.25	2.8 (8)	10.28	—
SSF[b]	1,100 (5)	6.43 (2)	NT	0

[a]Data courtesy of Maryland Environmental Services.
[b]Based on five replicates from Table 5; two additional replicates used for XANES testing.

A comparison of the XANES spectrum (Fig. 4) for chromium standards and the SSF materials show that there is no chromium(VI) *K*-edge peak present in the SSF media. The chromium(VI) concentration was thus estimated to be 0 in the SSF materials (Table 6). These results are similar to other steel slag XANES-Cr results that showed all Cr was present as chromium(III) (Chaurand et al. 2007).

All three oxidation states of iron exist in the SSF samples. Fig. 5 presents the iron *K*-edge spectrum for three iron standards and SSF media (two replicates) plotted using the processed XANES data from the ATHENA program. A well-defined preedge peak was observed of the iron standards was observed to start approximately at 7,112 eV, which is consistent with the XANES-Fe patterns observed in soil and solution samples (Mitsunobu et al. 2006; Thoral et al. 2005). XANES is sensitive to the oxidation state of the element, and the preedge position shifts toward higher energy with increasing oxidation state. The average iron(0), iron(II), and iron(III) concentrations in SSF were thus estimated to be 16,662 (12.7%), 60,942 (46.5%), and 53,660 mg/kg (40.9%), respectively.

ANC Testing

Fig. 6 shows the ANC curves for the DM, the SSF materials, and their blends. The SSF media consumes approximately 7 acid equivalents per kilogram (eq/kg) to reach a neutral pH (7) and approximately 11 to achieve pH ~ 3. The response of the milled SSF or SSFM sample is much stronger, requiring approximately 20 and 10 acid eq/kg to attain pH 3 and 7, respectively. This suggests that destroying the morphology of the SSF material liberates alkalinity, in the form of lime or other pH buffering minerals. The SSF material significantly increases the buffering capacity of the DM, and the family of curves parallels the 100% SSF curve above pH 4, showing a 2 eq/kg difference between the curves.

For comparison purposes, the TCLP and SPLP data of the SSF material are shown (Table 5), and they match well with the ANC result. The legend (Fig. 6) also shows the strength of an SPLP solution (1.12 meq/kg), which is approximately 1/1,765 the strength of the TCLP solution. Hence, a SPLP leach essentially abuts the Y-axis. Two portions of a DM curve are shown because of its moderate pH: an acidification curve (HNO_3) and an alkaline curve (NaOH). The steep ANC curves and their short range illustrate the weak buffering capacity of the DM.

Fig. 7 shows the ANC-As concentrations (dashed lines) for the raw DM and both SSF media to illustrate the role of milling on metals leaching. The U.S. EPA As drinking water standard is shown at 0.01 mg/L. The open symbols used for the concentration plots denote the detection limits for that particular sample, which varied because of the use of ICP versus ICP/MS for different samples, depending on the matrix interferences. The As in the DM is

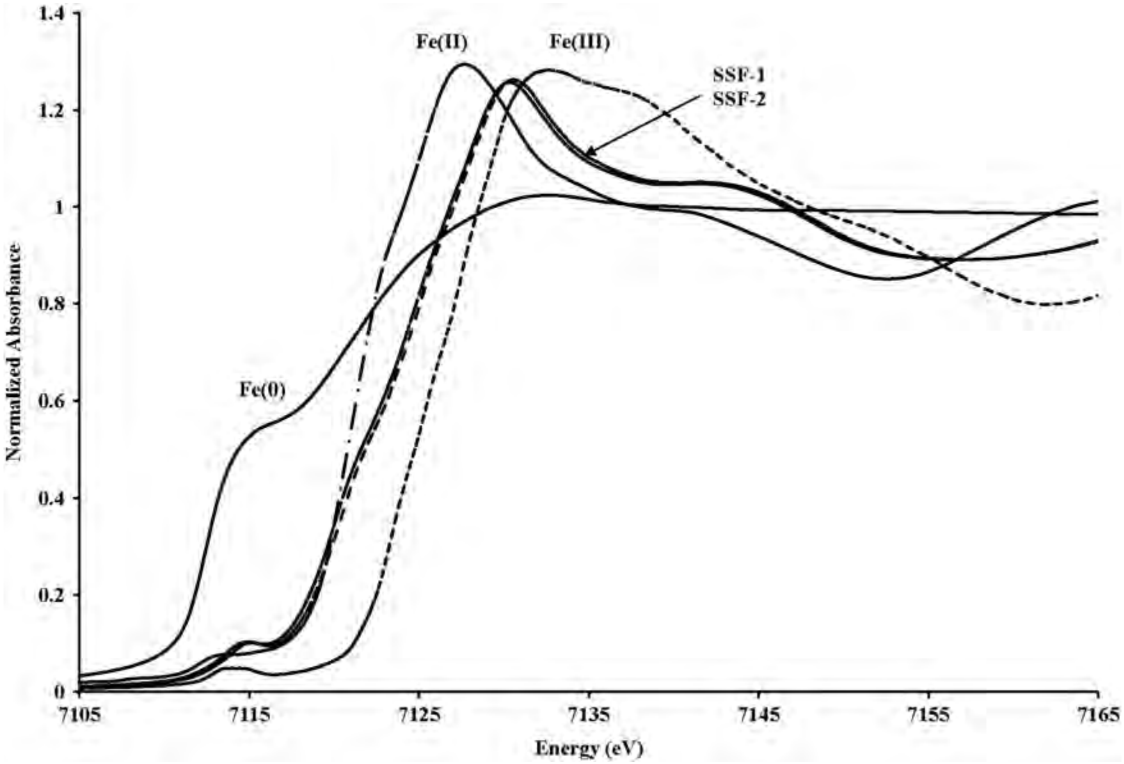


Fig. 5. Iron K-edge XANES spectra for calibration standards and fresh SFF media

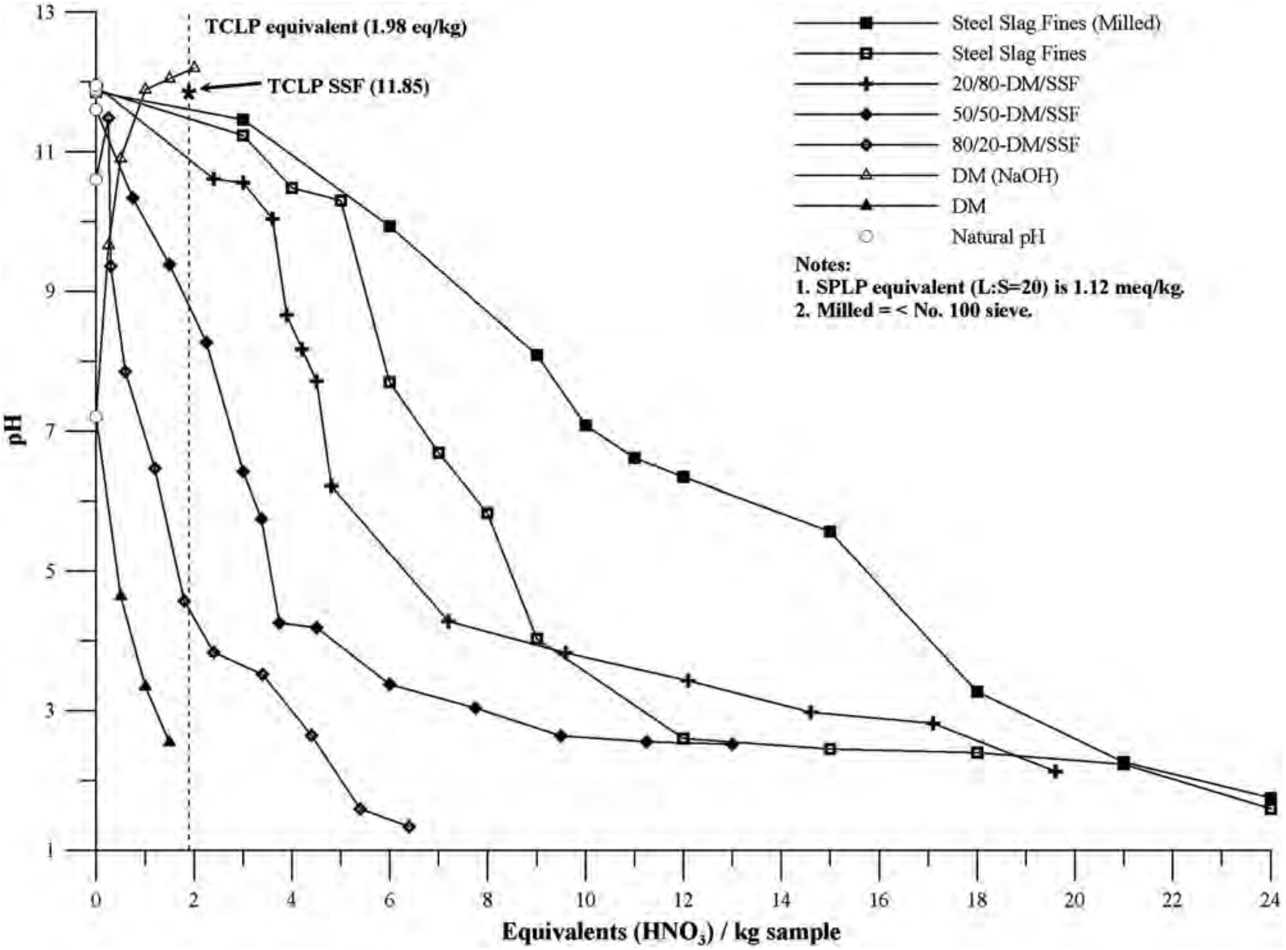


Fig. 6. Acid neutralization capacity of the DM, raw and milled SSF media, and three DM-SSF blends

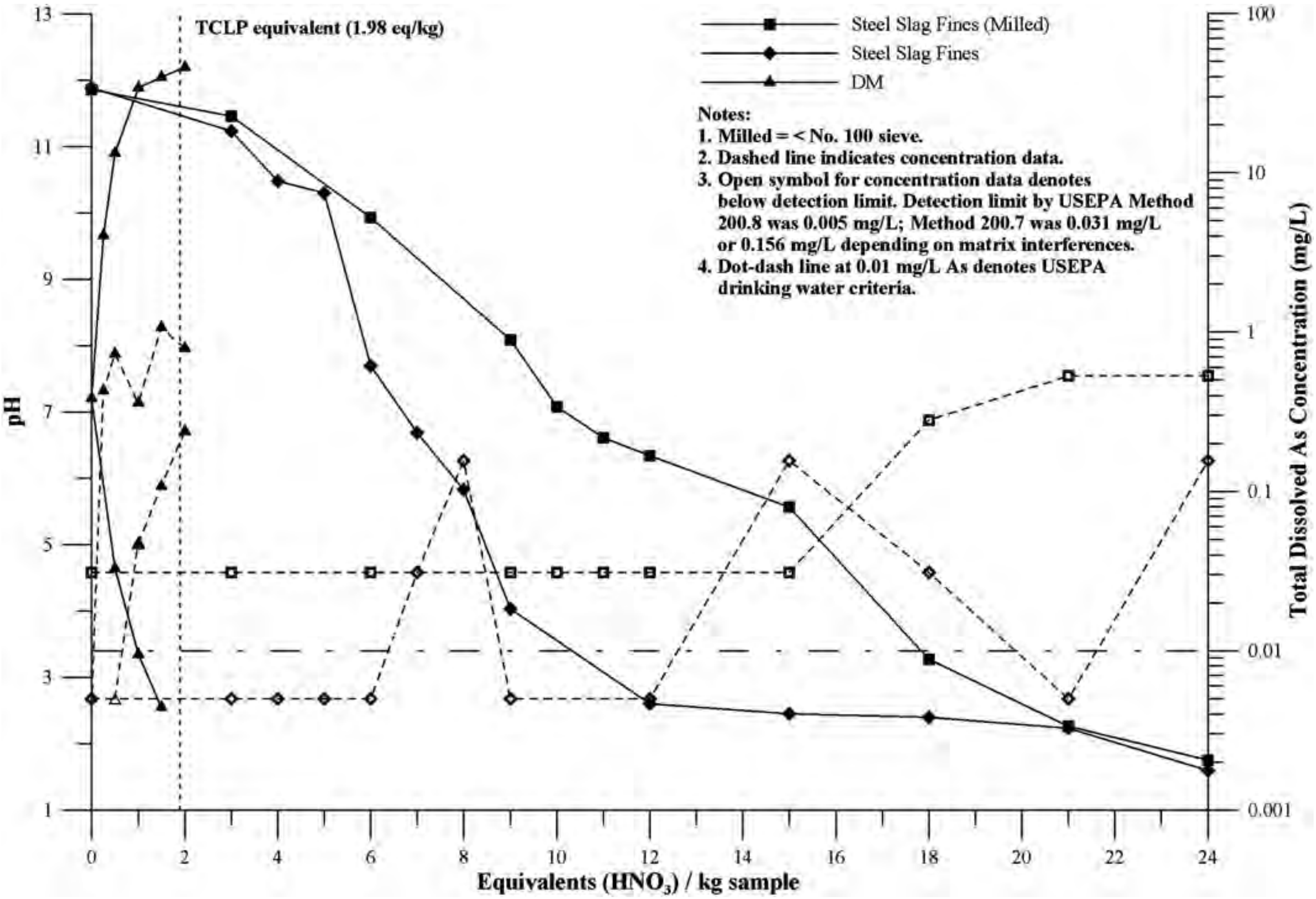


Fig. 7. Acid neutralization capacity leaching of arsenic from the DM, raw and milled SSF media, and three DM-SSF blends

liberated very easily and quickly exceeded the drinking water criteria, whereas the As concentration from the SSF and SSFM samples never exceeds the DL (which fluctuates because of matrix issues).

To put these ANC results in perspective, it takes approximately 20 eq/kg to lower the pH of COPR to 3 (Wazne et al. 2008). This would be the equivalent of approximately 17,850 SPLP extractions. However, even after the COPR has been in situ as fill or embankment material for up to 50–70 years in greater Baltimore and northern New Jersey, its pH is still above 11. Hence, we expect that the SSF media will likewise persist at an elevated pH for long periods. This has the double effect of preventing As leaching from the DM and, depending on the blending ratio, maintaining a pH above the range to suppress microbial transformations (~9) in the DM-SSF blends to prevent the natural acidification of DM.

Table 7. Arsenic Thresholding Suite—Totals (mg/kg)

		Arsenite spike (100 mg/kg As^{3+})				
Media	Raw control	Control	0.5% NC	1.0% NC	1.5% NC	2.0% NC
DM	25.5	125	72.2	113	120	128
80/20	21.2	112	114	98.1	51.3	102
50/50	< 15.8	71	48	69	76	73
20/80	< 18.0	< 16.7	7.82	< 15.3	< 15.2	< 14.6
SSF	< 5.62	54	NA			
		Arsenate spike (100 mg/kg As^{5+})				
	Raw control	Control	0.5% NC	1.0% NC	1.5% NC	2.0% NC
DM	25.5	144	141	127	137	131
80/20	21.2	95.7	93.6	83.4	83.6	106
50/50	< 15.8	71.3	69.6	65.3	70.7	58.3
20/80	< 18.0	< 7.75	< 30.4	33.3	< 31	< 27.5
SSF	< 5.62	80.8	NA			

Note: Totals by U.S. EPA Method 3050/6010B series.

Table 8. Arsenic Thresholding Suite—SPLP (mg/L)

Media	Raw control	Arsenite spike (100 mg/kg As^{3+})				
		Control	0.5% NC	1.0% NC	1.5% NC	2.0% NC
DM	< 0.050	< 0.050	< 0.050	0.061	0.061	< 0.050
80/20	< 0.050	0.112	0.122	0.098	0.127	0.124
50/50	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
20/80	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
SSF	< 0.050	< 0.050	NA			

	Raw control	Arsenate spike (100 mg/kg As^{5+})				
		Control	0.5% NC	1.0% NC	1.5% NC	2.0% NC
DM	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
80/20	< 0.050	0.054	0.079	0.056	0.053	0.071
50/50	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
20/80	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
SSF	< 0.050	< 0.050	NA			

Note: SPLP by U.S. EPA Method 1312/301B series.

Arsenic Thresholding

DM-SSF Suite

In this series of tests, we distinguish between raw controls and spiked controls. The raw controls reflect the natural As content of the DM, SSF, and their blending ratios. For the spiked controls, only the DM was spiked with a total As concentration of 100 mg/kg and was mellowed for 30 days prior to blending with SSF. Thus, the spiked DM control was expected to have approximately 25 + 100 or 125 mg/kg As. The theoretical As concentration of the DM-SSF blends was governed by the As content of the raw controls plus the As spike to the DM. Only in the case of the As-spiked SSF control was the SSF media spiked for quality assurance purposes; otherwise, it contributed (essentially) no As to the DM-SSF blends. Table 7 presents the total concentrations for the DM-SSF blend thresholding suite for the As^{3+} and As^{5+} spiked replicates. The slag cement doses are indicated by the 0.5–2.0% NC columns. Since the DM was the source of the As for all other replicates, the expected concentration of ~125 mg/kg in the DM was incrementally lowered (to zero) by increased blending with the SSF materials, as generally shown by the trends in the totals, even given the small doses of NC.

In every case (blends and NC dose) for both As oxidation states, the TCLP-As results were below the DL (< 0.25 mg/L), so the data are not shown. These results suggested that the DM and SSF media were able to immobilize As, i.e., slag cement was not required as an additional stabilizing agent. Table 8 shows that in every case for both oxidation states, the SPLP-As results were below the DL (< 0.05 mg/L). The exceptions are the 80/20 DM-SSF blends for both As spikes and two As^{3+} spiked DM replicates with intermediate doses of slag cement (the DL of SPLP is lower than TCLP due to matrix interferences). It appears that the slag dosage is related to the leachability rate of As. As increasing doses of the slag elevated the system pH, the As leachability consequently varies. Arsenic leachability is controlled by adsorption to metal oxide

Table 9. Raw Materials Thresholding Summary

					Arsenic dose								
			Detection limits		100 mg/kg			1,000 mg/kg			5,000 mg/kg		
	Spike	Analyte	TCLP	SPLP	Total	TCLP	SPLP	Total	TCLP	SPLP	Total	TCLP	SPLP
DM	As^{3+}	As	< 0.010	< 0.010	76 (5)	0.043 (5)	0.017 (5)	No testing					
		Cr	< 0.020	< 0.020	82.4 (5)	ND	0.0052 (5)						
		Fe	< 2.0	< 0.20	71,600 (5)	ND	0.58 (5)						
		pH	—	—	7.03 (4)	—	—						
	As^{5+}	As	< 0.010	< 0.010	85 (5)	0.058 (5)	0.020 (5)						
		Cr	< 0.020	< 0.020	75.4 (5)	ND	0.0042 (4)						
		Fe	< 2.0	< 0.20	69,600 (5)	27 (1)	0.32 (2)						
		pH	—	—	6.81 (5)	—	—						
SSF	As^{3+}	As	Same as above		142 (5)	ND	ND	2,000	ND	ND	7,900	0.029	ND
		Cr			718 (5)	ND	ND	830	ND	ND	700	ND	ND
		Fe			154,000 (5)	ND	ND	190,000	ND	ND	190,000	ND	ND
		pH			> 12 (5)	—	—	> 12	—	—	> 12	—	—
	As^{5+}	As			140 (5)	ND	ND	1,900	ND	ND	8,800	ND	ND
		Cr			700 (5)	ND	ND	730	ND	ND	810	ND	ND
		Fe			144,600 (5)	ND	ND	170,000	ND	ND	200,000	ND	ND
		pH			> 12 (5)	—	—	> 12	—	—	> 12	—	—

Note: Arsenic dosing level of 100 mg/kg based on five replicates. Parentheticals denote the number of replicate values averaged above detection limit.

Table 10. Quantitative XRPD Results for SSF Media and SSF Media Spiked with 5,000 mg/kg Arsenite and Arsenate

Phase	Molecular formula	PDF number[a]	CSD number[b]	SSF	As-3-5000	As-5-5000
Larnite	Ca_2SiO_4	97-001-0561	963	20.85	18.40	19.19
Magnesium ferrous oxide	$(MgO)_{0.432}(FeO)_{0.568}$	97-004-2976	60696	16.28	16.58	18.67
Srebrodolskite	$Ca_2Fe_2O_5$	97-001-4942	15059	11.70	12.64	11.26
Magnetite	$Fe_{2.942}O_4$	97-006-2364	82449	8.30	8.19	7.72
Calcite	$CaCO_3$	00-005-0586		7.87	7.18	9.07
Mayenite	$(CaO)_{12}(Al_2O_3)_7$	97-001-2803	6287	6.70	6.57	5.11
Wuestite	$Fe_{0.925}O$	97-006-2153	82235	4.36	2.83	4.17
Quartz	SiO_2	00-046-1045		2.66	1.92	1.56
Lime	CaO	97-002-1810	26959	2.66	1.92	2.40
Amorphous phase				18.6	23.8	20.8
Total				100.00	100.01	99.97

[a] Powder diffraction file number from ICDD (PDF-2).
[b] Crystal structure database number from ICSD.

surfaces at pH ≤ 7.5, whereas coprecipitation with calcium occurs at pH ≥ 10 (Jing et al. 2005). Moreover, As^{5+} adsorption rates appear greater than their As^{3+} counterparts, probably because of the higher concentration of the charged As^{5+} species versus the charged As^{3+} species in the neutral pH range (Meng et al. 2002). With respect to As^{3+} species, neutrally charged H_3AsO_3 predominates up to pH 8, but $H_2AsO_3^-$ and $HAsO_3^{2-}$ dominate thereafter. For As^{5+} species, neutrally charged H_3AsO_4 predominates at pH < 2, whereas $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} species dominate at greater pH values. The 20% SSF dosage increased the pH of the DM from approximately 7.4 to approximately 8.7 (data not shown). This pH shift would trigger As desorption (more significantly for As^{3+} than for As^{5+}) prior to the pH range associated with the onset of As-Ca coprecipitation for both species. The 50/50 and 20/80 DM-SSF blends were sufficiently alkaline and contained proportionally less As; therefore, they did not produce measurable concentrations of either As species.

Raw Materials Suite

Because the thresholding testing of the raw controls was somewhat limited, five additional replicates each of DM and SSF were retested at the 100 mg/kg target level for both As^{3+} and As^{5+}. Single replicates of the SSF media were individually dosed with each As species up to target concentrations of 5,000 mg/kg As in an attempt to establish an upper cap on As immobilization as a pure media. The DM (from the prior round) was mellowed for at least 80 days prior to testing, whereas the SSF material only mellowed for 30 days.

Table 9 presents the pH and concentrations of As, Cr, and Fe measured by total, TCLP, and SPLP analyses. The pH results for the DM are in the 6–7 range, whereas the pH of the SSF

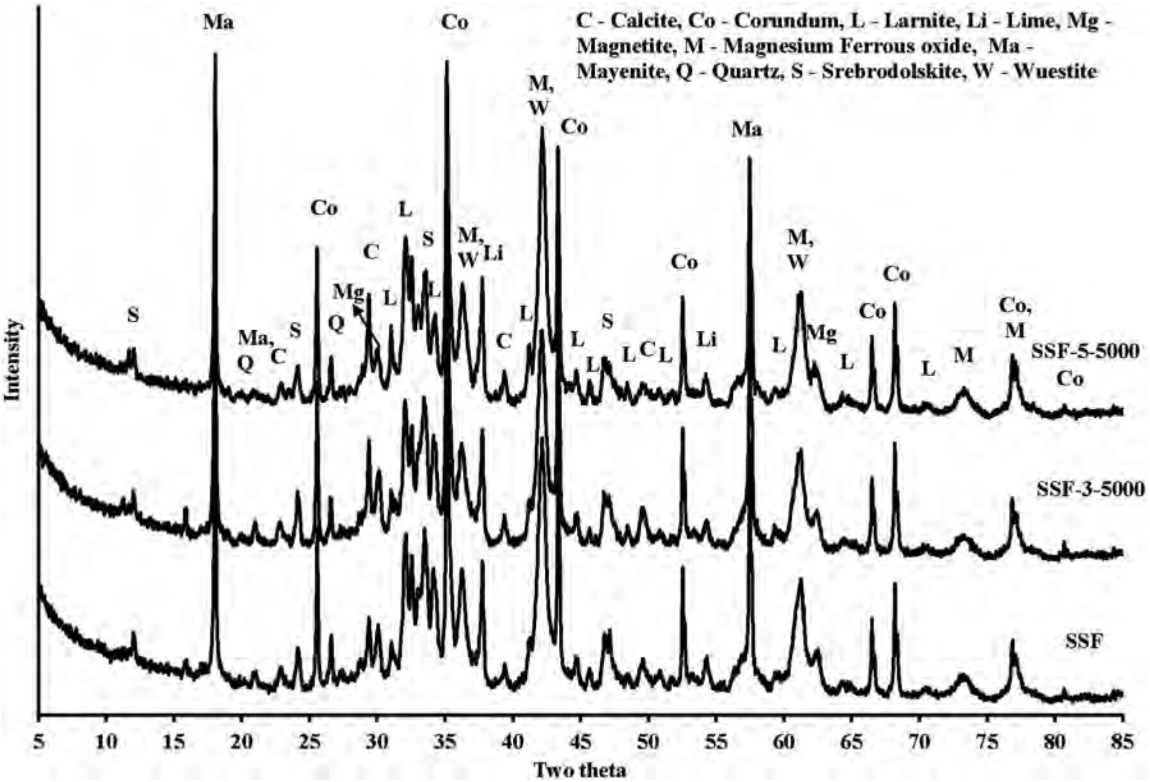


Fig. 8. Annotated diffractrograms for the raw SSF media and the SSF media spiked with 5,000 mg/kg As^{3+} and As^{5+} (SSF-3-5000 and SSF-5-5000 samples, respectively)

was greater than 12. From a totals perspective, it appears that the DM and SSF media were under- and overspiked with As, respectively. Given the sample size requirements for the totals test (0.5 g), it is usually the case that fine-grained media properly reflect their spiking targets. In the case of coarser grained media (unless ground), spiking dry samples usually results in the preferential uptake of the metals by the finer fractions due to surface area effects and the wicking (capillarity) of the aqueous solution. This would give the appearance of overspiking a sample even though the aqueous solutions were carefully measured and applied. The total

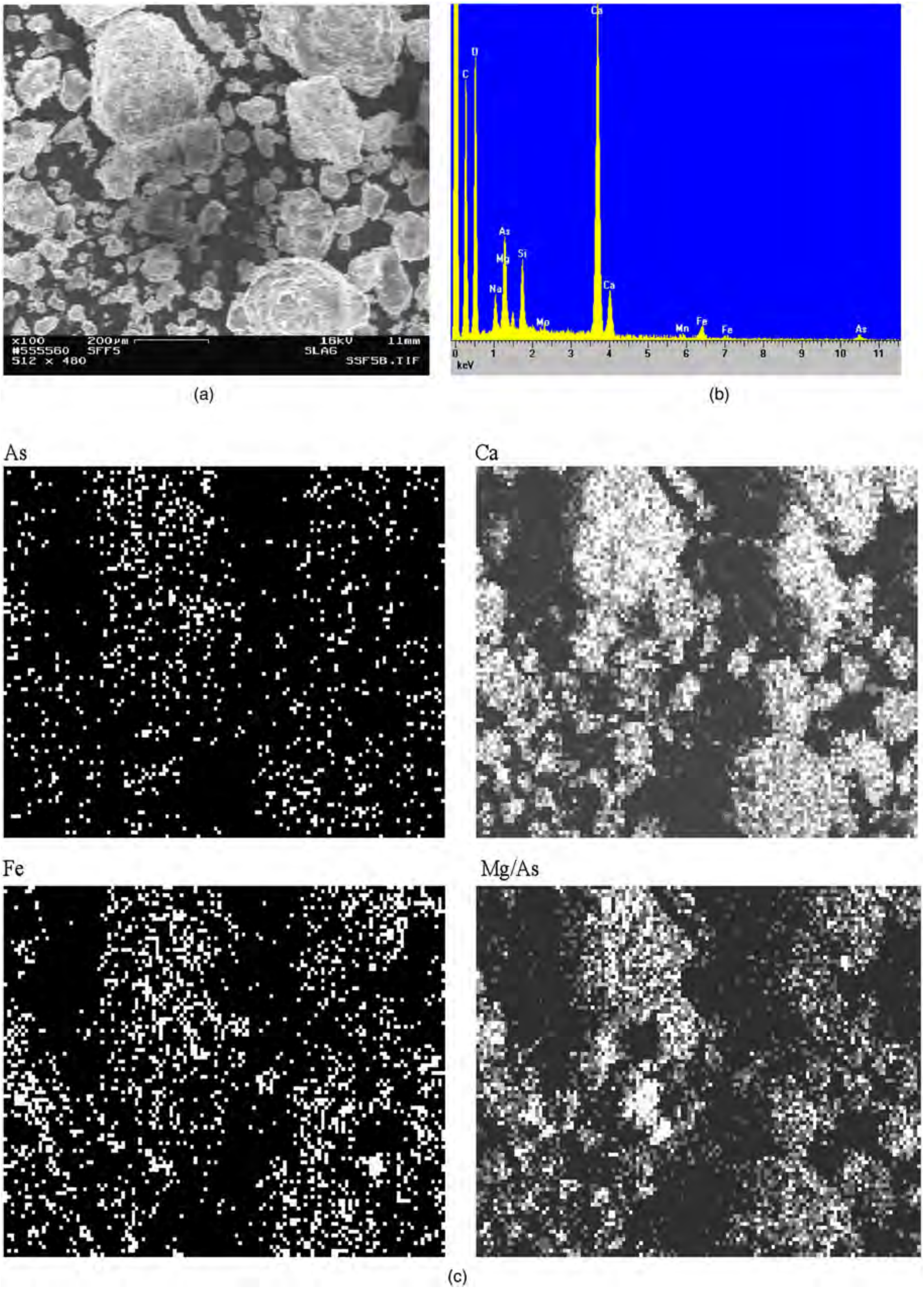


Fig. 9. (a) SEM image (100×); (b) EDX spectrum; (c) elemental mapping of the SSF-5-5000 sample

concentrations of Cr in the DM are approximately 50% and 60% of the values shown in Table 4, whereas the Fe concentrations are consistent.

The TCLP and SPLP DLs for As in Table 9 are lower than Tables 5 and 7. TCLP-As leaching from the DM (Table 9) is approximately four to six times the Maryland Type I/II aquifer criteria (Table 5), which coincides with the 5× spiking ratio (100 added to 20 mg/kg). The corresponding SPLP-As leaching also exceeds the Maryland Type I/II aquifer criteria for both As sources. Chromium and iron leaching from DM under both TCLP and SPLP conditions were within Maryland Type I/II aquifer criteria.

TCLP-Cr, -Fe leaching from the SSF all were nondetected and fully compliant with Maryland Type I/II aquifer criteria, despite the elevated totals concentrations of iron above Maryland nonresidential criteria. The arsenic leaching from the SSF media was also nondetected and fully compliant with Maryland Type I/II aquifer criteria under both TCLP and SPLP conditions, except for the TCLP-As^{3+} concentration from the 5,000 mg/kg As^{3+} spike, and even that result (0.029 mg/L) was approximately half of the leached As concentrations in the DM spiked with 100 mg/kg As.

XRPD

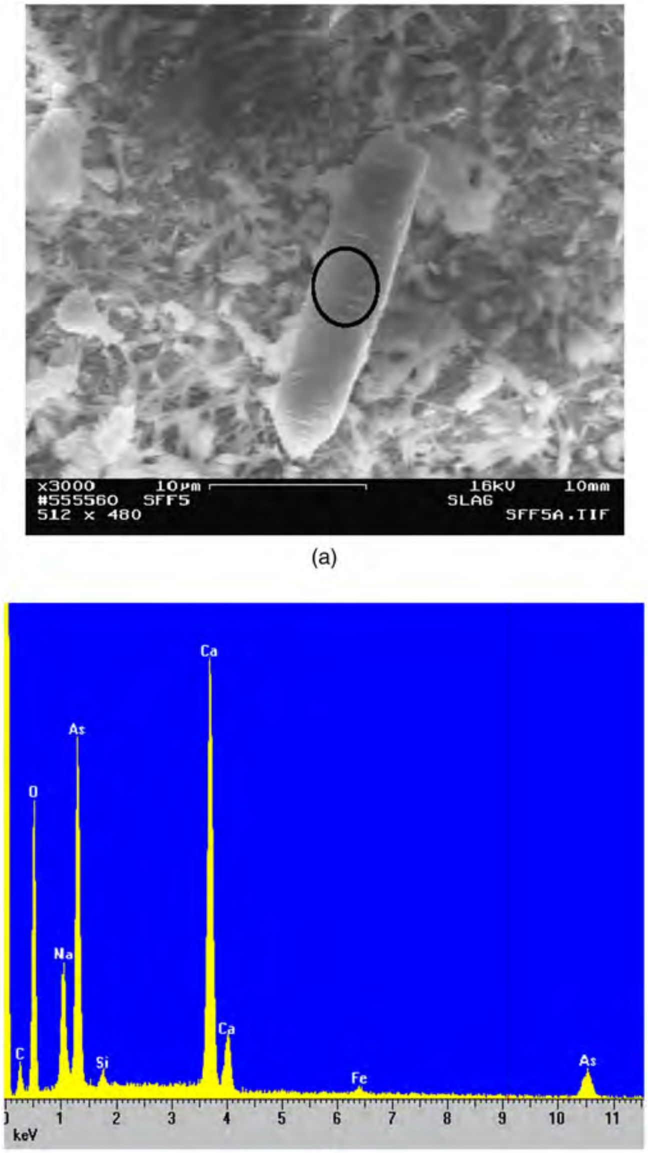
The quantitative results of the XRPD patterns of the raw and spiked SSF samples are presented in Table 10. The XRPD patterns of the raw and spiked SSF samples are presented in Fig. 8. The SSF media contained metallic iron, dicalcium silicates, dicalciumferrite, wuesite, and calcium oxides, which is consistent with the literature (Geiseler 1996; Motz and Geiseler 2001; Shen and Forssberg 2003). Tricalcium and calcium aluminum silicates were not detected. Larnite (dicalcium silicate, Ca_2SiO_4), and quartz (SiO_2) were the main silicate phases observed in these samples. Magnesium ferrous oxide [$(MgO)_{0.432}(FeO)_{0.568}$], wuestite ($Fe_{0.925}O$), srebrodolskite (dicalciumferrrite, $Ca_2Fe_2O_5$), and magnetite ($Fe_{2.942}O_4$) were the key iron phases observed in the SSF media. The quantity of total Ca and Fe calculated from the observed phases was approximately 21% and 23%, respectively. These numbers are close to the XRF results (Table 1), in which total Ca was 25%, and total Fe was 19%. Individual totals analysis indicated that the Fe content was approximately 12–27% (Tables 4 and 8, and other data not shown), depending on the replicates tested.

The TCLP and SPLP results (Table 9), showed no-to-trace leachable As concentrations, which suggests the possible presence of As precipitates. The literature reports that As immobilization from stabilization/solidification (S/S) treatments using combinations of cement, lime, and fly ash is associated with Ca-As precipitates (Akther et al. 1997; Dutre and Vandecasteele 1995; Moon et al. 2004, 2008; Kundu and Gupta 2008). Although the XRF results (Table 1) indicate the presence of approximately 25% Ca in the SSF, the XRPD results (Table 10) shows much of the Ca is bound to silicate and ferrite phases. As a result, the XRPD patterns of the unspiked SSF and As-spiked SSF are similar (Fig. 8), which might indicate that As spiking did not result in the formation of As-containing crystalline compounds above the XRD DL (approximately 1% by weight or 10,000 mg/kg) and/or As accumulated in the amorphous phase.

SEM-EDX

Although the XRPD analyses indicated that no As crystalline compounds occurred above the DL of the XRPD device, isolated crystals were observed by using SEM that showed arsenic was associated with Ca and Na elements. As an example, for the SSF media spiked with a target concentration of 5,000 As^{5+}, Fig. 9(a) presents the SEM image, Fig. 9(b) presents the EDX spectrum, and Fig. 9(c) shows the elemental mapping (XRF) of As, Ca, Fe, and Mg/As of the SSF-5-5000 sample, which show that As is uniformly distributed throughout the media. Fig. 10 shows the SEM image and EDX spectrum for one of the few As-rich crystals located in the SSF-5-5000 sample. The EDX spectrum illustrates the As association with Ca and Na, which allowed an estimate of the Ca/As molar ratio of the crystal (Fig. 10). Similar high magnification searches on the SSF-3-5000 sample (not shown) indicated As was closely associated with Ca and O.

The literature reports that As immobilization is primarily controlled by the formation of Ca-As precipitates at high pH (Akthar et al. 1997; Bothe and Brown 1999; Moon et al. 2004, 2008). On the basis of the assumption that As was immobilized by the formation of Ca-As precipitates, the molar ratios of Ca/As were determined by SEM-EDX to be 1.5 and 0.91 for the As^{3+} and As^{5+} spiked SSF media, respectively. Table 11 presents a literature



(a)

(b)

Fig. 10. (a) SEM image (3,000×); (b) EDX spectrum of isolated crystal located in the SSF-5-5000 sample

Table 11. Literature Summary of Ca-As Compounds

Compound name	Chemical formula	Crystal structure[a]	Ca:As molar ratio	Reference
Arsenic(III) compounds				
	$Ca(AsO_2)_2$		0.5^{c}	Stronach et al. (1997)
Calcium arsenite	$CaHAsO_3$		1^{c}	Dutre and Vandecasteele (1995)
	Ca-As-O		1	ICDD (PDF-2)
Arsenic(V) compounds				
	$CaNa_2(As_4O_{12})$		0.25	ICDD (PDF-2)
Calcium arsenate	$CaAs_2O_6$	Hexagonal	0.5	Kundu and Gupta (2008)
	$CaH_4(AsO_4)_2$		0.5	Kundu and Gupta (2008)
Calcium hydrogen arsenate hydrates	$Ca_2H_2(AsO_4)_4 \bullet 9H_2O$		0.5	Kundu and Gupta (2008)
Calcium diarsenate	$Ca_2As_2O_7$	Monoclinic	1	ICSD
Weilite (synthetic: precipitated with NH_3)	$Ca(HAsO_4)$	Triclinic	1^{c}	ICSD
Haidingerite (synthetic)	$CaHAsO_4 \bullet H_2O$	Orthorhombic	1^{c}	ICSD; Jing et al. (2003)
Pharmacolite (St. Andreasberg, Germany)	$CaHAsO_4 \bullet 2H_2O$	Monoclinic	1	ICSD; Kundu and Gupta (2008)
Calcium hydroxide arsenate hydrate	$CaAsO_3(OH) \bullet 2H_2O$		1	Kundu and Gupta (2008)
Calcium hydrogenarsenate trihydrate	$CaHAsO_4(H_2O)_3$	Orthorhombic	1	ICSD
	$Ca_2Na(HAsO_4)(AsO_4) \cdot 6H_2O$		1^{c}	Rodriguez et al. (2008)
	$NaCaAsO_4 \bullet 7.5H_2O$		1	Moon et al. (2004)
	$Ca_5H_2(AsO_4)_4 \bullet 5H_2O$		1.25	Kundu and Gupta (2008)
Sainfeldite (synthetic)	$Ca_5(HAsO_4)_2(AsO_4)_2(H_2O)_4$	Monoclinic	1.25	ICSD
Vladimirite (synthetic: from nonahydrate)	$Ca_5(HAsO_4)_2(AsO_4)_2(H_2O)_5$	Triclinic	1.25	ICSD
Ferrarisite (Sainte-Marie-aux Mines, France)	$Ca_5(HAsO_4)_2(AsO_4)_2(H_2O)_9$	Triclinic	1.25^{c}	ICSD
Guerinite (synthetic)	$Ca_5(HAsO_4)_2(AsO_4)_2(H_2O)_9$	Monoclinic	1.25^{c}	ICSD
Calcium arsenate	$Ca_3(AsO_4)_2$	Hexagonal	1.5	ICSD
	$Ca_3(AsO_4)_2 \bullet 4H_2O$		1.5^{b}	Jing et al. (2003)
	$Ca_3(AsO_4)_2 \bullet 3\frac{2}{3}H_2O$		1.5^{c}	Bothe and Brown (1999)
	$Ca_3(AsO_4)_2 \bullet 4\frac{1}{4}H_2O$		1.5^{c}	Bothe and Brown (1999)
	$Ca_3(AsO_4)_2 \bullet 6H_2O$		1.5^{c}	Parkhurst and Apello (1999)
Rauenthalite (Sainte-Marie-aux-Mines, France)	$Ca_3(AsO_4)_2(H_2O)_{10}$	Triclinic	1.5^{c}	ICSD
Phaunouxite (Sainte-Marie-aux Mines, France)	$Ca_3(AsO_4)_2(H_2O)_{11}$	Triclinic	1.5	ICSD
	$Ca_5(AsO_4)_3(OH)$		1.67^{c}	Bothe and Brown (1999)
	$Ca_4(OH)_2(AsO_4)_2 \bullet 4H_2O$		2^{c}	Bothe and Brown (1999)

[a] As indicated in the corresponding references and/or crystallography files.
[b] Phase in MINTEQ database.
[c] Phases added to MINTEQ database.

summary of the different possible Ca-As phases for Ca/As molar ratios between 0.5 and 2.0. Only three $Ca\text{-}As^{3+}$ phases [$Ca(AsO_2)_2$, Ca-As-O, $CaHAsO_3$] were found in the literature, but none of these compounds has a Ca/As molar ratio close to the 1.5 determined by the EDX. In the case of As^{5+}, the closest Ca/As molar ratio match for the As^{5+}-spiked SSF media was 1.0; this suggests that the observed crystal in Fig. 10 was $Ca_2As_2O_7$ or one of the hydrated forms of $CaHAsO_4$, although there is not a strong match with the crystal information shown in Table 11.

MINTEQ Simulations

In order to resolve the SEM-EDX data, geochemical model simulations using Visual MINTEQ (David and Allison 1999) were performed to ascertain which of the Ca-As solid phases controlled the solubility of As^{3+} and As^{5+} in the As-spiked SSF samples. The solid phase thermodynamic database of MINTEQ was augmented with additional relevant thermodynamic data for the Ca-As precipitates identified in the literature (Table 12). Although there are many Ca-As precipitates identified in the literature (e.g., Table 11), the thermodynamic data could not be located for all phases.

The average pH value of the SSF media was approximately 12, whereas the pH values of the corresponding TCLP and SPLP leachates were greater than 11, as shown in Table 9 and Fig. 6. Therefore, for simulation purposes, the lower bound on pH was set at 10 because of the strong buffering capacity of the SSF media. The Davies equation (Snoeyink and Jenkins 1980) was used to calculate the activity coefficients in the model. The model calculated ionic strengths (I) were used for $I < 0.5$ M. For $I < 0.5$ M, the ionic strength was fixed at 0.5 M (Geelhoed et al. 2002; Wazne et al. 2008). The values of As concentrations predicted by the model simulation did not change appreciably ($< 1\%$) when the higher ionic strengths were fixed at 0.5 M. The total elemental concentrations obtained by using XRF analyses (Table 1) were used as input for the simulation, and the L:S ratio was fixed at 20. To account for the reagent loading to the SSF, the total As and Na concentrations were simulated as 8,000 and 1,600 mg/kg, respectively.

This seemed appropriate as the presence of a sizeable sodium (Na) peak in Fig. 10(b) suggested that the crystal shown in Fig. 10(a) may be a sodium calcium arsenate even though the Na content of the SSF media, shown in Table 1, was extremely low (222 mg/kg Na). In this way, the search for possible precipitates had to be expanded beyond Ca-As phases to Na-Ca-As phases. Moreover, in lime-arsenic(V)-kaolinite slurries using $Na_2HAsO_4 \bullet 7H_2O$ as the As-spiking agent, Moon et al. (2004) confirmed the formation of $NaCaAsO_4 \bullet 7.5H_2O$ by XRPD,

Table 12. Reactions and Parameters Used in the Model Calculations

Precipitation reactions	Arsenic oxidation state	Ca/As molar ratio	log K
$Ca_3(AsO_4)_2 \bullet 4H_2O_{(s)} = 3Ca^{2+} + 2AsO_4^{3-} + 4H_2O$	5	1.5	−18.9[a]
$Ca_3(AsO_4)_2 \bullet 6H_2O_{(s)} = 3Ca^{2+} + 2AsO_4^{3-} + 6H_2O$	5	1.5	−19.1[b]
$Ca_3(AsO_4)_2 \bullet 10H_2O_{(s)} = 3Ca^{2+} + 2AsO_4^{3-} + 10H_2O$	5	1.5	−21.46[c]
$Ca_3(AsO_4)_2 \bullet 3\frac{2}{3}H_2O_{(s)} = 3Ca^{2+} + 2AsO_4^{3-} + 3\frac{2}{3}H_2O$	5	1.5	−21.02[c]
$Ca_3(AsO_4)_2 \bullet 4\frac{1}{4}H_2O_{(s)} = 3Ca^{2+} + 2AsO_4^{3-} + 4\frac{1}{4}H_2O$	5	1.5	−21.15[c]
$Ca_5(AsO_4)_3(OH)_{(s)} + H^+ = 5Ca^{2+} + 3AsO_4^{3-} + H_2O$	5	1.67	−24.3[c]
$CaHAsO_4 = Ca^{2+} + H^+ + AsO_4^{3-}$	5	1	−16.34[c]
$CaHAsO_4 \bullet H_2O = Ca^{2+} + H^+ + AsO_4^{3-} + H_2O$	5	1	−16.34[c]
$Ca_5H_2(AsO_4)_4 \bullet 9H_2O = 5Ca^{2+} + 2HAsO_4^{2-} + 2AsO_4^{3-} + 9H_2O$	5	1.25	−31.17[d]
$Ca_2Na(HAsO_4)(AsO_4) \bullet 6H_2O = 2Ca^{2+} + Na^+ + HAsO_4^{2-} + AsO_4^{3-} + 6H_2O$	5	1	−13.83[d]
$Ca_4(OH)_2(AsO_4)_2 \bullet 4H_2O + 2H^+ = 4Ca^{2+} + 2AsO_4^{3-} + 6H_2O$	5	2	−0.13[c]
$CaHAsO_3 + 2H^+ = Ca^{2+} + H_3AsO_3$	3	1	14.37[e]
$Ca(AsO_2)_2 + 2H_2O = Ca^{2+} + 2H_2AsO_3^-$	3	0.5	−6.52[f]

[a] MINTEQ database.
[b] Parkhurst and Apello (1999).
[c] Bothe and Brown (1999).
[d] Rodríguez et al. (2008).
[e] Dutre and Vandecasteele (1995).
[f] Stronach et al. (1997).

Table 13. Dissolved As Concentration as Predicted by the Model at Different pH

pH	10	11	12	13	TCLP	SPLP
As^{3+} mg/L	19.98	1.86	0.32	3.76	0.029	< 0.01
As^{5+} mg/L	0.0044	0.0003	0.0002	0.1656	< 0.01	< 0.01

although it is unclear if the detected phase was merely an artifact of the spiking agent itself (Na:As = 2), not the S/S system, as kaolinite is also Na deficient ($Na_2O \sim 0.15\%$ by weight or 1,110 mg/kg Na; Moon et al. 2009) and could not make Na available in the necessary quantities to exceed the XRPD detection limit (~1% by weight typically). The literature search (Table 11) identified two other possible sodium calcium arsenate phases [$CaNa_2(As_4O_{12})$ and $Ca_2Na(HAsO_4)(AsO_4) \bullet 6H_2O$] with $0.25 \le Na/As \le 1.0$, but the thermodynamic data were only available in the last case.

The MINTEQ simulations predicted that $CaHAsO_3$ and $Ca_5(AsO_4)_3(OH)$ phases were the respective As^{3+} and As^{5+} precipitates between $10 \le pH \le 13$, with corresponding Ca:As molar ratios of 1 and 1.67, respectively. The prevalence of sodium calcium arsenates was not predicted in either case. The model-predicted concentrations (mg/L) of the corresponding dissolved As species are summarized in Table 13. The dissolved As^{5+} concentrations are significantly less than the dissolved As^{3+} concentrations, and they compare more favorably to the TCLP/SPLP extractions, but the concentrations are still off by almost a factor of 100.

To assess the source(s) of this discrepancy, the obtained Ca/As ratio for the As^{3+} species was 1.5 by SEM-EDX, nevertheless MINTEQ predicted the formation of $CaHAsO_3$ (Ca:As = 1) over $Ca(AsO_2)_2$ (Ca/As = 0.5), when comparing the known As^{3+} compounds in Table 11 (no thermodynamic data for Ca-As-O was available). The SEM-EDX results for the As^{5+} crystal analysis indicated that the As phase had a Ca/As ~ 1 that allowed for $Ca_2As_2O_7$ to be the possible crystal phase (albeit not included in MINTEQ) or one of the hydrated forms of $CaHAsO_4$. However, the latter phase did not precipitate during the MINTEQ runs. Instead, $Ca_5(AsO_4)_3(OH)$ with a Ca/As = 1.67 precipitated.

Given the combination of synthetic versus natural minerals containing Ca-As in Table 11, and more specifically, for the Ca/As molar ratios determined by SEM-EDX, it is uncertain whether they would have been predicted by MINTEQ simulations even if the thermodynamic data for the compounds had been available. It is quite well known that the K_{sp} values reported in the literature are determined from experimental procedures using synthetic solutions, which are often remote from the conditions encountered in the field. Solid solutions rather than pure solid phases may exist in the field in addition to possible dynamic field conditions. Even for the same solid phases under well-controlled experimental conditions, researchers have reported K_{sp} values for some As compounds that differ by five orders of magnitude (Zhu et al. 2006).

Although the SEM-EDX is quite accurate in determining the molar ratios of specific crystals, which, in turn, impact dissolved concentrations, it is clear from the elemental mapping in Fig. 9 that various surface solid phases containing Ca, Fe, Mg, and Mn may be associated with As precipitates, which will also influence the apparent aqueous concentrations of arsenic. The bulk Ca/As molar ratio from XRD (Table 1) inputted to the simulation is, therefore, not the same as the effective Ca/As ratio when the SSF composition and surface species are accounted for, with the excess going to specific mineral formation, both amorphous and crystalline. Despite the identified issues with K_{sp} values, the potential surface precipitation of As would obviously create a situation in which the effective Ca/As molar ratio can be skewed in either direction, producing disagreement between the simulated precipitates and the empirically determined phases by EDX. Thus, using multiple lines of evidence (quantitative XRPD, SEM-EDX, leached concentrations, MINTEQ simulations) to understand the ultimate disposition of As in the SSF samples has not produced strong agreement on the observed phases. Moreover, it is not known if techniques that can report on average atomic bond lengths (which can also be used in mineral identification analyses), such as EXAFS, would provide conclusive information on the As-containing minerals. However, through additional study of these and like systems, there is collective room for improvement for generating consensus on the mechanisms responsible for immobilization of As among the traditional and newer microscale investigative techniques.

Discussion

The goal of this work was to document the coupled geotechnical and geoenvironmental enhancements that SSF media provides to DM. From a density perspective, the SSF media significantly improved the compaction indices of the DM, and its high frictional strength will obviously add to that of the DM, when blended. While additional geotechnical data are being collected in ongoing phases of this project, the measured increases in unit weight, by corollary, already signal expected improvements in strength and drainage (this was the case with the cited CG-DM blends). Moreover, the extended swell tests illustrated that the SSF materials reduced the swell of the DM.

The SSF media was found to be of equal or better environmental quality than the DM itself from a major anions, totals, chromium (VI) content, and TCLP/SPLP leaching perspective. The As-thresholding experiments demonstrated that the DM spiked with 100 mg/kg As on its own, and in combination with SSF materials, leached very low As concentrations under TCLP (all nondetected) and SPLP (~75% nondetected) conditions. On its own, however, the As-spiked DM could not satisfy regional aquifer media (0.010 mg/L) under both TCLP and SPLP conditions (Table 9), whereas the SSF media demonstrated a significant ability to immobilize As. The SSF media immobilized 7,900 mg/kg As^{3+} (measured) to TCLP-As leaching levels lower than the average DM spiked with 100 mg/kg As^{3+} and As^{5+}, or 0.029 mg/L, whereas the corresponding SPLP-As leach was nondetected (< 0.010 mg/L). The SSF media also immobilized up to 8,800 mg/kg As^{5+} (measured) to corresponding TCLP-As and SPLP-As leaches of < 0.010 mg/L. That the SSF media is granular and not a commercial cementitous or fine pozzolanic material makes these As-immobilization results all the more profound for drainage, filtering, reactive media, and soil blending applications.

On the basis of the arsenic thresholding studies performed in this study and the results shown in Tables 7 and 8, it appears that DM with an As total concentration of approximately 100–125 mg/kg could be safely used. Here we are speaking of the DM quality as mined from the CDF, not the navigation channel or private berth conditions, which could be higher. The sedimentation processes that occur by hydraulic placement of DM in a CDF afford important contaminant dilution, sediment dewatering, cost, and other advantages that make large-scale DM beneficial-use applications viable and competitive in urban coastal, river, or estuarine regions. If analytical resolution and/or compliance on arsenic is required to the regional aquifer level (0.010 mg/L; Table 5), one approach would be to apply a factor of safety of two ($FS = 2$) on the DM-only SPLP-As results, shown in Table 9. This would yield a corresponding total As value of approximately 50–60 mg/kg, which is consistent with the regulated DM beneficial-use criteria of neighboring states (e.g., Pennsylvania = 53 mg/kg). For situations (hotspots) in which the DM exceeds this As criterion, DM beneficial use could still be possible by for instance mandating a minimum SSF content (e.g., 50%), which, by blending, would bring the net total As concentration of the DM-SSF blend back into overall alignment with the foregoing compliance scheme.

Microscale investigation techniques and modeling techniques were used to assess the ultimate disposition of high concentrations of arsenic in the SSF media. The total concentrations of arsenic were still sufficiently low enough to be less than the mineral DLs of the XRPD device. Elemental mapping (Fig. 9) showed that As was ubiquitous; however, the associations of As with surface phases, such as Ca, Fe, Al, and Mg, were not modeled. SEM-EDX also showed isolated crystal formation, but their corresponding empirical formulas could not be reconciled with currently recognized minerals and their equilibria.

Despite identification of the exact As crystals, the documented As-immobilization potential of the granular SSF media was nonetheless impressive. That both the DM and SSF media are low cost makes them attractive for fill construction in urban, coastal areas. Thus, more detailed study of the DM-SSF blends and their combined geotechnical and metals leaching behavior is warranted.

Conclusions

A beneficial-use evaluation of steel slag fines (SSF) to geotechnically and geoenvironmentally improve the quality and characteristics of dredged material (DM) for large scale recycling was completed. The SSF media improved the compacted unit weights of the DM above MDSHA minimum requirements and reduced the volume change behavior of DM during extended swell tests while itself exhibiting compression (no swell). After some small ($< 3\%$) initial movement (< 24 hours), the volume change of the DM-SSF blends was observed to be essentially constant for more than 200 days. Of the PPL metals evaluated in both media, arsenic was determined to be a key constituent of concern, requiring focused study to understand its leaching and mobilization from the DM and DM-SSF blends.

Because the arsenic concentrations in the DM are variable, arsenic thresholding analyses were undertaken to reverse engineer an acceptable As total concentration in the DM on its own and when blended with the SSF. DM and DM-SSF blends were successful in immobilizing As^{3+} and As^{5+} to below the TCLP DL (< 0.25 mg/L) in all combinations, whereas only the 20/80 and 50/50 DM-SSF blends consistently were below the SPLP detection limit (0.05 mg/L). As a raw material, the As-spiked DM (100 mg/kg spike) on its own could not satisfy regional groundwater criteria under TCLP or SPLP conditions, however, the SSF media showed a tremendous ability to immobilize arsenic. More specifically, the SSF media immobilized 7,900 mg/kg As^{3+} to TCLP-As leaching levels lower than the average DM spiked with 100 mg/kg As^{3+} and As^{5+}, or 0.029 mg/L. The SSF media also immobilized up to 8,800 mg/kg As^{5+} to a corresponding SPLP-As leach of < 0.010 mg/L.

A forensic analysis of the As distribution in the SSF media by quantitative XRPD showed that As crystalline phases did not exceed the DL of the device. Elemental mapping provided by SEM-EDX showed that As was ubiquitous throughout the SSF media, including the formation of isolated crystals. The crystals' empirical formula, determined by EDX, could not be matched with the open literature on known Ca-As phases, including the modeling of potential precipitates and their equilibrated aqueous concentrations predicted by MINTEQ.

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Notation

The following symbols are used in this paper:

c = cohesion, kPa;

G_s = specific gravity, dimensionless;

$\gamma_{d,\max}$ = maximum dry density, kN/m^3;

w_{opt} = optimum water content, %; and

σ_n = applied effective normal stress during direct shear testing, kPa.

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Aging Effects in Field-Compacted Dredged Material: Steel Slag Fines Blends

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Abstract: This paper contains the results of aging study performed on 365-day-old trial highway embankments constructed of field-compacted dredged material (DM), steel slag fines (SSF), and three DM-SSF blends. Key findings include that moisture content of the internal core at 365 days was essentially unchanged from the as-built conditions, and the bulk (major oxide) chemistry of the DM-SSF blends matched what was predicted by the field blending ratios. The addition of SSF to the 100% DM resulted in significant pH buffering and in strength increases up to a factor of 2, as measured by the average cone penetrometer test (CPT) tip resistance. Refusal (>115 MPa or >1,200 t/ft^2) was encountered in the 100% SSF embankment at a depth of approximately 1.5 m. The 365-day aged 100% DM and 80/20 DM-SSF blend had effective friction angles on the order of 34 and 52°, respectively, where the dry DM content is reported first. Quantitative X-ray diffraction analyses indicated that no new crystalline phases were observed in the DM-SSF blends, such as those commonly associated with typical cementation reactions. For 365-day-old DM-SSF blends containing between approximately 1 mg/kg (100% SSF) and 26 mg/kg (100% DM) total arsenic, the 95% upper confidence limit on the average. As concentration from the combined toxicity characteristic leaching procedure/synthetic precipitation leaching procedure (TCLP/SPLP) leaching results was less than the SPLP detection limit (0.028 mg/L), suggesting that the environmental risk associated with beneficially using the DM-SSF blends may be negligible. **DOI: 10.1061/(ASCE)HZ.2153-5515.0000154.**

CE Database subject headings: Arsenic; Dredging; Recycling; Aging (material); Slag.

Author keywords: Arsenic; Dredged spoil; Slag; Recycling; Aging.

Introduction

This paper is the last in a series of publications (Grubb 2009, 2011; Grubb et al. 2010a, b, c; 2011a, b; Malasavage et al. 2012) aimed at exploring the possibility of large-scale recycling of dredged material (DM), steel slag fines (SSF; <9.5 mm fraction), and several DM-SSF blends for a variety of geotechnical and earthwork applications. The focus was to explore and report on the properties of these synthetic, recycled fill materials to assess a suitable range of beneficial use applications and to provide the data sets necessary to enable the creation of a rationally-based beneficial use permit framework. Emphasis was placed on understanding the raw and blended materials because of the potential need for additional controls to be protective of human health and the environment and not regulatory compliance, per se.

The main motivation for this work arose from the Maryland Port Administration (MPA) having to identify several options to beneficially use upwards (e.g., >400,000 m^3/yr) of DM from the Baltimore harbor on an annual basis by 2023. The source of the DM will principally be the Cox Creek Dredged Material Containment Facility (DMCF) because of its limited capacity (~4.8 million m^3). Under Maryland state law, DM from the Baltimore harbor can only be placed in a DMCF, such as Cox Creek. Recycling on such a large scale speaks to the need to develop sustainable, high volume commercial outlets for DM in the greater Baltimore metropolitan area to minimize transportation costs. Because of the significant volumes of material involved, the development of safe and sustainable applications for DM management and/or beneficial use (uncontaminated or contaminated DM) is an important regional challenge. Accordingly, a three-phase demonstration project was conducted to evaluate the environmental, geotechnical, and constructability issues associated with potentially using the DM-SSF blends as a geotechnical fill for a variety of end uses, as detailed in the aforementioned publications.

A two-phase field demonstration project was completed. Malasavage et al. (2012) describes the construction of five 3.5-m (12-ft) high trial, single-lane highway embankments: 100% DM, 100% SSF and 80/20, 50/50, and 20/80 DM-SSF blends, in which the DM content is reported first (dry % by weight basis). The feasibility of blending the DM and SSF media (by using a portable

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soil pugmill) at specified blending ratios was successfully demonstrated at high throughputs. The subsequent construction and inspection of the compacted DM-SSF blend embankments revealed they were extremely competent—several embankments met regional highway embankment criteria. The second part of the field project (this paper) was to report on the aging effects of the constructed 100% DM, 100% SSF, and the DM-SSF blend embankments at 365 days.

Geotechnical Methods

Field Sample Collection and Preparation

Samples of the 365-day-old trial embankment materials were collected at three locations along the long axis of each trial embankment by using a small excavator positioned on the top of the embankment. The two outer locations were situated approximately 2 m from the crest of each end slope of the embankment, while the third location was taken at the center (locations were approximately 7 m apart). The test pits were excavated to approximately the mid-height of each aboveground trapezoidal embankment (depth of approximately 2 m below the embankment crest) to collect samples from the compacted, inner core.

Once each test pit was completed, the bottom was smoothed out, and a 0.6-m long, 7.62-cm diameter, stainless steel thin-walled tube was advanced into the embankment by using the excavator bucket. Because of the high strength and stiffness of several of the embankments, tube samples (TS) could only be collected from the 100% DM (3), 80/20 DM-SSF Blend (3), and 50/50 DM-SSF Blend (1) embankments, for a total of 7 TS samples. After collection, the thin-walled tubes were cleaned, sealed with microcrystalline wax, capped, and labeled for transport. The TS samples served as the source material for subsequent geotechnical, environmental, and mineralogical tests. Where TS samples could not be recovered, freshly excavated material from the bottom of the test pit was placed in sealable 0.453 kg (16-oz) glass and plastic jars for environmental and mineralogical testing, respectively.

Cone Penetrometer Testing

Three locations along the long axis of each trial embankment were tested according to ASTM D5778-07 (ASTM 2007) for their cone penetrometer test (CPT) resistance at testing locations adjacent to those tested by Malasavage et al. (2012) for the newly constructed embankments in the Fall 2010. Tip resistance (q_t), sleeve friction (f_s), and dynamic pore pressure (u) were measured continuously from the top of each embankment to depths of at least 3.5 m (12 ft), depending on the undulating ground surface beneath each embankment. The bottom of each embankment was identified by sudden changes in the q_t.

$\mathrm{CI\bar{U}}$ Triaxial Strength Testing

The 365-day old field samples of 100% DM and the 80/20 DM-SSF blend were subjected to isotropically consolidated $\mathrm{CI\bar{U}}$ shear tests with pore water measurements in general accordance with ASTM D4767 (ASTM 2004). First, each thin-walled tube sample was cut by using an electric saw to a height of approximately 14.8 cm (5.6 in.). Each sample was then extruded intact from the tube, except for the only 50/50 DM-SSF blend sample, which was compromised. Saturation of specimens was verified through B-value (>0.9) check and by tracking volumetric water intake relative to available air-pore space at the time of extrusion. Specimens were tested at three confining pressures, 69, 207, and 345 kPa (10, 30, and 50 psi). Failure was reported for two criteria: 15% axial strain and maximum stress obliquity.

Analytical Methods

Representative sample splits of the 365-day-old 100% DM, 100% SSF, and their blends were collected from their respective storage devices (tube sample/jars) in accordance with ASTM D6323-98 (ASTM 1998). The environmental suite consisted of priority pollutant list (PPL) total metal concentrations, toxicity characteristic leaching procedure (TCLP), and synthetic precipitation leaching procedure (SPLP) tests. The mineralogical suite included X-ray fluorescence (XRF) and quantitative X-ray powder diffraction (XRPD) and scanning electron microscopy-energy dispersive X-ray (SEM-EDX), the latter of which did not offer additional insight into the DM-SSF blends and will not be presented in this paper.

Environmental Analyses

Total PPL metals were determined by using the U.S. EPA (USEPA) 3050B method (USEPA 1996). The TCLP and SPLP tests were performed according to USEPA Methods 1311 and 1312 (USEPA 1986b, a), respectively, with metals digestion by the USEPA 3015A (USEPA 2007) method series. Metals concentrations were determined by using Inductive Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), except for total As, Tl, and Se concentrations, which were determined by using Inductive Coupled Plasma-Mass spectrometry (ICP-MS). Method detection limit (MDL) calibrations were based on a series of seven lab-fortified blanks ran at a spiked amount 1–4 times the detection limit (DL) (or instrument DL if the first time). The standard deviation was then multiplied by 3.314. If the response was within 10–100% of the spike, then the MDL was determined to be acceptable. Otherwise the spike value was changed and the process repeated.

XRF Analyses

The bulk chemistry determinations incorporated XRF analyses, free lime (CaO), and loss on ignition (LOI) reporting at 950°C by ASTM C114-11b (ASTM 2011). Material densities were likewise determined by using helium pycnometry.

XRPD Analyses

Air-dried subsamples (50 g) of each media were taken and first hand-pulverized to pass the 2-mm screen, of which 2 g were mechanically-pulverized in a McCrone micronizing mill for 10 min by using 7 mL cyclohexane as the milling fluid. The resulting slurry was air-dried and then mixed with corundum ($\alpha - \mathrm{Al_2O_3}$, Sawyer, Lot No. C04-AO-41) on an 80:20 ratio by weight and then subjected to XRPD.

Step-scanned XRPD data was collected on each subsample by using a Rigaku Ultima 4 computer-automated diffractometer using Bragg-Brentano geometry. Diffractometry was conducted at 40 kV and 40 mA by using a diffracted beam graphite-monochromator with Cu radiation. The data was collected in the 2θ range of 5–85° with a step size of 0.03° per 8 s. The qualitative and quantitative analyses of the XRPD patterns were performed by using the *Jade Version 7.5* (Materials Data Inc.) and the Whole Pattern Fitting function of *Jade*, which is based on the Rietveld method (1969). The reference databases for powder diffraction and crystal structure data were the International Center for Diffraction Data (ICDD) database (ICDD 2004) and the Inorganic Crystal Structure Database (ICSD) (ICSD 2011), respectively.

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Results and Discussion

Geotechnical

Other than their self-weight, the DM-SSF blend embankments were not subject to any loading. Moreover, the trial highway embankments remained uncovered and exposed to ambient weather conditions for a period of at least 365 days. On the basis of field observations at 365 days, no significant heave or settlement occurred in the trial embankments, consistent with the consolidation and swell testing results of the DM-SSF Blends (Grubb et al. 2011a). Additionally, the moisture content of the 0-day and 365-day embankments were very similar, indicating no net uptake of moisture, based on the 100% DM and 80/20 DM-SSF blend data shown in Tables 1 and 2. Table 2 actually suggests a loss of moisture on the order of 2%, but the exhumed sample data set at 365 days was much smaller than the compaction control data set. On the whole, these observations taken collectively suggest a relatively constant volume (i.e., density) and moisture throughout the curing period and that the surface crust formation and hydraulic conductivity of the embankments were sufficiently low to promote surface runoff over infiltration.

Fig. 1 shows the tip resistance results for each DM-SSF blend embankment average over three locations for the postconstruction (0-day; 2010) and 365-day aged (2011) conditions. All CPT soundings were advanced without difficulty, except for the 100% SSF embankment, which began encountering refusal a 1.5-m depth, where the maximum limit on the CPT readout device was clearly exceeded (115 MPa; ~1,200 tsf). Many attempts were repeated, including putting the full weight (20 t) of the truck on the CPT tip. Two of the 100% SSF CPT soundings were terminated at 2.1 and 2.7 m, respectively. To determine whether or not there was a possible lens of high strength 100% SSF media preventing penetration, the third sounding was drilled out with a hollow stem auger from approximately 2.75–3 m of depth. The CPT sounding was then reattempted and refusal was almost immediately encountered.

Fig. 1 shows that the CPT tip resistance results for the 100% DM embankment remained essentially unchanged between the 0- and 365-day measurements. The corresponding sleeve friction (f_s) and dynamic pore pressure (u) were <0.5 and 0 MPa, respectively. The average CPT tip resistance of the 80/20, 50/50, and 20/80 DM-SSF Blends increased in strength between 30–90% (up to a factor of almost 2x), as shown in Fig. 1, based on the average CPT tip resistances measured below 0.3 m (surface crust). Discontinuous positive pore water pressures were measured at what appeared to be lift interfaces in the deeper portions of each embankment, and the f_s values were less than 1 MPa for all DM-SSF blend embankments. The 100% SSF embankment appears to have doubled in strength up to a depth of 1.5 m; thereafter, the 365-day aged embankment achieved refusal (>115 MPa), which constitutes at least a doubling of the strength below 1.5 m. The corresponding f_s and u values were <0.5 and 0 MPa, respectively, identical to the 100% DM.

By comparison, aged unconfined compressive strength (UCS) test samples of laboratory-prepared DM-SSF blends, which had a slightly higher DM fines content, were found to increase in strength by a factor of 1 to almost 3 over 360 days. In direct CPT performance, the aged crushed glass-dredged material (CG-DM) blends tested by Grubb et al. (2008a, b) at the U.S. Army Corps of Engineers Fort Mifflin site in Philadelphia were determined to increase in strength by a factor of 2 to 3. However, in actual magnitude, the strongest embankment (80/20 CG-DM Blend) was only a quarter as strong as the 20/80 DM-SSF blend (both had 80% coarse material, CG or SSF), or approximately 6 MPa versus 24 MPa, as shown in Fig. 2. The average CPT values shown in Fig. 2 were calculated from depth 0.5 m (1.6 ft) beneath to 3.2 m (10.5 ft) beneath the top surface of each embankment to avoid the potential contribution from the hardened surface crust on several of the embankments and variable thicknesses up to 4 m. Thus, although the DM sources were not significantly different (both USCS OH soils), the main factors contributing to differences in strength were likely associated with specific gravity ($SG_{SSF}/SG_{CG} \sim 1.4$), which impacts blend unit weights, and reactivity (residual lime content of SSF), which may potentially contribute to cementation.

Table 1 summarizes the triaxial testing data for the 365-day aged 100% DM and the 80/20 DM-SSF Blend from the trial

Table 1. Strength Parameters for 100% DM and 80/20 DM-SSF Blend

	Water content		CIŪ triaxial			
	D2974		D4767			
			15% Axial strain		Maximum stress obliquity[a]	
Media	$\bar{X}$ (%)	σ (%)	c' kPa (psf)	ϕ' (°)	c' kPa (psf)	ϕ' (°)
100% DM	41.14	2.85	10 (202)	27	15 (317)	34
80/20 DM-SSF blend	28.15	1.76	0	39	0	52

[a] Occurred at approximately 7.3% and 2.3% axial strain, respectively, for 100% DM and 80/20 DM-SSF blend.

Table 2. Comparison of Geotechnical Parameters from Laboratory and Field Samples

Media tested	Aging condition	γ_d kN/m^3 (lb/ft^3)	w (%)	% RC (%)	% Fines (%)	c' kPa (lb/ft^2)	ϕ' (°)
100% DM	Lab (28-day)	12.6 (80)	38	95	98.8[a]	41[b] (856)	27.3[b]
	Field (365-day)	11.6[c] (73.9)	41.1 ± 2.85[c]	85[c]	74.4 ± 8.8[d]	15[e] (317)	34[e]
80/20 DM-SSF	Lab (28-day)	13.5 (86.2)	35	95	83.4[a]	48[b] (1,003)	32.4[b]
	Field (365-day)	14.4[c] (91.7)	28.15 ± 1.76[c]	85[c]	60 ± 8.1[d]	0[e]	52[e]

[a] From Grubb et al. (2011a, Table 2).
[b] From Malasavage et al. (2012, Table 2).
[c] From Malasavage et al. (2012, Table 4).
[d] From Malasavage et al. (2012, Table 6).
[e] From Table 1.

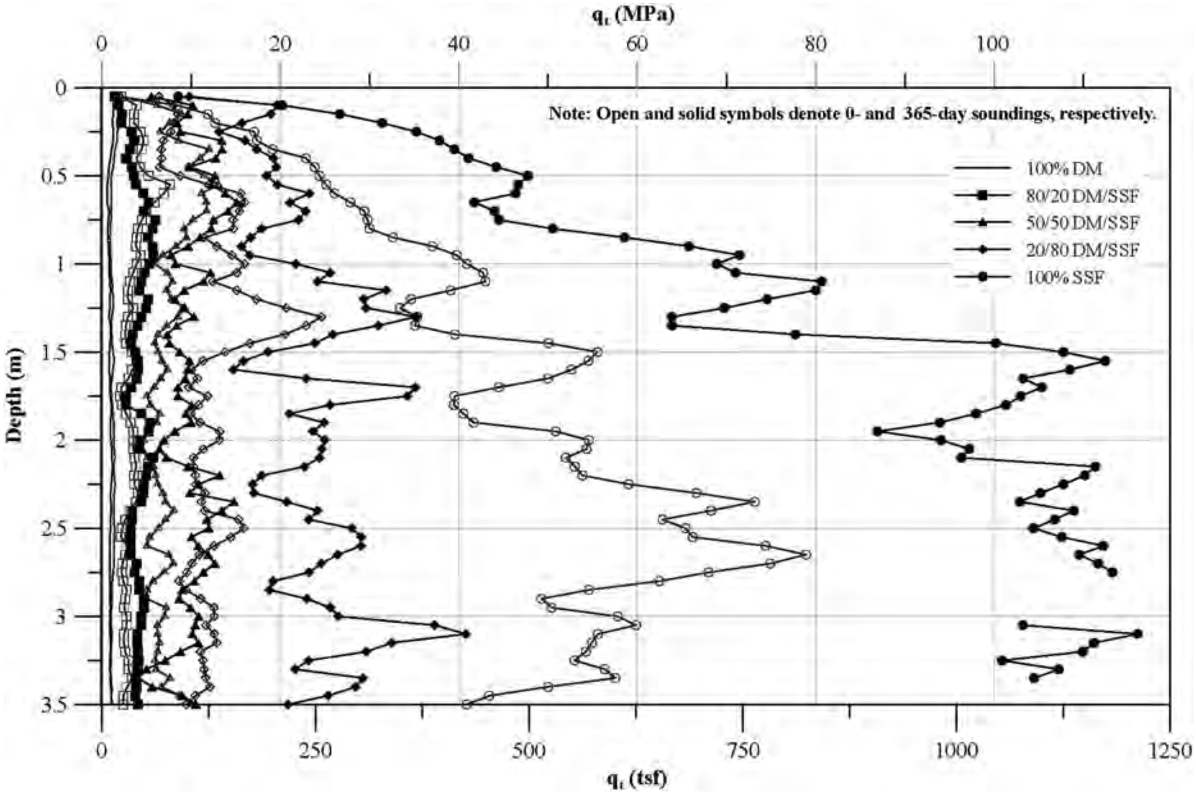

Fig. 1. Average CPT sounding results for trial embankments constructed with 100% DM, 100% SSF, and DM-SSF blends

embankments. On the basis of the maximum stress obliquity criterion, the 100% DM had a $c'_{\mathrm{CI\bar{U}}}$ of 15.17 kPa (317 psf) and $\phi'_{\mathrm{CI\bar{U}}}$ of 34°, whereas the 80/20 DM-SSF blend was cohesionless with a $\phi'_{\mathrm{CI\bar{U}}}$ of 52°. As such, the 100% DM appears suitable for landscaping or general fill construction, such as the dikes and berms it is typically used for. On the other hand, the addition of 20% SSF

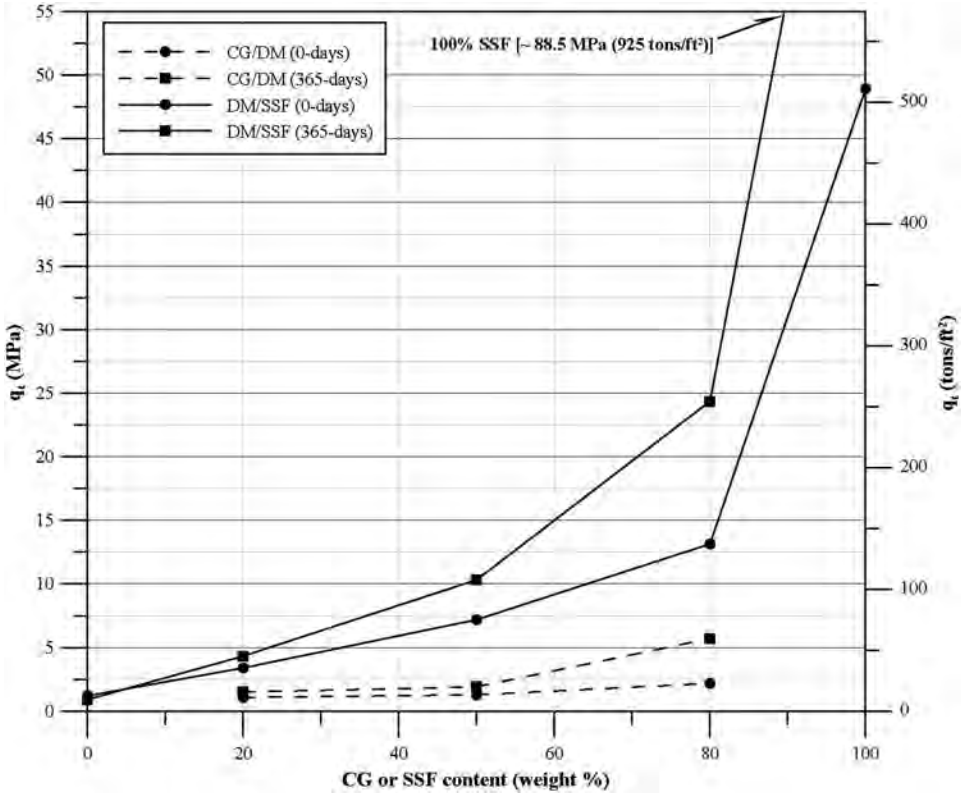

Fig. 2. Average CPT tip resistance of DM-containing blends versus coarse fraction content

to the DM produced an 18° increase in the $\phi'_{\mathrm{CI\bar{U}}}$ value from 34° (100% DM) to 52° (80/20 DM-SSF blend). So although the as-constructed 80/20 DM-SSF blend trial embankment did not satisfy the minimum compaction criteria of 15.7 $\mathrm{kN/m^3}$ (100 $\mathrm{lb/ft^3}$) by ASTM D1557 (ASTM 2012) for borrow (embankment) material as specified by Maryland State Highways without seeking a variance to the Section 916 specification (MDSHA 2008), the effective friction angle at 365 days proves the 80/20 DM-SSF blend to be a superior construction material. That is, compacted unit weight specifications are a surrogate for strength, and the attained strengths for the 80/20 DM-SSF blend itself exceeded that of compacted natural sands, or $\phi'_{\mathrm{DS}} \sim 35$–45° (Holtz and Kovacs 1981).

That said, the evaluation of aging effects based on triaxial strength comparisons were less straightforward than the CPT results. Table 2 presents a summary of the geotechnical parameters for 28-day cured 100% DM and 80/20 DM-SSF blends in the laboratory and field blends at 0 and 365 days. A key difference between the laboratory and field testing suites is that the DM source material used in the field project had approximately 25% more sand, making it difficult to tease out pure aging effects.

For the 100% DM, the lab triaxial testing samples were approximately 1 $\mathrm{kN/m^3}$ denser and contained 23% more fines than the field. So although the aged field triaxial samples were less dense (on the basis of embankment compaction data) and its lower effective cohesion value probably reflects both the lower density and increased sand content, its effective friction angle was nevertheless 7° higher, as shown in Table 2. Thus, aging effects may have offset differences in compaction from a triaxial perspective, even though the CPT results showed essentially no change.

For the 80/20 DM-SSF blend, the field triaxial samples were approximately 1 $\mathrm{kN/m^3}$ denser and contained 23% less fines than the laboratory triaxial samples. Although the coarser nature of the field samples allows the elimination of effective cohesion to be understandable, a 20° increase in the effective friction angle to 52° is difficult to attribute entirely to a 1 $\mathrm{kN/m^3}$ (5 $\mathrm{lb/ft^3}$) difference in unit weight. On the basis of the similarity in the results for the 100% DM aged samples and the 80/20 DM-SSF blend sample from the lab, one might expect the contribution of the additional sand fraction to the DM may lead to an effective friction angle increase on the order of 5–10° to the field blended materials. This leaves up to 10°, which may be purely associated with aging effects in the 80/20 DM-SSF blend sample based on the data shown previously for dense sands.

Environmental

The total PPL metal concentrations of the 365-day-old 100% DM, 100% SSF, and DM-SSF blends are shown in Table 3, and the numerical values either denote the average or the highest-valued detection limit associated with three replicates. To establish a context for beneficial use of materials, such as DM and steel slag, it is helpful to compare their environmental quality to the natural chemistry of regional soils, in this case the Eastern United States. Accordingly, also shown in Table 3 for comparison (from left to right) are several measured ranges and average total metal concentrations for Eastern U.S. soils (Dragun and Chekiri 2005) and regional soil cleanup criteria because several states take their soil cleanup standards to be synonymous with DM management.

As the beneficial use of DM, SSF, and DM-SSF blends will likely be to limited commercial, industrial, and highway construction sites (where additional engineering controls can be implemented to mitigate exposure conditions and risk), nonresidential criteria are normally taken to apply. The first set of criteria shown in Table 3 are the nonresidential soil cleanup criteria promulgated by the Maryland Department of the Environment (MDE) voluntary cleanup up program (VCP) (MDE 2008) followed by the New Jersey nonresidential soil cleanup criteria (NJDEP 2009). The neighboring Pennsylvania clean and regulated fill standards are also shown, which cover unrestricted and permitted uses of soils and soil-like media (PADEP 2004). Lastly, the Delaware Department of Natural Resources and Environmental Control (DNREC) uniform risk-based standards

Table 3. Summary of Total Metal Concentrations Results for 100% DM, 100% SSF, and DM-SSF Blends (mg/kg)

	Eastern U.S. soils[a]		MDE[b]	NJ[c]	PA[d]		DE[e]	365-day				
PPL metal	Range	Average	Non-Res	Non-Res	Clean	Regulated	URS NC RU	100% DM	80/20 DM-SSF	50/50 DM-SSF	20/80 DM-SSF	100% SSF
Antimony (Sb)	<1.0–8.8	0.76	41	19	12	53	82	<3.30	<2.91	<2.84	<2.43	<2.67
Arsenic (As)	<0.1–73	7.4	1.9	19	12	53	4	26.0	23.6	12.9	3.15	<1.84
Beryllium (Be)	<1.0–7.0	0.85	20	140	320	320	410	1.90	1.55	0.983	<1.74	<1.12
Cadmium (Cd)	ND-4.0	—	100	78	38	38	100	0.709	0.367	<0.966	<1.74	<2.10
Chromium (Cr tot)	1.0–1,000	52	310	NR	NR	NR	NR	132	363	612	908	1,133
Chromium (Cr III)	—	—	150,000	NR	190,000	190,000	310,000	—	—	—	—	—
Chromium (Cr VI)	—	—	310	6,100	94	190	610	—	—	—	—	—
Copper (Cu)	<1.0–700	22	4,100	45,000	8,200	36,000	8,200	221	371	170	71.4	49.5
Iron (Fe)	100–100,000	25,000	72,000	NR	NR	190,000	61,000	58,600	100,133	114,433	181,333	221,000
Lead (Pb)	<10–300	17	1,000	800	450	450	1,000	86.6	75.7	47.2	19.8	<19.9
Mercury (Hg)	<0.01–3.4	0.12	31	65	10	10	610	0.245	0.203	<0.143	<0.116	<0.101
Nickel (Ni)	<5.0–700	18	2,000	23,000	650	650	4,100	333	521	245	73	<18.0
Selenium (Se)	<0.1–3.9	0.45	510	57,000	26	26	1,000	2.42	1.59	0.933	<0.729	<1.38
Silver (Ag)	—	—	510	4,100	84	84	1,000	<2.15	1.85	<3.58	<3.06	<6.36
Thallium (Tl)	—	—	7.2	79	14	14	220	0.23	0.172	<0.142	<0.122	<0.230
Zinc (Zn)	<50–2,900	52	31,000	1,500	12,000	12,000	61,000	274	232	280	125	146

Note: Totals by USEPA 6000/7000 Method series; values below detection limit shown with "<" symbol; values are either numerical averages based on actual measurements, or the maximum non-detect limit for three replicates.

[a] Dragun and Chekiri (2005).

[b] MDE (2008).

[c] NJDEP (2009).

[d] PADEP (2004).

[e] DNREC (1999).

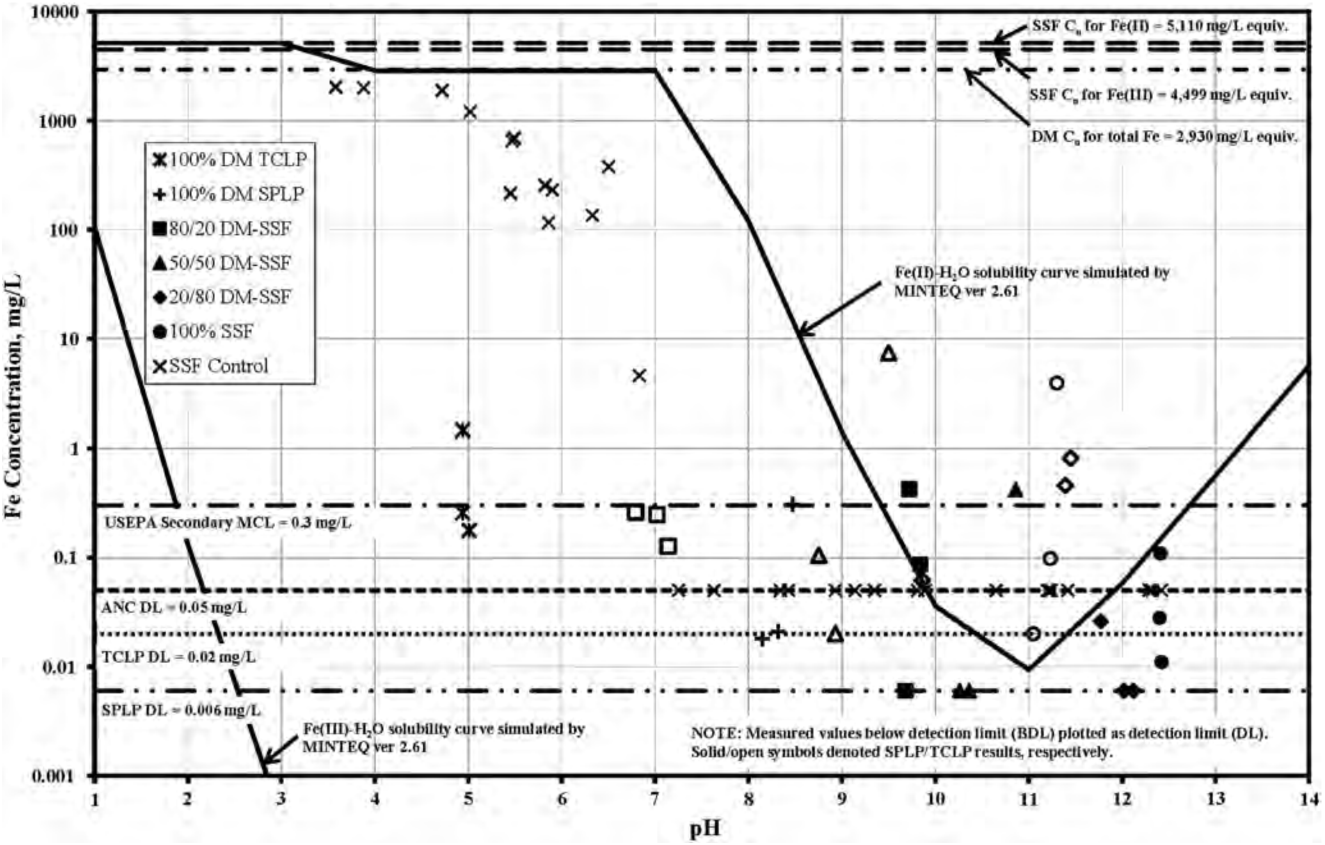

Fig. 3. Comparison of ANC, TCLP, SPLP leaching results for iron (Fe) from 100% DM, 100% SSF, and DM-SSF blends

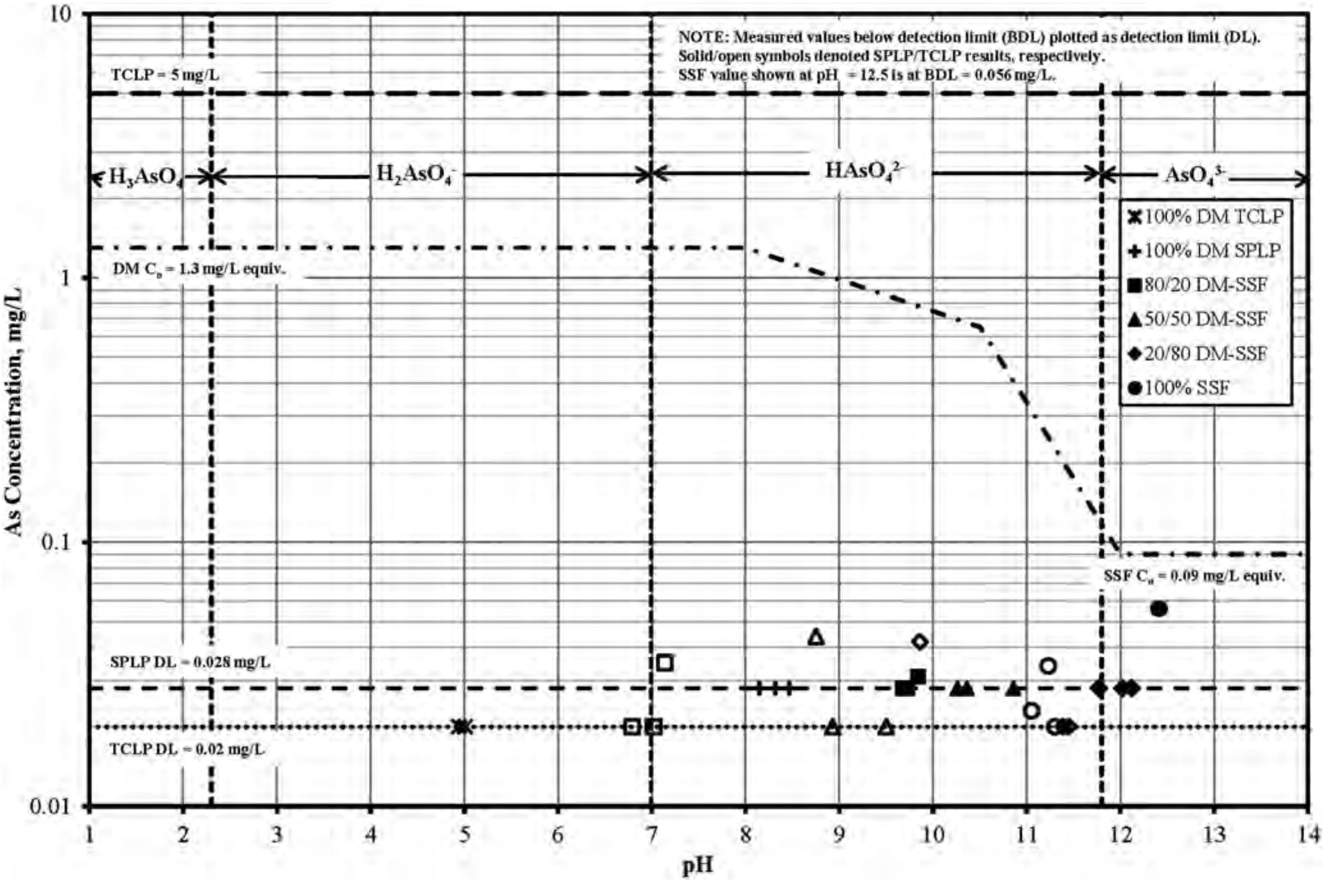

Fig. 4. TCLP-As and SPLP-As results as a function of pH and As(V) speciation for 100% DM, 100% SSF, and DM-SSF blends

(URS) for noncritical water resources areas with restricted uses (NC RU) are shown because the numerical criteria for surface and subsurface soils (for PPL metals) are equally valued. The DM beneficial use criteria for agricultural purposes has been proposed in Virginia (Daniels et al. 2009) where the recommended clean fill standard for total As is 20 mg/kg (proposed exclusion limit is 40 mg/kg; VA background is approximately 5 mg/kg).

Reviewing the total PPL metal concentration results from the 365-day aged 100% DM, 100% SSF, and their blends from the field project, at first glance, the synthetic fill media fail on three potential criteria for the PPL metals shown: As, Cr, and Fe. The latter of the two metals will be discussed first. For chromium, Grubb et al. (2011a) reported that <25% and ≤10% of the total Cr in the 100% DM and 100% SSF was Cr(VI), respectively, including direct solid phase measure measurements. Thus, all blends comply with the MDE criteria for chromium.

Iron Leaching Analysis

Iron is recognized for its ability to immobilize arsenic, which is partly why the SSF media was selected for blending with DM. Grubb et al. (2010b, c, 2011a, b) and Jagupilla et al. (2012) showed that the SSF is capable of immobilizing a wide range of heavy metals and metalloids (including PO_4) at industrial dosing levels. Grubb et al. (2010b, 2011a) performed acid neutralization capacity (ANC) tests on the 100% SSF media (total Fe ~220,000 mg/kg) by using an extended leach time (48 h versus 18 h for TCLP) to mitigate against the nonequilibrium effects for which the TCLP/SPLP procedures have been criticized (Vipulanandan 1995; Kosson et al. 2002; Cao and Dermatas 2008). In the SSF media, iron is speciated as Fe(0), Fe(II), and Fe(III) in the ratios of approximately 12.7, 46.5, and 40.9%, respectively (Grubb et al. 2011a). If fully leachable, dissolved Fe(II) and Fe(III) concentrations of approximately 5,110 and 4,499 mg/L would result, on the basis of a liquid:solid ratio of 20:1 identical to the TCLP/SPLP protocol, as shown by the respective SSF C_o limits in Fig. 3, in which C_o denotes the initial concentration. By analogy, if all of the dissolved Fe was derived from the DM, a maximum concentration of 2,930 mg/L would result based on the data shown in Table 3.

Also shown on Fig. 3 are the modeled Fe(II) and Fe(III) solubility curves for a pure water system using MINTEQ (ver. 2.61), which indicate that the soluble Fe concentrations emanating from the SSF media are likely dominated by Fe(II). Thus, although the SSF media and its leachates are a complex system (fail dilute assumption, contain solids), the pH-dependent solubility curves remain a useful framework for benchmarking leaching behavior. To the point, iron concentrations plotting above Fe(II) solubility line suggest that: (1) an experimental and/or procedural error

Table 4. Summary of As Data from Aged UCS and Field Samples

Media tested	UCS—360 day[a]			Field samples—365 day[b]			
	Totals (mg/kg)	TCLP (mg/L)	SPLP (mg/L)	Totals $\bar{X}$ (mg/kg)	Totals σ (mg/kg)	TCLP[c] (mg/L)	SPLP[c] (mg/L)
100% DM	42.5	<0.100	<0.056	26.0	1.4	<0.020 (3)	<0.028 (3)
80/20 DM-SSF	42.6	<0.111	<0.056	23.6	2.7	0.035, <0.020 (2)	0.031, <0.028 (2)
50/50 DM-SSF	24.5	<0.111	<0.056	12.9	1.8	0.044, <0.020 (2)	<0.028 (3)
20/80 DM-SSF	10.7	<0.111	<0.056	3.45	1.4	0.042, <0.020 (2)	<0.028 (3)
100% SSF		<0.500	<0.056	<1.84, <1.07, <0.889	—	0.034, 0.023, <0.020	<0.056 (3)

[a] Data reproduced from Grubb et al. (2011b).

[b] Average based on 3 replicates, $\bar{X}$ and σ denote average and standard deviation, respectively.

[c] Parentheticals denote number of similar-valued measurements.

Table 5. Summary of XRF Results for 100% DM, 100% SSF, and DM-SSF Blends (Percent by Weight)

Analyte	100% DM control	100% DM		80/20 DM-SSF		50/50 DM-SSF		20/80 DM-SSF		100% SSF		100% SSF control
		$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	
SiO_2	53.94	57.54	1.49	47.19	2.81	31.96	2.07	19.44	1.06	10.82	0.34	10.65
Al_2O_3	17.17	13.99	1.10	10.66	0.66	7.47	0.13	4.75	0.74	3.59	0.33	4.09
Fe_2O_3	9.79	9.62	0.25	13.87	1.48	22.28	1.24	26.90	0.84	31.84	2.48	26.84
CaO	0.45	0.92	0.46	9.22	1.97	18.81	1.48	28.02	0.83	33.22	1.24	37.21
MgO	1.88	1.52	0.09	3.37	0.39	5.81	0.56	8.19	0.34	9.49	0.42	10.31
SO_3	0.09	0.75	0.31	2.09	0.06	1.40	0.09	0.66	0.04	0.21	0.02	0.16
Na_2O	0.85	0.63	0.04	0.15	0.25	0.12	0.20	0.03	0.04	0.01	0.01	0.03
K_2O	2.74	2.31	0.08	1.58	0.13	0.88	0.11	0.29	0.05	0.03	0.01	0.02
TiO2	0.89	0.75	0.06	0.66	0.04	0.52	0.03	0.42	0.01	0.34	0.02	0.46
P_2O_5	0.23	0.21	0.02	0.27	0.02	0.38	0.01	0.48	0.01	0.54	0.02	0.78
Mn_2O_3	0.21	0.17	0.02	1.36	0.25	2.65	0.38	4.02	0.13	4.67	0.09	3.97
SrO	0.02	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.02
Cr_2O_3	0.04	0.03	0.00	0.11	0.01	0.20	0.01	0.30	0.02	0.48	0.23	0.34
ZnO	0.05	0.20	0.01	0.23	0.05	0.03	0.01	0.02	0.01	0.02	0.00	0.03
BaO	0.06	0.04	0.01	<0.01	0.00	<0.01	0.00	<0.01	0.00	<0.01	0.00	<0.01
LOI (950°C)	11.23	10.95	0.73	8.00	0.46	7.42	1.32	5.56	0.90	3.78	1.00	5.49
Total	99.64	99.62		98.78		99.91		99.11		99.06		100.40
Free CaO				0.40	0.06	0.85	0.00	2.05	0.40	5.14	0.61	7.86
Density (g/cm^3)		2.68	0.05	2.80	0.04	2.98	0.10	3.26	0.06	3.44	0.03	3.27
pH	8.72	5.90	1.10	10.78	0.22	11.59	0.13	12.09	0.02	12.26	0.04	12.08

Note: $\bar{X}$ and σ, respectively, denote average and standard deviation; all samples aged for 365 days except controls (no aging).

Table 6. Summary of Quantitative XRPD Results for 100% DM, 100% SSF, and DM-SSF Blends (Percent by Weight)

Phase	Molecular formula	PDF[a]	CSD[b]	100% DM control	100% DM		80/20 DM-SSF		50/50 DM-SSF		20/80 DM-SSF		100% SSF		100% SSF control
					$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	
Silicon dioxide	SiO_2	97-002-9817	39830	31.84	42.81	2.54	33.08	6.30	24.50	4.79	10.76	1.36	4.34	0.24	2.66
Muscovite/Illite	$KAl_2(Si_3Al)O_{10}(OH)_2$	00-043-0685		48.56	41.06	5.69	24.93	4.59	12.51	1.58	12.57	1.83	—	—	—
Clinochlore 1B	$(Mg_5Al)(Si, Al)_4O_{10}(OH)_8$	00-024-0506	63193	11.74	8.63	2.20	5.42	0.87	6.30	0.71	—	—	—	—	—
Cronstedtite 2T	$Fe_3(FeSi)O_4(OH)_5$	97-001-6963	18194	3.00	3.67	0.59	—	—	—	—	—	—	—	—	—
Qunitinite 2H	$Al_2Mg_4(OH)_{12}(CO_3)(H_2O)_3$		82874	2.87	2.67	0.62	2.98	1.49	—	—	—	—	—	—	—
Albite	$NaAlSi_3O_8$	00-019-1184		2.00	1.17	0.44	—	—	—	—	—	—	—	—	—
Larnite	Ca_2SiO_4	97-001-0561	963	—	—	—	2.00	0.98	4.02	2.62	10.67	1.32	12.52	0.97	20.85
Magnesium Ferrous Oxide	$(MgO)_{0.432}(FeO)_{0.568}$	97-004-2976	60696	—	—	—	3.69	2.69	5.23	1.47	12.80	1.13	14.85	3.00	16.28
Srebrodolskite	$Ca_2Fe_2O_5$	97-001-4942	15059	—	—	—	2.57	2.20	5.63	2.38	10.71	0.90	12.87	0.63	11.7
Magnetite	$Fe_{2.942}O_4$	97-006-2364	82449	—	—	—	2.53	1.98	4.35	1.44	7.23	0.86	8.91	0.48	8.3
Calcite	$CaCO_3$	00-005-0586		—	—	—	—	—	4.95	1.67	5.72	0.35	7.94	1.82	7.87
Mayenite	$(CaO)_{12}(Al_2O_3)_7$	97-001-2803	6287	—	—	—	—	—	—	—	0.65	0.34	0.42	0.07	6.7
Wuestite	$Fe_{0.925}O$	97-006-2153	82235	—	—	—	—	—	1.75	0.76	2.77	1.06	4.35	1.85	4.36
Lime	CaO	97-002-1810	26959	—	—	—	—	—	—	—	1.09	0.10	1.50	0.31	2.66
Portlandite	$Ca(OH)_2$	97-007-9620	202225	—	—	—	—	—	—	—	1.76	0.77	4.63	2.21	—
Amorphous phase				0	0	0	22.77	2.11	30.77	5.91	23.27	3.89	27.67	4.97	18.6
Total				100.01	100.01		99.98		100.00		99.99		99.99		99.98

Note: $\bar{X}$ and σ, respectively, denote average and standard deviation; all samples aged for 365 days except controls (no aging).

[a] Powder diffraction file no. from ICDD (2004).

[b] Crystal structure database no. from ICSD (2011).

has occurred; (2) significant differences exist between the modeled, dilute aqueous system and the real system; (3) the extracted solution was oversaturated with respect to Fe (II); and/or (4) the system had not yet achieved equilibrium.

Although there are certainly heterogeneity issues at stake, the most plausible explanations for the Fe concentrations plotting above the Fe(II) solubility line are likely associated with oversaturation (as has been observed in Cr-containing systems) and nonequilibrium effects (Cao and Dermatas 2008). More specifically, the ANC-Fe experiments described by Grubb et al. (2011a) illustrated that the 100% SSF (control) does not leach Fe above pH ~ 7.3 (<0.05 mg/L), as shown in Fig. 3, a factor of 6 times below the USEPA secondary drinking water criteria of 0.3 mg/L. Comparison of the ANC, TCLP, and SPLP values shows that many dissolved Fe values were below the detection limit (BDL) for the respective tests. Two TCLP outliers occur in the Fe insolubility region at a similar pH to the longer duration acid neutralization capacity (ANC) test, suggesting that these TCLP solutions were oversaturated or were not close to equilibrium. Likewise, for the DM-SSF blends at pH > 7, the TCLP values almost always plot higher than the SPLP values (many BDL), again suggesting that those replicates had not attained or approached equilibrium. Because the ANC tests performed on 100% SSF involved greater amounts of iron than any of the DM-SSF blends and the extraction time was more than twice as long as the TCLP/SPLP procedure, it seems reasonable to conclude that the iron concentrations for the DM-SSF blends should be less than 0.05 mg/L for pH > 7. However, as the 100% DM is increasingly acidified (TCLP versus SPLP data), a strong Fe leaching potential is indicated by Fig. 3, as expected.

Arsenic Leaching Analysis

Now, arsenic will be discussed. Arsenic background concentrations in MD are 4–11 mg/kg (MDE 2008), yet the nonresidential cleanup criteria was, nevertheless, promulgated at least 2 times below the lower bound (Table 3). Thus, for the PPL suite of metals, the As content of the DM is the only remaining exceedance related to the MDE criteria, even though several DM-SFF blends and the 100% SSF could be potentially used as-is in neighboring PA, VA, and DE; short truck hauls and barge trips from the Cox Creek DMCF. However, it is commonly recognized that total metal concentrations occurring in soils, byproducts, or other construction materials rarely have anything to do with metals leachability, bioavailability, or hazard in its final configuration. Thus, it is more fruitful to focus on actual metals leaching to evaluate and anticipate arsenic behavior under different exposure conditions. In this way, appropriate engineering controls and permitting strategies can be applied, if necessary.

Fig. 4 presents the TCLP-As and SPLP-As leaching results from the 365-day old field samples of 100% DM, 100% SSF, and the DM-SSF blends by using open and solid symbols, respectively. For comparison purposes, the TCLP-As criterion (5.0 mg/L) and the DLs of the TCLP and SPLP tests are shown. The DM C_o limit (1.3 mg/L) denotes the equivalent aqueous concentration of arsenic when assumed to be fully leachable from the 100% DM based on Table 3 and a liquid:solid ratio of 20:1 (or, 26.0 mg/kg divided by 20). The maximum leachable As concentration varies with the DM-SSF blending ratio, eventually taking on the value of 0.09 mg/L for the 100% SSF (SSF C_o limit). From Fig. 4, it becomes clear that the concepts of TCLP and SPLP are relative. The postextraction (final) pHs are strongly dependent on the buffering capacity of the solid, as illustrated by the overlapping horizontal spreads in the As concentration data by test procedure and blend ratio.

All total dissolved As concentrations shown in Table 4 plot at or near the DL for either extraction test. This makes it difficult to assess the significance of the As concentrations considering that aggressive acids (not water) were added to the solids. The results, nevertheless, approach the USEPA maximum contaminant level (MCL) for arsenic in drinking water of 0.01 mg/L, despite the significant matrix interferences occurring in these concentrated, nonideal extraction solutions. As shown in Table 4, 67% (10/15) and 93% (14/15) of the TCLP-As and SPLP-As concentrations were BDL. Note that the DLs in this study were less than the previously tested UCS specimens aged for 360 days (Grubb et al. 2011b). However, in longer duration ANC tests on 100% SSF using concentration nitric acid, the ANC-As concentrations were BDL (<0.005 mg/L) for pH > 7 (Grubb et al. 2011a).

To evaluate the significance of the TCLP-As and SPLP-As results, the thirty As concentrations shown in Table 4 were used to estimate a 95% upper confidence limit of the mean TCLP/SPLP extraction concentration [95% upper confidence limit (UCL)]. Specifically, because of the significant pH overlap in the data, all 30 As concentrations were input into USEPA's UCL Pro software (USEPA 2009), yielding a 95% UCL concentration of 0.0214 mg/L on the basis of the Student's t-UCL method. This 95% UCL value is less than the SPLP DL and close to the TCLP DL (worst-case exposure condition), further corroborating the likelihood that As concentrations would remain BDL when water is equilibrated with the compacted 100% DM, 100% SFF of the DM-SSF blends. The natural low permeability ($<10^{-5}$ cm/s) of the DM-SSF blends (Malasavage et al. 2012) coupled with the use of cover soils further reduces the likelihood that significant environmental threats will be posed by arsenic, even when 100% DM is used (highest total As content).

Lastly, the authors consider the % As extraction based on the total As available versus leaching results. The pK_{a1} of arsenite is approximately 9.17 (Cornelis et al. 2008), so As(III) persists as neutral (inorganic) species below the pK_{a1}, making it essentially nonsorptive and less prone to interactions with dissolved Ca, Mg, and Fe, which tend to promote precipitation reactions with oxyanions (including As). In fact, As(III) concentrations leached from 100% SSF dosed with 500 mg As/L where essentially uniform below pH 11 (Grubb et al. 2010b). By analogy, in the DM-SSF system (Fig. 4), the As(III) would likely increase monotonically with decreasing pH because the total As concentration in the DM-SSF blend is proportional to the DM content. This trend, however, was not observed.

For As(V), leaching appears to be related to both pH controls and sorption. The acidity constants of triprotic arsenic acid (H_3AsO_4) are respectively 2.3, 6.99, and 11.8, as shown in Fig. 4. Thus, for the 100% DM (26 mg/kg), the TCLP-As and SPLP-As results were both BDL, indicating an As extraction ratio <1.5% from the DM below pH = 8.5. This result makes sense because the prevailing species of As(V) is $H_2AsO_4^-$, which strongly sorbs to iron containing media and clay minerals below pH = 6.99 (Manning and Goldberg 1996; Waltham and Eick 2002).

Mineralogy

Tables 5 and 6, respectively, present the average and standard deviation of the XRF and quantitative XRPD results for the 100% DM, 100% SSF, and their blends on the basis of three replicates from each trial highway embankment. The XRF results of the virgin (unaged) 100% DM and 100% SSF laboratory controls from Grubb et al. (2011a) are presented in both tables for comparison purposes. The XRF results were used in two main ways: (1) to confirm the effectiveness and accuracy of the DM-SSF blending process on the basis of chemistry, which was conducted on the basis of particle gradation, and (2) for mass balance purposes for quantitative XRPD.

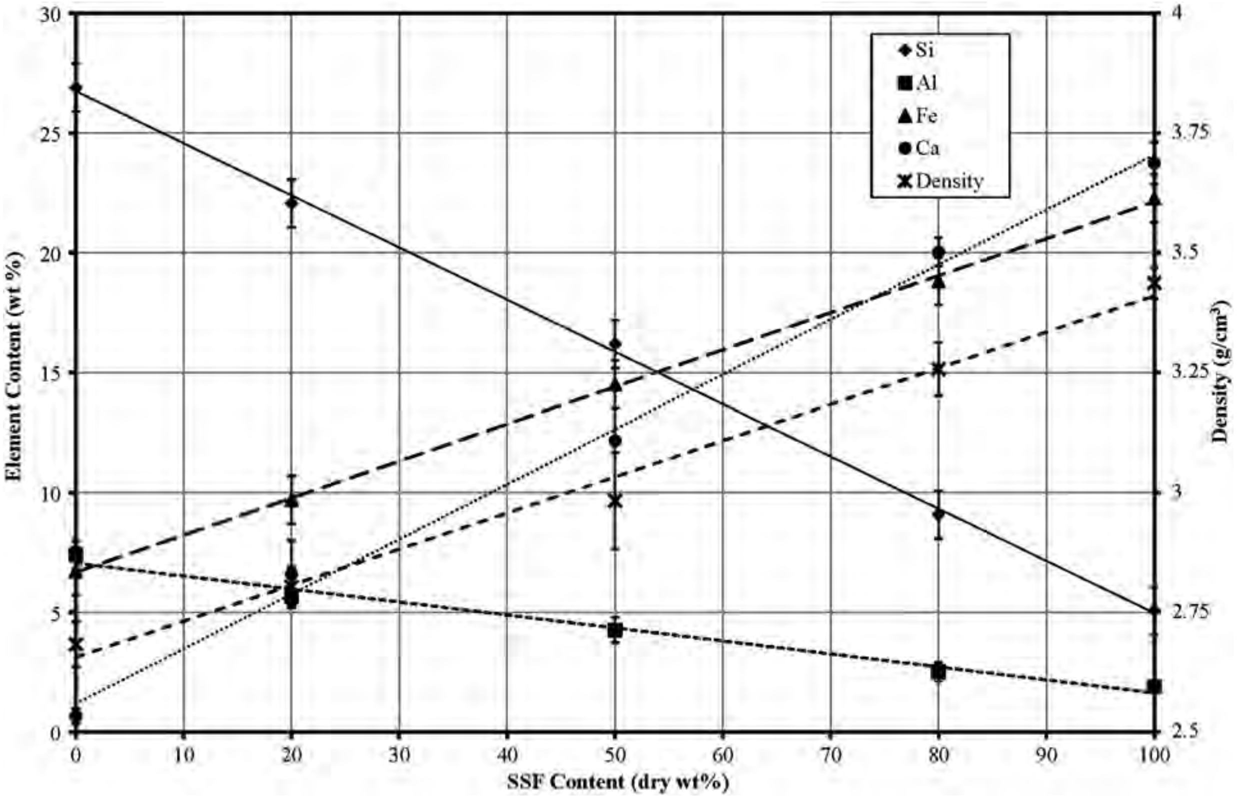

Fig. 5. Bulk chemistry and density of DM-SSF blends as a function of SSF content

Table 5 shows the mineralogy of the 100% DM control sample has less silica and more alumina than that 100% DM from the field project, mainly because the latter had a greater sand content (Malasavage et al. 2012) and thus, more silica. Fig. 5 shows the bulk chemistry data for the major cations (Si, Al, Fe, Ca) and density versus a straight line interpolation on the basis of the endpoint

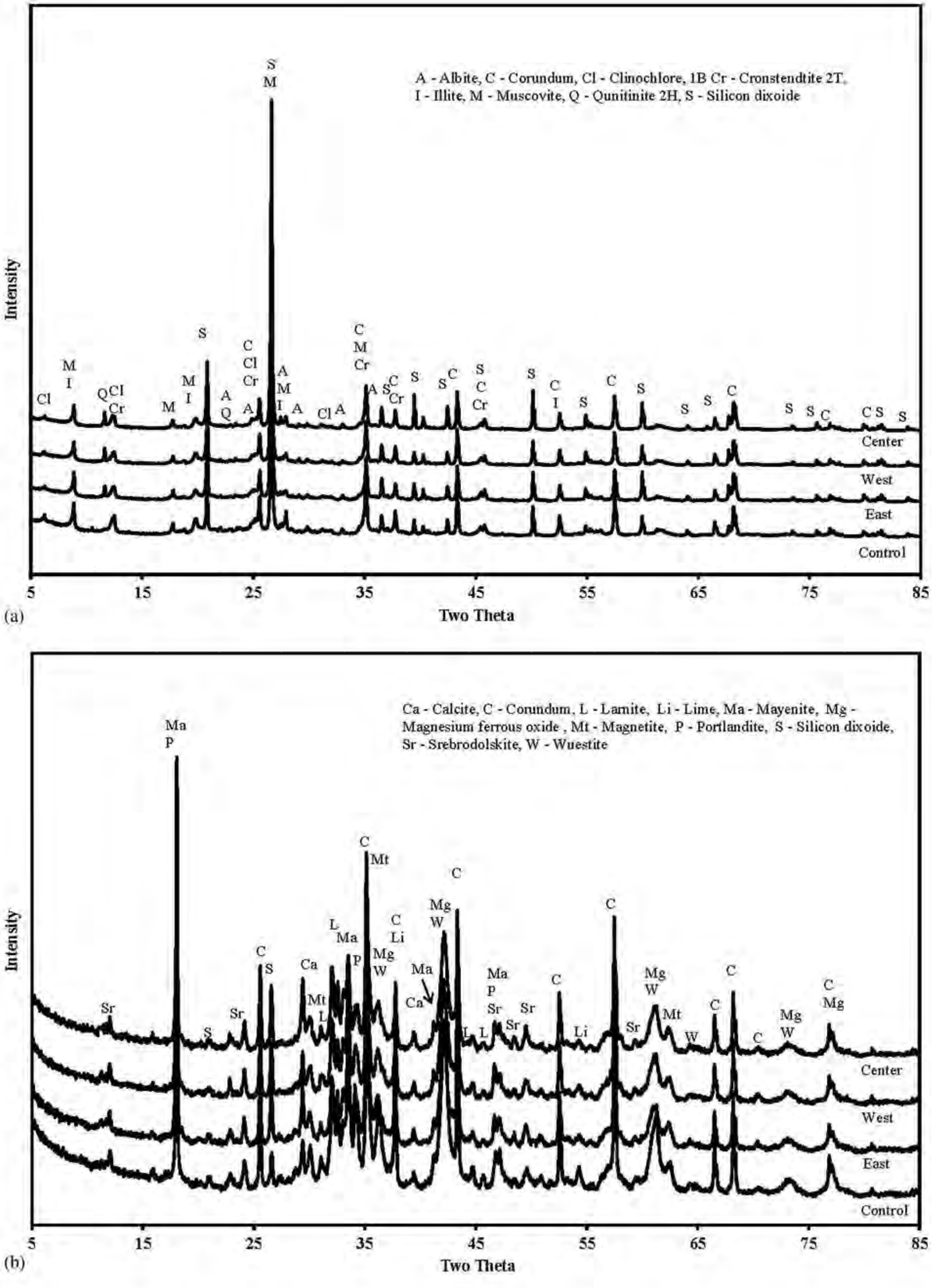

Fig. 6. Annotated diffractograms of 100% DM and 100% SSF media replicates and controls

chemistries of the 100% DM and 100% SSF. The proximity of the data to the trend-lines (especially density) confirms that the field blending criteria established on the basis of gradation curves appear to be an effective quality assurance/quality control approach. The only anomalous data set is sulfur (Table 5), which is parabolic in nature, and the exact reason for this is not known because both 100% DM and 100% SSF have low SO_3 contents (Table 5). The pH data of the exhumed trial highway embankment blends (Table 5) indicates that low doses of the SSF media have a significant ability to buffer the otherwise acidic DM to alkaline pH values for extended periods of time (e.g., a year).

Fig. 6 shows the annotated diffractograms for each 100% DM and 100% SSF field replicate sample versus their respective controls. Visually, there are very subtle differences that contribute to the average values and standard deviations shown in Table 6 for the raw materials. The influence of materials bending on the diffractograms is reflected in Fig. 7, which presents the XRPD data from each 365-day aged field sample taken from the central location of each embankment. The transition from a silica/alumina dominated chemistry (100% DM) to calcium/iron dominated system (100% SSF) is evident.

Table 6 shows that the major crystalline phases identified in the 365-day-old 100% DM were silicon oxide (SiO_2) and muscovite/illite [$KAl_2(Si_3Al)O_{10}(OH)_2$]. The minor phases observed were clinochlore [$(Mg_5Al)(Si,Al)_4O_{10}(OH)_8$], cronstedtite [$Fe_3(FeSi)O_4(OH)_5$], quintinite [$Al_2Mg_4(OH)_{12}(CO_3)(H_2O)_3$], and albite ($NaAlSi_3O_8$). The respective quantities of total (elemental) Si and Al calculated from the observed phases were approximately 31 and 9% compared to 27 and 7% based on the XRF results. There was no amorphous content associated with the 100% DM and no significant compositional differences from the 100% DM control. The exceptions to this were the quartz and muscovite/illite contents, very likely caused by the difference in the sand contents between the lab control and field samples. From a bulk chemistry perspective, it appears that aging had no effect on the 100% DM, save perhaps pH (acidification), as previously report by Grubb et al. (2011a) and as observed by Daniels et al. (2009).

Larnite (dicalcium silicate, Ca_2SiO_4) and quartz (SiO_2) were the main silicate phases observed in the the 365-day-old 100% SSF media. Likewise, magnesium ferrous oxide [$(MgO)_{0.432}(FeO)_{0.568}$], srebrodolskite (dicalciumferrrite, $Ca_2Fe_2O_5$), magnetite ($Fe_{2.942}O_4$), and wuestite ($Fe_{0.925}O$) were the key iron phases. The quantities of total (elemental) Fe and Si calculated from the observed phases were approximately 22 and 4%, respectively, which were almost identical to the XRF results. Other calcium containing phases included calcite ($CaCO_3$), lime (CaO), and portlandite [$Ca(OH)_2$]. The quantity of total Ca calculated from the observed phases was approximately 16%, somewhat lower than the XRF result (~24%). This suggests that the remaining Ca content was likely associated with the amorphous content. Although the SSF source materials for the laboratory (control) and field demonstration project were selected at different intervals (2009 versus 2010), which may have contributed slightly to their differences in composition, the disappearance of larnite, persistence of portlandite, and high amorphous content (27.7%) of the 365-day-old 100% SSF media are indicative of ongoing reactions and therefore, aging.

As expected, the major phases associated with the 100% DM and 100% SSF were observed in all DM-SSF blends in concentrations that generally reflected the blending ratios (Table 6, Fig. 7). Most significantly, no new crystalline phases were observed in the DM-SSF blends, such as those commonly associated with typical cementation reactions. Thus, although it appears that the lime contained in the 100% SSF media hydrated to portlandite, its quantities were likely insufficient to produce cementitious end products with Si and/or Al. Not surprisingly, when the DM-SSF system is Ca-rich (high SSF content), it is Si and Al poor in the bulk chemistry sense (as shown in Fig. 5). This opposing constraint exists because of blending, regardless of whether the silica and alumina are even physically or chemically available for reaction.

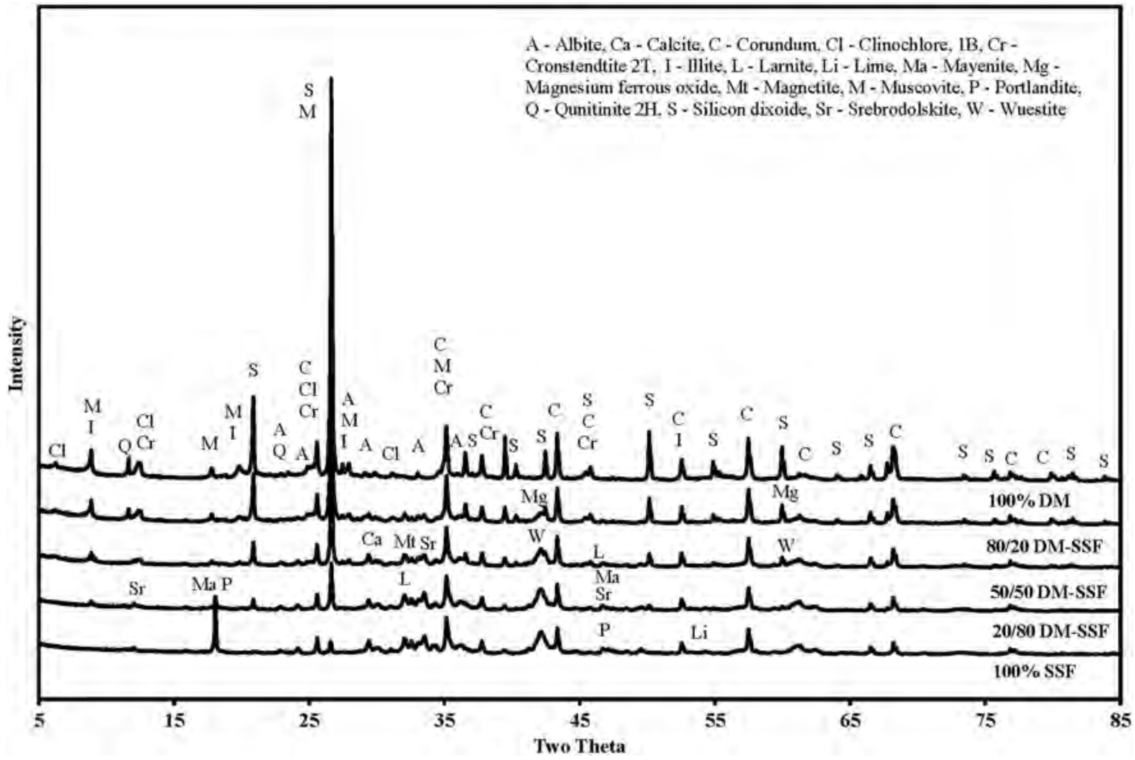

Fig. 7. Annotated diffractograms for 100% DM, 100% SSF, and DM-SSF blends

These trends are consistent with Chrysochoou et al. (2010), who showed that 10% lime in stabilized dredged material (SDM) blends readily hydrated to portlandite but progressed no further after 6 months of curing because of the limited reactivity of DM (slow release of soluble Si/Al). Although the SDM study involved the blending of two fine grained media (lime, DM) at much higher water contents, potential cementitious reactions will likely progress even slower (if at all) in the DM-SSF blends because of particle size effects and the low in situ moisture contents of the compacted blends. Also, it is possible that lime in the SSF media could be embedded in other phases and therefore, not available for reaction despite its detection by XRPD. This was evident when milling of the SSF media to pass the Number 100 sieve (<0.15 mm) significantly increased the ANC of the 100% SSF because of the dissolution of lime and/or other pH buffering minerals (Grubb et al. 2011a). Lastly, the lime and silica in the DM-SSF blends may have been passivated by the formation oxide coatings, which would limit their reactivity. Thus, while no cementitous crystalline phases were observed in the DM-SSF blends after 365 days in the field, reactivity cannot be ruled out, even though it appears unlikely and without geotechnical consequence [e.g., inundated DM-SSF blends showed no swell after 240 days (Grubb et al. 2011a)].

Conclusions

On the basis of these multiple lines of evidence, analyses, and the prior research involving these media (especially Grubb et al. 2010b, 2011a), arsenic leaching from the 100% DM, 100% SSF, and the DM-SSF blends is extremely low to negligible on the basis of the expected concentrations of total As in the Baltimore harbor DM (up to 100 g/kg). The fluctuating detection limits in these studies, although inconvenient, have illustrated that the behavior of As in the DM-SSF blends appears to be largely independent of the blending ratio. As little as 20% SSF blending promotes significant geotechnical improvement while maximizing the DM content such that the resulting 80/20 DM-SFF blend could be used for large-scale highway embankment construciton, port facility construction, and similar geotechnical uses. The geoenvironmental improvements are immediate and increase with aging, and perhaps more significantly, appear to exclude the formation of crystalline cementitious end-products, significant changes in moisture content, or the potential for swell (Grubb et al. 2011a).

Thus, although the SSF has a high capacity to immobilize arsenic (Grubb et al. 2010b), on its own the 100% DM containing up to ~125 mg/kg did not leach above SPLP detection limits (0.05 mg/L). The UCS aging study (Grubb et al. 2011b) showed aged DM-SSF blends containing up to approximately 45 mg/kg were BDL on SPLP-As leaching (<0.056 mg/L). This field aging study has shown the 95% UCL on the average leached As concentration to be less than the SPLP DL (0.028 mg/L) and almost matching the TCLP DL (0.02 mg/L) for DM containing approximately 26 mg/kg As. Given the standard permit approaches for beneficial use, which would likely entail that the proposed uses of the DM-SSF blends exclude residential sites, would occur under paved surfaces with limited infiltration and/or require a cover soil of at least 15.2 cm (6 in.) to support vegetative cover, it appears that the opportunity to promote large-scale recycling of these materials in the urban/development environment (already on potable water) far outweighs any potential risk using these materials on the basis of arsenic issues.

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Notation

The following symbols are used in this paper:

$c'_{\mathrm{CI\bar{U}}}$ = effective cohesion, kPa;
f_s = sleeve friction, MPa;
q_t = tip resistance, MPa;
u = dynamic pore pressure, MPa;
w = water content, %;
γ_d = dry density, kN/m^3; and
$\phi'_{\mathrm{CI\bar{U}}}$ = effective friction angle.

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Immobilization of Lead, Tungsten, and Phosphate by Steel Slag Fines: Metals Thresholding and Rate Studies

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Abstract: This study presents an evaluation of 9.5-mm minus steel slag fines (SSF) to immobilize lead (Pb), tungsten (W), and phosphate (P as PO_4) at total contaminant dosing concentrations of 10,000 mg/kg (W, PO_4) and 100,000 mg/kg (Pb), as a potential new construction material for firing-range backstop berms (or treating firing-range soils). Direct contaminant uptake and kinetic rate, rerelease, and mineralogical studies were undertaken for metal loadings totaling up to six combinations of Pb, W, and PO_4. Batch rate studies showed that >95% of Pb and W were removed from aqueous solution within 2 h in the presence of the SSF media. For equivalent aqueous doses of 500 mg/L (W, PO_4) and 5,000 mg/L (Pb), the TCLP-Pb concentrations for all multielement suites were <0.3 mg/L, which is much less than the TCLP-Pb criterion of 5.0 mg/L. For the P-Pb-W suite (all three contaminants present simultaneously), the SPLP-W concentrations (<0.35 mg/L) were lower than the TCLP-W concentrations (<1.1 mg/L) regardless of PO_4 dose. Leached phosphate concentrations from the P-Pb-W suite were below or hovered at the detection limit (0.5 mg/L) under SPLP and TCLP conditions, respectively. A mineralogical evaluation revealed that lead pyromorphite $[Pb_5(PO_4)_3OH]$ and scheelite $[Ca(WO_4)]$ were the key PO_4-containing, Pb-containing, and W-containing phases. **DOI: 10.1061/(ASCE)HZ.2153-5515.0000214.**

Author keywords: Steel slag fines (SSFs); Immobilization; Lead; Tungsten; Phosphate.

Introduction

The U.S. Department of Defense (DoD) operates more than 2,600 small arm firing ranges (SAFRs) (ITRC 2003). The types of munitions (shot, pellets, and small/large caliber) used at SAFRs (and the other 9,000 nonmilitary outdoor firing ranges) invariably results in the deposit of many heavy metals and metalloids throughout the range (floor, backstop berms), which vary in particle size from whole projectiles to microscopic metallic dust. Spent bullet loading at SAFRs is estimated to be on the order of 80,000 tons per year (Larson et al. 2005) and the key metals of environmental interest are lead (Pb), copper (Cu), nickel (Ni), tungsten (W), antimony (Sb), and zinc (Zn) (Dermatas et al. 2004a, b, c; Bednar et al. 2009), although other metals may be present depending on the exact alloys (and their quality) used for jacketing, tracers, incendiary devices, and armor penetration (Ag, As, Ba, Bi, Co, Sn, U) (Robinson et al. 2008; Felt et al. 2011; Griggs et al. 2011).

Typically, the earthen backstop berms behind the target locations are composed of native soil and therefore can result in significant regulatory challenges for environmental range management; acidic soils have resulted in elevated levels of heavy metals in both leachate and surface water from SAFRs (Larson et al. 2005), and neutral to basic soil pH can produce storm-water runoff with significant amounts of metals associated with suspended solids (Tessier et al. 1982). In 2001, the U.S. EPA issued a best management practice (BMP) for the management of firing ranges that included the application of natural alkaline minerals and phosphate synthetic compounds (USEPA 2001). Generally, alkaline materials such as cement, lime (both costing approximately \$100/ton), and crushed limestone are used to raise soil pH to precipitate Pb, Cu, and Ni, whereas phosphate compounds are used to promote the immobilization of Pb as lead phosphates, or pyromorphites $[Pb_5(PO_4)_3X$ where $X = Cl^-, OH^-, F^-]$, which are the thermodynamically most stable and most insoluble Pb minerals over a large pH and Eh (redox) range (Nriagu 1974). While steel slag fines (SSF) media and limestone may have similar costs, the SSF media is not only the more sustainable option, it also produces much more reactive calcium (Ca) than limestone (Grubb et al. 2011b; Huijen and Comans 2006).

Studies have shown that W is highly soluble under neutral to alkaline conditions, whereas Pb is amphoteric; i.e., soluble under strongly acidic and alkaline conditions (Bednar et al. 2009; Koutsospyros et al. 2006; Karachalios et al. 2011). Therefore, raising soil pH to immobilize Pb may mobilize W; but lowering soil pH to immobilize W can mobilize Pb. Moreover, the unintended consequences of the application of phosphates to SAFR soils are that it can result in (1) a secondary phosphate contamination of surface waters and groundwaters that ultimately promotes eutrophication of the receiving streams, rivers, high-valued wetlands, and estuaries (Larson et al. 2005; Chrysochoou et al. 2007; Clausen and Korte 2009); and (2) enhanced mobilization of toxic oxyanions (such as Sb, W, and U) by factors up to 100 depending on soil conditions (Koutsospyros et al. 2006; Chrysochoou et al. 2007; Bednar et al. 2009; Griggs et al. 2011). In fact, PO_4 is a reagent known to solubilize W in analytical procedures (e.g., OSHA method ID-213) (OSHA 1994).

Since the mobilization of oxyanions such as W and Sb was not necessarily anticipated by prior phosphate (PO_4 or P) applications

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targeting Pb immobilization, it remains a potentially sizable problem given that a minimum of 85 million rounds of W-containing rounds have been fired in SAFRs since 1999 (Clausen and Korte 2009), and the quantities of the traditional Pb/Sb rounds could be substantially higher. While the DoD and environmental remediation communities have come to grips with this reality, few options are available for SAFR soil treatment, including conventional stabilization/solidification (S/S) using cement, lime, and pozzolanic materials (Battelle 1997). Likewise, the research and development (R&D) of SAFR soil treatments/amendments, including various alkaline materials, phosphorus, sulfur, and iron-containing media of both natural and synthetic origin, have shown mixed results (Bednar et al. 2009; Karachalios et al. 2011).

Interestingly, slag media have demonstrated the ability to immobilize numerous heavy metals rapidly (Grubb et al. 2010b, c, 2011a, b, c; Jagupilla et al. 2012a, b) and have removed PO_4 successfully (Oguz 2004; Hedstöm and Rastas 2006; Pratt et al. 2007; McDowell et al. 2008; Jha et al. 2008; Bowden et al. 2009) and Pb (Dimitrova 2002; Kang et al. 2004; Liu et al. 2010a, b) from aqueous streams. More specifically, SSF media are a low-cost (approximately \$10/ton), widely available, and granular recycled material from the steel-making industry having a sand-sized (9.5 mm minus fraction) gradation, which makes it a good geotechnical substitute for the sands and native soils currently used as firing range backstop berm media. Accordingly, the objective of this research was to evaluate the SSF media for the simultaneous immobilization of P, Pb, and W for potential use in SAFR management and remediation.

Materials and Methods

The geotechnical characteristics of the SSF media used in this study have been evaluated extensively in the literature (e.g., Grubb et al. 2010c, 2011c). Briefly, the SSF media were derived from the basic oxygen furnace (~1,700°C) at the Sparrows Point steel mill complex in Baltimore, Maryland. Typically, after the molten slag from the kettles is dumped on the slag pile, it air-cools for a minimum of 24 h. Afterward, the bulk steel slag is processed through a conventional aggregate crushing and screening plant, with the coarse-sized aggregates going to commercial construction. The screenings from this plant, or fines (9.5 mm minus fraction), are stockpiled in dedicated locations. The resulting SSF media are granular and nonplastic, classifying as an SP or SW soil by the Unified Soil Classification System (USCS), typically with less than 10% material passing the No. 200 (0.075-mm) sieve (Grubb et al. 2011c).

Thresholding Experiments

Freshly crushed SSF media were used at its natural moisture content (approximately 16%). Two series of thresholding (metal immobilization) experiments were conducted. First, the immobilization of each element (Pb, PO_4, and W) was evaluated (in a single-element suite). A multielement suite involving combinations of P, Pb, and W (P-Pb, P-W, Pb-W, and P-Pb-W) then was evaluated due to its potential relevance to firing range contamination scenarios. Single aqueous metal solutions were prepared by dissolving each individual highly soluble salt in deionized (DI) water to achieve target doses equivalent to 100–100,000 mg/kg to the SSF media, depending on the metal. The following metal salts were used: $NaH_2PO_4 \cdot H_2O$ (99% purity); $Pb(NO_3)_2$ (>99%purity); and, $Na_2WO_4 \cdot 2H_2O$ (99.3% purity), all from Fisher Scientific (Cambridge, MA). In practice, the equivalent aqueous doses of the target metals were used based on a liquid:solid ratio of 20:1, consistent with EPA Method 1311 (U.S. EPA 1986). Thus, a Pb target dose of 100,000 mg/kg was added as a 5,000-mg/L solution.

The SSF media was first individually wetted (sprayed) with each metal-spiked DI water solution and was mixed thoroughly using a stainless steel spoon. Each batch of metal-spiked SSF media was then stored in sealable plastic bags and allowed to mellow for 30 days. After mellowing, all the samples were air-dried and used for analytical testing. To batch sufficient SSF media at the 100,000 mg/kg Pb level, equivalent aqueous solutions of Pb were prepared based on the solubility of the $Pb(NO_3)_2$ salt (~52 g/100 mL at 20°C). Due to the volume required, the solution was contacted with the SSF media in a 500-mL polypropylene bottle that was rotated for 18 h in a standard TCLP tumbler [U.S. EPA Method 1311 (U.S. EPA 1986)]. The mixture then was transferred to an open stainless steel bowl in a vacuum hood for approximately 24 h until the free liquid evaporated. Using a spatula, the moist SSF media next was returned to its polypropylene bottle and mellowed for the balance of the 30 days. A total metals analysis of the process revealed negligible loss of Pb.

For the multielement suite, the W and Pb concentrations were fixed at 10,000 and 100,000 mg/kg, respectively. W spiking always occurred first, using the procedure previously described. For the Pb-W suite, the W-spiked SSF media was allowed to mellow and air-dry for approximately 24 h prior to Pb application by this procedure. In this way, the joint deposition of Pb and W on the SSF media was simulated. The Pb-W spiked SSF media was allowed to mellow for a total of 30 days in sealed containers prior to analytical testing. For the P-Pb and P-W suites, the Pb-spiked and W-spiked media were mellowed for 30 days prior to PO_4 application, at rates of between 100 and 10,000 mg/kg. The P-Pb and P-W spiked media then were allowed to mellow for an additional 30 days in sealed bags (60 days total), as previously described. For the P-Pb-W suite, the Pb-W spiked media was air-dried after 30 days, spiked with PO_4, and mellowed for an additional 30 days (60 days total) in sealed bags prior to analytical testing. After 60 days of mellowing, the samples were air-dried and used for analytical testing. In each case, the mellowed pH of the contaminant-spiked SSF media and the post extraction pH values were measured by ASTM D4972-01 and U.S. EPA Method 1311/1312, respectively.

TCLP and SPLP analyses were conducted in accordance with U.S. EPA Methods 1311 (U.S. EPA 1986) and 1312 (U.S. EPA 1986). In all cases, the sample size for the TCLP and SPLP analyses was reduced to 25 g and the samples were analyzed in triplicate. TCLP and SPLP analyses were followed by ICP-OES analysis for all metals (U.S. EPA Method 6010c). Prior to analysis, the solutions were acidified using 1% HNO_3. After each triplicate series, the ICP was sequentially flushed with 1% HNO_3 and DI water to avoid cross-contamination from previous runs.

A modified OSHA method (ID-213) (OSHA 1994) was used for total digestion of the SSF media to determine the W concentrations. The procedure was amended by adding 2 ml of H_2O_2 after step 8 in Section 3.5.3 of the ID-213 procedure to improve the W recoveries (Betancur 2007; Grubb et al. 2009). Also, a watch glass was used to cover the samples on the hot plate to promote refluxing. The procedure also included the digestion of W powder, and a matrix spike was used for quality control. W concentrations were determined by ICP-OES analysis [U.S. EPA Method 6010c (U.S. EPA 2007)].

Batch Kinetics

Batch kinetics experiments were conducted using individually prepared aqueous solutions containing the aforementioned W and Pb salts fixed at doses equivalent to 10,000 mg/kg (W) and

100,000 mg/kg (Pb). Sacrificial samples were prepared for each metal and time interval. The selected sampling intervals were 1, 2, 5, 10, and 60 min, and 3, 6, 12, and 18 h. Procedurally, 6.5 g of dry SSF media was placed in a 130-mL bottle. The aqueous metal solution was added to each sample (total liquid volume of 130 mL) using an L:S ratio of 20:1. The resultant slurries (in triplicate; A to C) were mixed in a standard TCLP tumbler at 30 revolutions per minute (rpm). At each interval, designated samples were removed and the supernatants were passed through a 0.45-μm nylon membrane filter. The pH of the leachate was recorded using an Accumet AR20 pH–meter (Accumet Engineering, Hudson, NH). All samples were stored in the refrigerator at a temperature of 4°C before analysis by ICP-OES by U.S. EPA Method 6010c.

Acid Neutralization Capacity

Acid neutralization capacity (ANC) testing (Isenberg and Moore 1992) was conducted on the P-Pb-W spiked SSF media (aged 60 days) at the 10,000 mg/kg PO_4 dosing level. The procedure consisted of equilibrating the P-Pb-W spiked SSF media with increasing equivalents of reagent (acid or base) per kilogram of dry solids. Specifically, 6.5 g dry weight of each sample was placed in a series of 130-mL bottles. Incremental amounts of 15.8N nitric acid (HNO_3) were added to the sample using an L:S ratio of 20:1, as in the TCLP procedure. As the pH of the mellowed P-Pb-W spiked SSF media was approximately 10, base neutralization capacity (BNC) testing also was undertaken by adding incremental amounts of 10N sodium hydroxide (NaOH) to the sample to illustrate the impacts of additional alkalinity on the metal-spiked SSF media. All ANC/BNC samples were prepared in duplicate. The resultant slurries were tumbled in a standard TCLP tumbler for 48 h. The supernatants then were passed through a 0.45-μm nylon membrane filter, and the pH of the leachate was recorded using an Accumet AR20 pH-meter. All samples were stored in the refrigerator at a temperature of 4°C before they were analyzed by ICP-OES.

X-ray Powder Diffraction

X-ray powder diffraction (XRPD) and Rietveld quantification analyses (RQAs) were used to assess the mineralogical composition of all contaminant-spiked SSF media. XRPD sample preparation involved pulverizing 20 g of air-dried SSF media using a standard compaction hammer to break the larger particles to less than 2 mm. Afterward, a 2 g subsample from the pulverized SSF sample (<2 mm in size) then was micronized in a McCrone micronizing mill for 10 min using 7 mL cyclohexane as the milling fluid. The resulting slurry was air dried and then mixed with an internal standard (corundum, α-Al_2O_3, Sawyer, Lot No. C04-AO-41) on an 80:20 weight basis prior to XRPD analyses.

Step-scanned XRPD data was collected by a Rigaku Ultima 4 computer-automated diffractometer (Rigaku, Tokyo, Japan) using Bragg-Brentano geometry. Diffractometry was conducted at 40 kV and 40 mA using a diffracted beam graphite-monochromator with Cu radiation. The data was collected in the 2θ range of 5°–85° with a step size of 0.03° per 8 s. The qualitative and quantitative analyses of the XRPD patterns were performed using the *Jade* software version 7.5 (*Jade 7.5*) and the whole pattern fitting function of *Jade*, which is based on the Rietveld method (Rietveld 1969). The reference databases for powder diffraction and crystal structure data were the International Center for Diffraction Data database (ICDD 2004) and the Inorganic Crystal Structure Database (ICSD 2011), respectively.

Results

Thresholding Results

The results for the contaminant thresholding suites are summarized in Tables 1 and 2 and Figs. 1–5. All presented data denote the average of triplicate samples.

Table 1 shows the PO_4 thresholding results. Here, total PO_4 concentrations were not used as the basis for comparison because the SSF media itself contained approximately 10,334 ± 712 mg/kg PO_4, and comparisons made on the basis of aqueous concentrations were determined to be more reproducible and meaningful (Grubb et al. 2010a, b). The combination of the acidity associated with the PO_4 solution itself (3.86–4.32), and the TCLP solution depressed the TCLP-pH of the SSF media into the mid-7 range in some cases, while the SPLP-pH values remained above pH 12, consistent with the strong buffering capacity of the SSF media (Grubb et al. 2011c). All SPLP-PO_4 concentrations were below the detection limit (BDL; 0.5 mg/L) for all doses up to 500 mg/L (90%–99.9% removal). While the PO_4 removal exceeded 99.5% under TCLP conditions at the highest PO_4 doses, the TCLP-PO_4 concentrations nevertheless remained above 1 mg/L. The ability of SSF to immobilize PO_4 (alone) was very high, consistent with the literature on PO_4 removal by slags (Oguz 2004; Hedstöm and Rastas 2006; Pratt et al. 2007; McDowell et al. 2008; Jha et al. 2008; Bowden et al. 2009).

Table 2 shows the leaching results of the P-Pb-W thresholding suite for SSF media initially containing 100,000 mg/kg Pb and 10,000 mg/kg W. The results of the Pb-W only control also are shown for comparison purposes (see $PO_4 = 0$ mg/L). The data shown in Table 2 is visually reproduced in Figs. 1–5. When relevant, these figures show the single-element (e.g., PO_4, Pb, W only) and dual-element (e.g., Pb-W) control values arbitrarily plotted for

Table 1. PO_4 Thresholding Results for SSF Media

	PO_4 target dose[a]		PO_4				
	Totals (mg/kg)	Equivalent (mg/L)	Concentration (mg/L)	Removal (%)	Solution pH	Mellowed pH	Extracted pH
TCLP	100	5	0.62	87.65	4.32	11.49	6.94
	500	25	0.85	96.59	4.32	10.96	7.46
	1,000	50	0.84	98.33	3.86	11.01	8.53
	5,000	250	1.14	99.54	3.86	10.95	7.84
	10,000	500	1.72	99.66	3.86	10.85	7.55
SPLP	100	Same as above	<0.5	90.00	Same as above	Same as above	12.39
	500		<0.5	98.00			12.37
	1,000		<0.5	99.00			12.41
	5,000		<0.5	99.80			12.40
	10,000		<0.5	99.90			12.27

[a] Assumes liquid:solid ratio of 20:1.

Table 2. PO_4 Thresholding Results for SSF Media Spiked with 100,000 mg/kg Pb and 10,000 mg/kg W

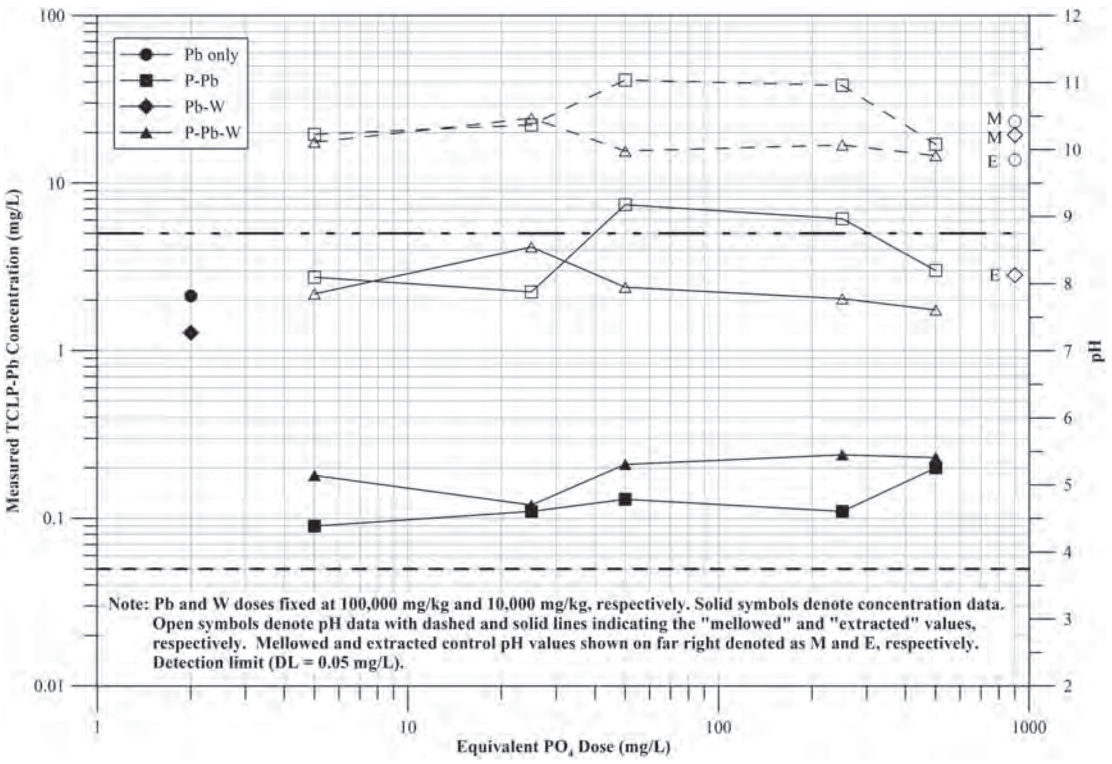
	PO_4 target dose[a]		PO_4		Pb		W			
	Totals (mg/kg)	Equivalent (mg/L)	Concentration (mg/L)	Removal (%)	Concentration (mg/L)	Removal (%)	Concentration (mg/L)	Removal (%)	Mellowed pH	Extracted pH
TCLP	0	0	NA	NA	1.28	99.97	3.52	99.30	10.22	8.13
	100	5	0.54	89.25	0.18	100.00	0.69	99.86	10.11	7.85
	500	25	0.51	97.97	0.12	100.00	1.09	99.78	10.47	8.55
	1,000	50	0.61	98.79	0.21	100.00	0.92	99.82	9.98	7.95
	5,000	250	0.5	99.80	0.24	100.00	0.95	99.81	10.07	7.78
	10,000	500	<0.5	99.90	0.23	100.00	0.85	99.83	9.91	7.61
SPLP	0	Same as above	NA	NA	124.67	97.51	1.28	99.74	Same as above	11.60
	100		<0.5	90.00	115.53	97.69	0.26	99.95		11.51
	500		<0.5	98.00	182.57	96.35	0.24	99.95		11.67
	1,000		<0.5	99.00	76.20	98.48	0.15	99.97		11.49
	5,000		<0.5	99.80	101.97	97.96	0.22	99.96		11.47
	10,000		<0.5	99.90	45.08	99.10	0.31	99.94		11.37

[a] Assumes liquid:solid ratio of 20:1.

visual comparison purposes at a PO_4 concentration of 2 mg/L. Likewise, the corresponding mellowed pH values of the Pb, W and Pb-W controls typically are shown in the rightmost locations of Figs. 1–5.

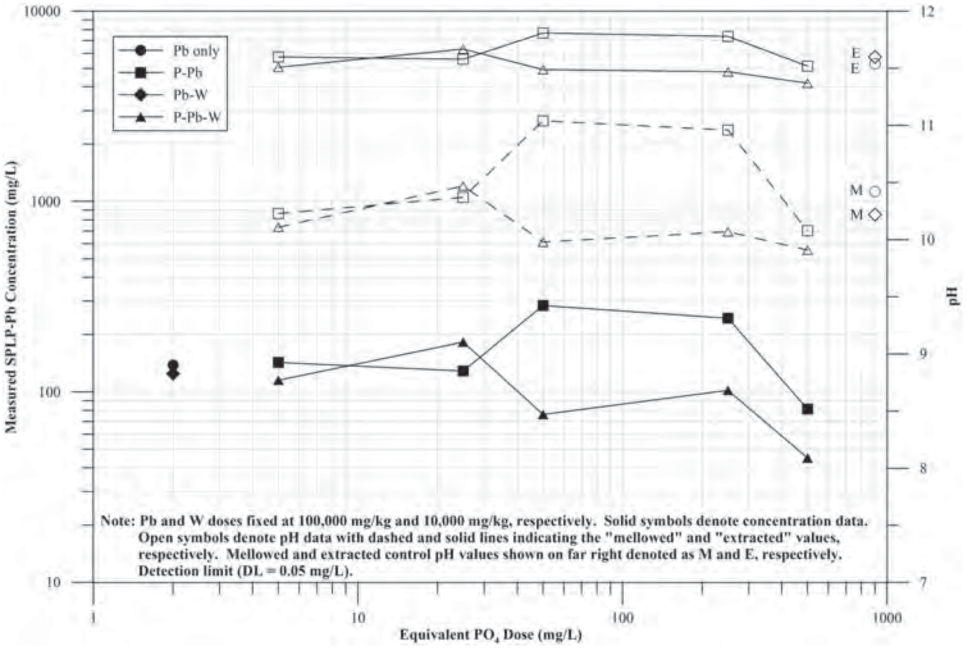
The primary goal of this research was to document the immobilization of Pb and W, followed by any adverse impacts that the application of PO_4 had on W leaching and the corresponding potential for secondary PO_4 contamination. Accordingly, Fig. 1 presents the TCLP-Pb concentrations along with the mellowed and extracted pH for the entire P-Pb-W thresholding suite. The Pb concentrations satisfied the TCLP-Pb criterion of 5.0 mg/L for all testing conditions, with no concentration greater than 0.3 mg/L. Adding W to the Pb-only suite produced a small decrease in the TCLP-Pb concentration. Adding PO_4 to the Pb-only and/or Pb-W suites promoted approximately an order of magnitude reduction in the TCLP-Pb concentrations, with the P-Pb suite producing the lowest overall concentrations for each PO_4 dose. The extracted pH values were approximately 2 units lower than the mellowed conditions for all PO_4 doses, with the pH almost always lower in the P-Pb-W suite. Note that the PO_4 solution is acidic (Table 1), and the combined effect of its acidity along with the TCLP solution lowered the pH of the SSF media by approximately 3–3.5 units (to near-neutral conditions) at the highest PO_4 doses. Thinking ahead to possible field applications, this is about the same time that the SSF media potentially used as a filter medium or SAFR backstop berm could be designed for changing out based on the system pH (7.5–9.5) as this coincides with the minimum Pb solubility (below this pH range, Pb remobilizes).

Fig. 2 presents the SPLP-Pb concentrations along with the mellowed and extracted pH for the entire P-Pb-W thresholding suite. The SPLP testing conditions were approximately 3.5–4 pH units higher that the corresponding TCLP conditions (Fig. 1), which



Note: Pb and W doses fixed at 100,000 mg/kg and 10,000 mg/kg, respectively. Solid symbols denote concentration data. Open symbols denote pH data with dashed and solid lines indicating the "mellowed" and "extracted" values, respectively. Mellowed and extracted control pH values shown on far right denoted as M and E, respectively. Detection limit (DL = 0.05 mg/L).

Fig. 1. TCLP-Pb concentrations in the P-Pb-W thresholding suite as a function of the initial PO_4 dose



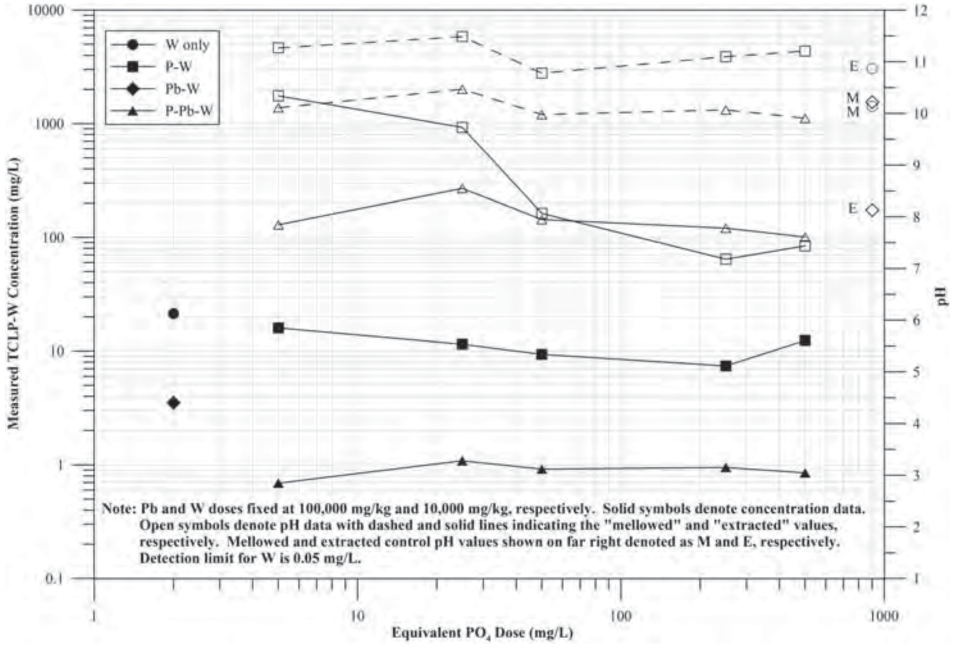
Note: Pb and W doses fixed at 100,000 mg/kg and 10,000 mg/kg, respectively. Solid symbols denote concentration data. Open symbols denote pH data with dashed and solid lines indicating the "mellowed" and "extracted" values, respectively. Mellowed and extracted control pH values shown on far right denoted as M and E, respectively. Detection limit (DL = 0.05 mg/L).

Fig. 2. SPLP-Pb concentrations in the P-Pb-W thresholding suite as a function of the initial PO_4 dose

resulted in significantly higher Pb concentrations. The SPLP-Pb concentrations were on the order of 100–150 mg/L for all suites up to a PO_4 dose of approximately 25 mg/L, at which point the SPLP-Pb concentrations in the P-Pb-W suite decreased by up to a factor of approximately 3. Conversely, the SPLP-Pb concentrations in the P-Pb suite increased somewhat due to pH effects (increases) before being lowered at approximately $\text{pH} = 10$ due to the acidity associated with the highest PO_4 dose.

Fig. 3 presents the TCLP-W concentrations along with the mellowed and extracted pH for the entire P-Pb-W thresholding suite. Beginning with the W-only data (approximately 21 mg/L), Pb addition produced approximately a sevenfold decrease in the TCLP-W concentration (approximately 3.5 mg/L), whereas adding PO_4 to the W-only system had very little impact—at most a threefold decrease in the TCLP-W concentration (7–16 mg/L). When all three elements were present, TCLP-W concentrations leaching from the SSF media averaged below 1 mg/L, regardless of the PO_4 dose.

Likewise, Fig. 4 presents the SPLP-W concentrations along with the mellowed and extracted pH for the entire P-Pb-W system. The SPLP-pH was up to 2 units higher than the mellowed condition, fluctuating between approximately pH 9.5–10.5 depending on



Note: Pb and W doses fixed at 100,000 mg/kg and 10,000 mg/kg, respectively. Solid symbols denote concentration data. Open symbols denote pH data with dashed and solid lines indicating the "mellowed" and "extracted" values, respectively. Mellowed and extracted control pH values shown on far right denoted as M and E, respectively. Detection limit for W is 0.05 mg/L.

Fig. 3. TCLP-W concentrations in the P-Pb-W thresholding suite as a function of the initial PO_4 dose

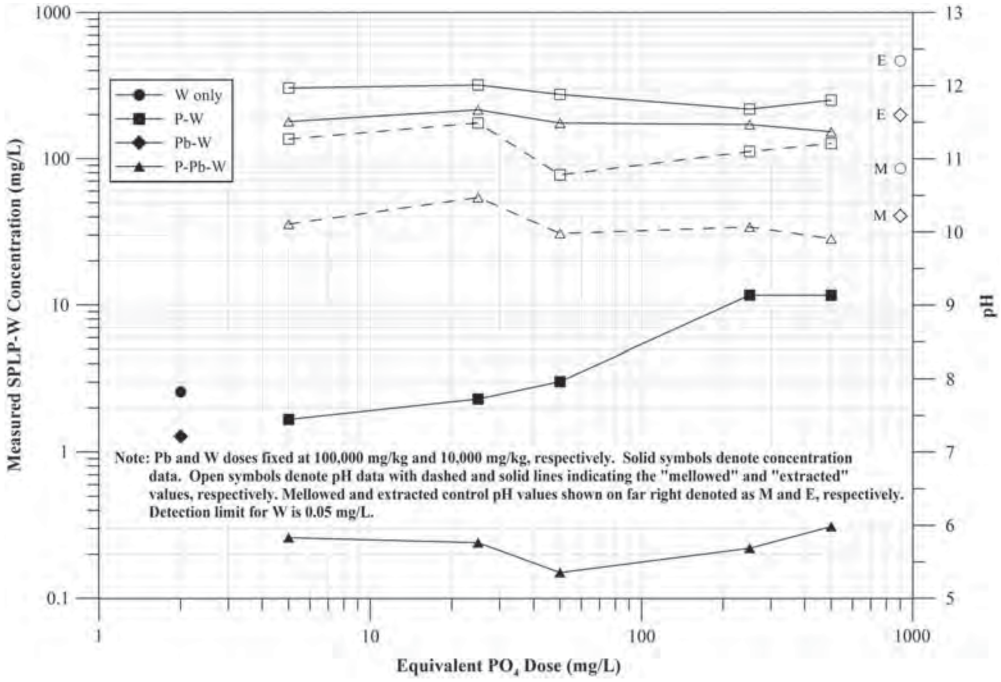


Fig. 4. SPLP-W concentrations in the P-Pb-W thresholding suite as a function of the initial PO_4 dose

the PO_4 dose (Table 2). The addition of PO_4 to the W-only suite (no Pb present) increased the SPLP-W concentrations by up to an order of magnitude, presumably due to oxyanionic competition for dissolved cations (Ca, Mg, and Fe). For all tested suites, the SPLP-W concentrations were almost always lower than the corresponding TCLP-W concentrations (one exception) indicating the broad ability of SSF media to immobilize W under neutral to alkaline conditions (approximately $7 \leq pH \leq 11.5$).

Interestingly, Bednar et al. (2009) found that WO_4 (700 mg/kg, or 35 mg/L equivalent aqueous) was very mobile (up to 50 mg/L) in sand columns under near neutral (approximate pH of 6) to strongly alkaline (approximate pH of 11) conditions regardless of the presence of PO_4. Under acidic conditions (approximate pH of 3), they observed that the WO_4 concentrations were significantly less (e.g., 1–2 mg/L), unless PO_4 was present, in which case the WO_4 concentrations essentially returned to their prior levels (40–50 mg/L). Such WO_4 (oxyanion) leaching behavior does not occur in the SSF media because it contains large concentrations of reactive cations (Ca, Mg, and Fe) (Grubb et al. 2011c, d, 2103), and is strongly buffered down to neutral pH (at which point it likely

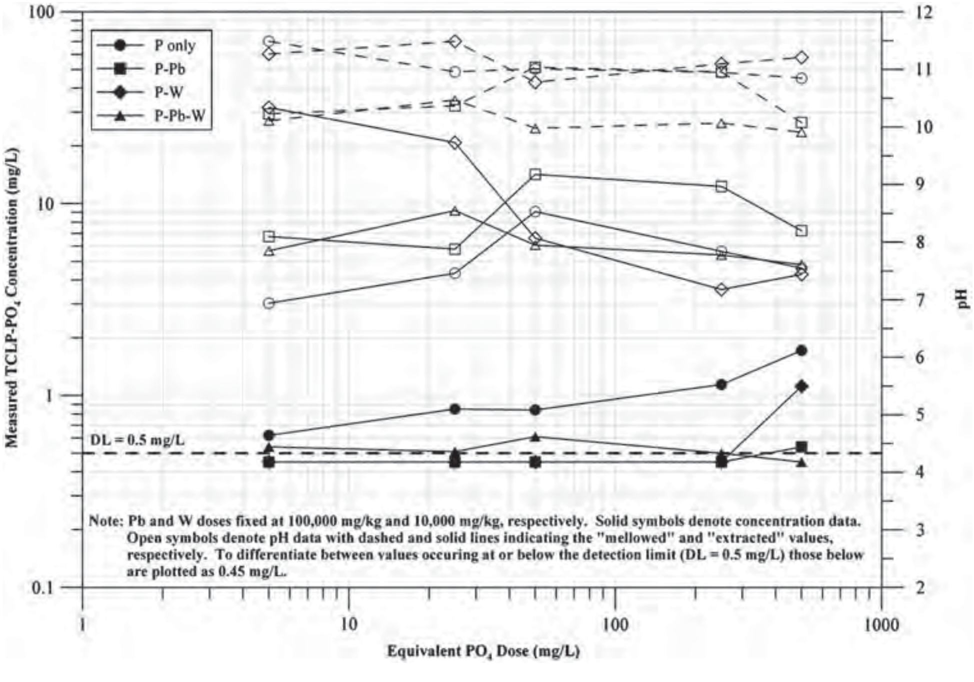


Fig. 5. TCLP-PO_4 concentrations in the P-Pb-W thresholding suite as a function of the initial PO_4 dose

will be changed due to increased TCLP-Pb leaching). Put differently, W is highly mobile in sandy soils typical of firing range soils and PO_4 aggravates this condition. Bednar et al. (2009) did not report the corresponding PO_4 leached concentrations from their soil columns, but they did state that there is ample evidence from batch tests that the PO_4 concentrations would be on the order of 2–3 mg/L or greater, as would be the case under highly contaminated conditions (e.g., 7,000 mg/kg W; 1,000 mg/kg PO_4).

Unlike the sandy soils typical of firing-range soils (where W may have been present and PO_4 was applied to immobilize Pb), the SSF media has been shown to be effective in immobilizing PO_4 without significant reduction in (and even enhancement to) Pb and W immobilization (Fig. 5). PO_4 concentrations were BDL (<0.5 mg/L) under SPLP conditions and fluctuated around the DL (<0.5 mg/L) under TCLP conditions for all PO_4 dosing levels when Pb was present. It is important to note that PO_4 is not required to achieve high Pb and W immobilization levels (or TCLP-Pb compliance) in SSF media. Instead, the findings of this paper show that any combination of PO_4, Pb, W is highly immobilized in the SSF media, whereas W and PO_4 remain highly mobile in sandy media. Finally, under SPLP conditions for the P-Pb-W suite, which would simulate outdoor exposure to acid rain conditions, the SPLP-Pb concentrations ranged between approximately 45 and 185 mg/L, which is consistent with the results from the other Pb-containing suites. However, the performance of the SSF media is expected to improve significantly as the system pH decreases with weathering (acidification of the SSF media and carbonation), as suggested by Table 1.

Batch Kinetics Results

Figs. 6 and 7 present the percentage of removal of Pb and W by the SSF media and the pH shift of the slurries as a function of time. Each figure shows the measured concentration (C_o) of each metal along with the DL (0.05 mg/L) of the ICP-OES, respectively. BDL concentrations were plotted as the DL and also were used as a basis to develop percentage removal estimates calculated as $(C_o - C)/C_o$.

The initial pH of the Pb and W salt solutions (pH_o) were 4.12 and 7.14, respectively. The pH of the Pb-only system gradually increased from approximately pH 6 to 12 between 1 min and 18 h, but exceeded an approximate pH of 11 within 3 h. The percentage removal of Pb by the SSF media exceeded 90% within 2 h and stabilized at approximately 93% by 18 h. The removal of W by the SSF media (Fig. 7) was quite rapid (65%) at the early contact times (<5 min) and eventually tapered off to approximately 99.5% at 18 h. These timeframes for metal removal (for the concentrations tested) are certainly within the residence times of conventional water treatment technology.

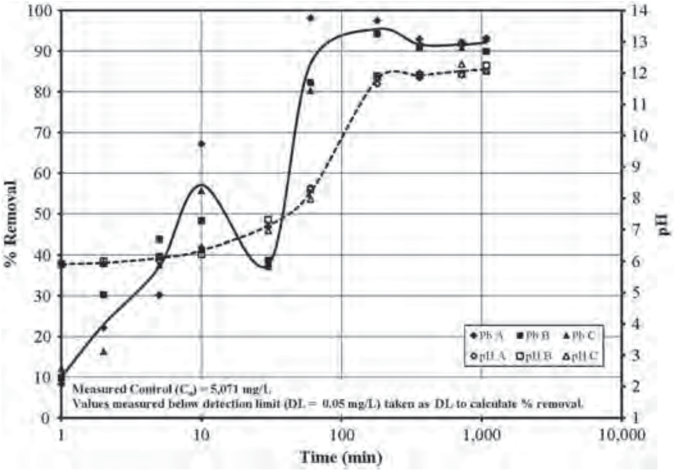


Fig. 6. Removal rate of Pb by raw SSF media in batch equilibration experiments (L:S = 20:1)

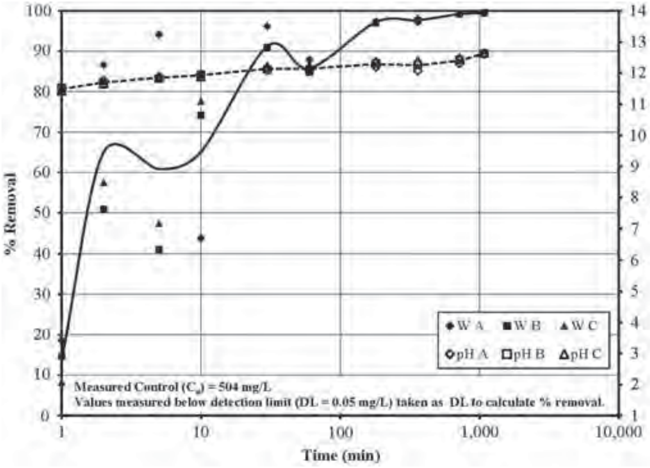


Fig. 7. Removal rate of W by raw SSF media in batch equilibration experiments (L:S = 20:1)

The concentrations of Ca, Mg, and Fe indigenous to SSF media that can react with and precipitate phosphate and tungstate also were measured during the batch experiments. The Ca concentrations in the Pb and W systems varied log-linearly between 200 to 1,300 mg/L and 100 to 700 mg/L, respectively. The dissolved Mg concentrations were low (<1.0 mg/L) for both Pb- and W-spiked systems, while the dissolved Fe concentrations were BDL (<0.5 mg/L).

ANC Results

ANC testing was conducted to assess the leaching behavior of Pb, PO_4, and W from the P-Pb-W suite to simulate the effects of the weathering process (acidification). The test results are shown in Figs. 8–10, respectively. The release of Pb from the P-Pb-W suite appears to be solubility controlled, similar to the trends observed during experiments for the Pb-H_2O system under open conditions (Dermatas and Meng 2003) (Fig. 8). The TCLP-Pb criteria were satisfied between approximately $6.5 \leq pH \leq 10$. However, as shown in Fig. 9, W was virtually insoluble (BDL) at all pH values tested versus equilibrium modeling of the equivalent dose of W using MINTEQ (David and Allison 1999). Similar to Pb, PO_4 expressed amphoteric behavior with respect to pH. The concentration of PO_4 under all tested pH conditions was essentially ≤ 15 mg/L. Between approximately pH 6 and 11, PO_4 concentrations were below 1 mg/L. When deployed in the field, the pH of the SSF media will likely to buffer around pH 8–9 due to absorption of atmospheric CO_2. Under such conditions, PO_4 concentrations were BDL, which also coincides with the minimum dissolved Pb concentration (Fig. 8).

XRPD Results

XRPD analyses were conducted to evaluate the P, Pb, and W immobilization mechanisms occurring in the SSF media versus the bulk slag control by Grubb et al. (2010b). The XRPD results

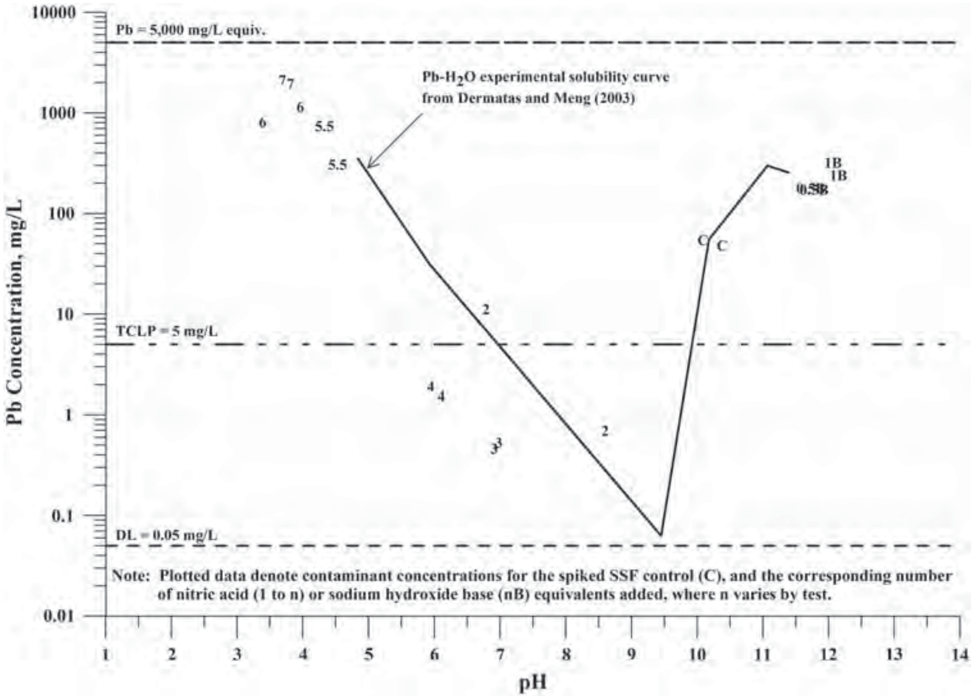


Fig. 8. ANC-derived total Pb concentrations equilibrated with SSF media containing 100,000 mg/kg Pb, 10,000 mg/kg W, and 10,000 mg/kg PO_4 spike

of all SSF-spiked media are presented in Table 3. Fig. 11 presents the annotated XRPD diffractograms for the raw SSF media, Pb-only, Pb-W, and P-Pb-W suites. The quantitative XRPD results presented in Table 3 were directly adjusted for sample dilution effects due to elevated contaminant spiking (1 and 10 wt%) and atmospheric CO_2 absorption. The crystalline solid phase percentage changes were normalized to the crystalline solid phases in the raw SSF media to enable direct comparison between the suites. The normalized crystalline solid phase percentages were calculated by multiplying the measured weight percentages by the corresponding dilution factors. The dilution factors were determined by dividing the mass of the raw SSF samples by the mass of

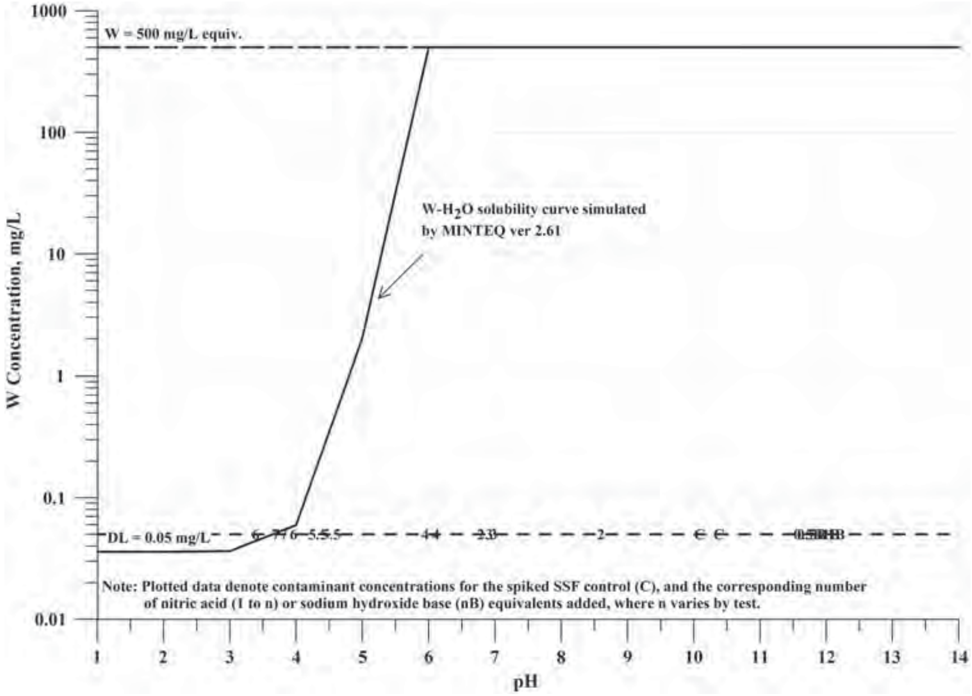


Fig. 9. ANC-derived total W concentrations equilibrated with SSF media containing 100,000 mg/kg Pb, 10,000 mg/kg W, and 10,000 mg/kg PO_4 spike

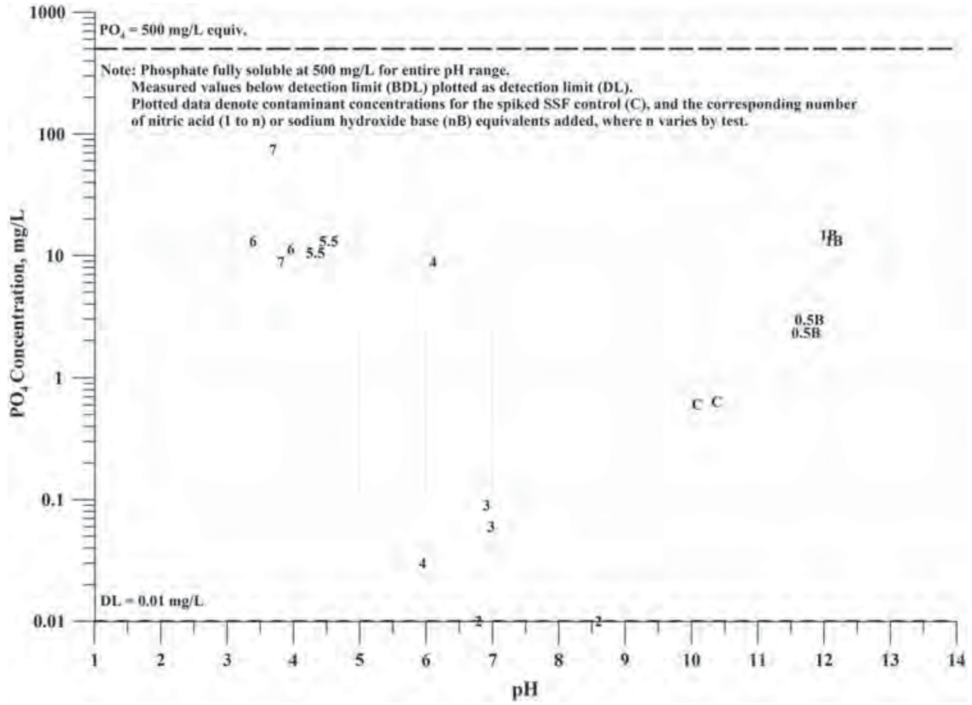


Fig. 10. ANC-derived total PO_4 concentrations equilibrated with SSF media containing 100,000 mg/kg Pb, 10,000 mg/kg W, and 10,000 mg/kg PO_4 spike

the SSF in an equivalent mass of spiked-SSF samples. The mass of the SSF in the spiked-SSF samples were determined by subtracting the mass of the spiked salts and the absorbed CO_2 from the mass of the spiked-SSF media. The amounts of CO_2 absorbed were calculated from the difference between the $CaCO_3$ content in the SSF control and the spiked samples. The $CaCO_3$ content increased from approximately 8% in the fresh SSF media up to approximately 19% for the P-Pb suite sample. The increase in $CaCO_3$ content occurred most likely during the sample spiking, drying, and mellowing processes.

Table 3. Quantitative XRPD Results (%) for Raw and Metal-Spiked SSF Media

Phase/parameter	Formula	PDF[a]	CSD[b]	SSF[c]	Pb-only	W-only	PO_4-only	Pb-W	P-Pb	P-W	P-Pb-W
Larnite	Ca_2SiO_4	97-001-0561	963	20.85	16.85	13.28	15.82	13.85	14.15	17.04	18.03
Magnesium ferrous oxide	$(MgO)_{0.432}\ (FeO)_{0.568}$	97-004-2976	60,696	16.28	14.22	11.22	17.07	14.72	17.25	16.98	13.21
Srebrodolskite	$Ca_2Fe_2O_5$	97-001-4942	15,059	11.70	15.02	10.50	14.88	11.55	13.81	13.80	15.81
Magnetite	$Fe_{2.942}O_4$	97-006-2364	82,449	8.30	8.31	9.06	5.62	8.90	8.21	8.10	11.61
Mayenite	$(CaO)_{12}(Al_2O_3)_7$	97-001-2803	6,287	6.70	—	8.13	1.66	6.38	3.92	4.49	4.82
Wuestite	$Fe_{0.925}O$	97-006-2153	82,235	4.36	5.46	4.84	6.03	3.95	4.64	3.84	2.09
Quartz	SiO_2	00-046-1045		2.66	2.39	2.16	2.28	3.85	3.81	3.40	4.07
Lime	CaO	97-002-1810	26,959	2.66	—	—	—	—	—	—	
Calcite	$CaCO_3$	00-005-0586		7.87	14.57	15.55	7.70	11.76	18.92	13.47	16.18
Aragonite	$CaCO_3$	00-041-1475		—	—	—	6.65	—	—	—	
Tridecalead octaoxide hexahydrate tetranitrate	$Pb_{13}O_8(OH)_6(NO_3)_4$	97-003-7036	51,473	—	3.87	—	—	—	—	—	
Massicot	PbO	03-065-0129		—	1.03	—	—	—	—	—	
Lead oxide	Pb_2O_3	00-023-0331	23,760	—	1.59	—	—	2.97	0.95	—	
Lead oxide	Pb_5O_8	00-052-0772		—	—	—	—	—	—	—	NQ
Scheelite	$CaWO_4$	97-001-5457	15,586	—	—	1.75	—	1.21	—	1.97	1.98
Hydroxypyromorphite	$Pb_5(PO_4)_3(OH)$	00-008-0259	87,518	—	—	—	—	—	1.19	—	3.58
Amorphous phase[d]				18.60	32.10	28.10	26.20	35.70	32.10	22.10	28.80
Dilution factor[e]				—	1.23	1.06	1.05	1.23	1.28	1.07	1.28
Mellowed pH				12.05	10.42	10.87	10.85	10.22	10.08	11.21	9.91

Note: Dashes indicated nondetection; NQ = not quantified.

[a] Powder diffraction file (ICDD 2004).

[b] Crystal structure data (ICSD 2011).

[c] Control values from Grubb et al. (2010c). Actual wt% values shown. All other data columns show corrected values to account for metals spiking and carbonation effects versus raw SSF quality.

[d] Values based on raw (uncorrected) XRPD data.

[e] Dilution factor to normalize against SSF control due to metals spiking and carbonation.

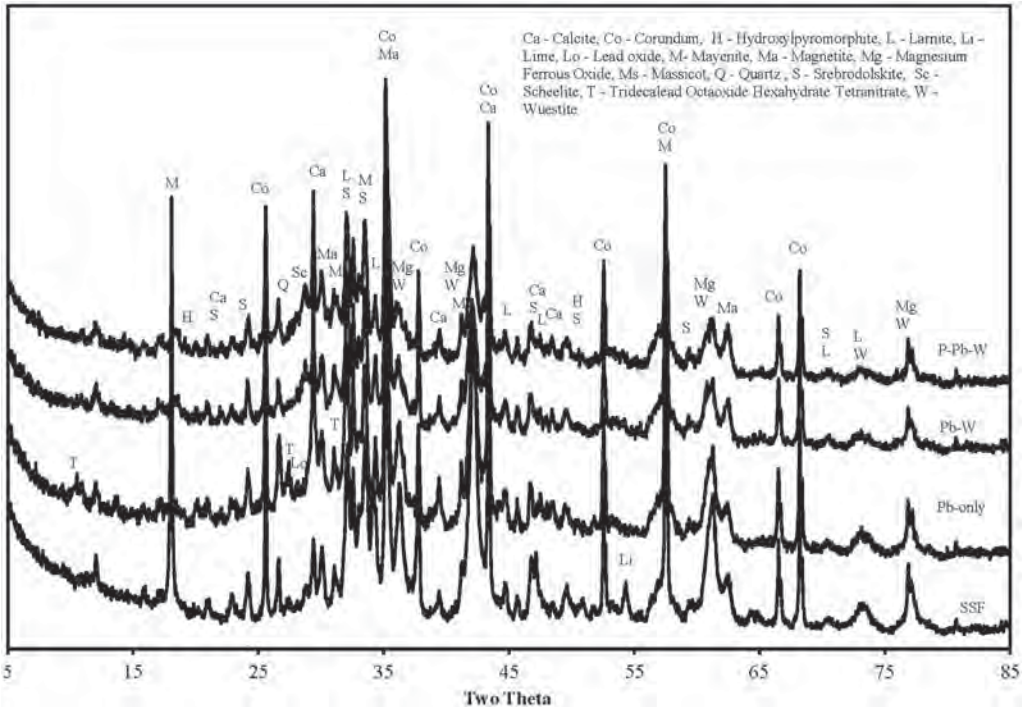


Fig. 11. Annotated diffractograms of raw, Pb-only, Pb-W, and P-Pb-W-spiked SSF media

The major solid phases identified in the raw SSF media were larnite (Ca_2SiO_4), magnesium ferrous oxide [$(MgO)_{0.432}(FeO)_{0.568}$], and srebrodolskite ($Ca_2Fe_2O_5$), quantified at approximately 21%, 16%, and 12%, respectively. Upon spiking, the larnite phase content decreased for all suites (13.5%–36.3%), indicating that it may not be stable under the experimental conditions. Even though the other two major phases experienced slight changes, no significant trend was observed.

On the other hand, some other minor phases experienced significant changes. Lime in the raw SSF media (2.6%) completely dissolved, most likely incongruently to other Ca-containing phases such as calcite due to the elevated pH conditions, and as evidenced by the low dissolved Ca concentrations in the SPLP leachates (data not presented). Conversely, new minor phases were formed upon metals spiking such as tridecalead octaoxide hexahydrate tetranitrate [$Pb_{13}O_8(OH)_6(NO_3)_4$], Pb-hydroxypyromorphite [$Pb_5(PO_4)_3(OH)$] and scheelite ($CaWO_4$).

Tridecalead octaoxide hexahydrate tetranitrate was observed at approximately 4% in the Pb-only-spiked sample, and it may be an artifact of lead nitrate salt use in the experiments. This phase appeared to be metastable and likely dissolved incongruently to other phases, as it did not appear in other thresholding suites. Minor amounts of lead oxide also were observed in the Pb-containing suites, such as PbO, Pb_2O_3, and Pb_5O_8, ranging between 1%–3%; however, the Pb_5O_8 phase was not quantified due to the lack of ICSD data. Pb-hydroxypyromorphite was formed in the PO_4-containing systems and was quantified at approximately 1.2% and 3.6% in the P-Pb and P-Pb-W suites, respectively, or approximately 9.2% and 27.7% of the initial Pb mass (Table 4).

Scheelite emerged as a minor but dominant WO_4-containing phase between approximately 1.2%–2% in the all-W-spiked suites. These ratios correspond to approximately 76% and 126% of the initial W mass, respectively, which indicates that $CaWO_4$ was the primary sink for W (Table 4).

Discussion

The most common Pb phases identified at firing-range soils and Pb-contaminated soils treated by S/S processes are massicot (PbO),

Table 4. % Mass Estimates for Pb, W, and PO_4 in Quantifiable Crystalline Phases

		Pb-only	W-only	PO_4-only	Pb-W		P-Pb		P-W		P-Pb-W		
Phase	Chemical formula	Pb	W	PO_4	Pb	W	Pb	PO_4	W	PO_4	Pb	W	PO_4
Tridecalead octaoxide hexahydrate tetranitrate	$Pb_{13}O_8(OH)_6(NO_3)_4$	32.87	—	—	—	—	—	—	—	—	—	—	—
Massicot	PbO	9.60	—	—	—	—	—	—	—	—	—	—	—
Lead oxide	Pb_2O_3	14.25	—	—	26.62	—	8.51	—	—	—	—	—	—
Lead oxide	Pb_5O_8	—	—	—	—	—	—	—	—	—	—	—	—
Scheelite	$CaWO_4$	—	117.40	—	—	77.26	—	—	125.79	—	—	126.46	—
Hydroxypyromorphite	$Pb_5(PO_4)_3(OH)$	—	—	—	—	—	9.21	25.34	—	—	27.72	—	76.33
Total		56.72	117.40	BDL	26.62	77.26	17.73	25.34	125.79	BDL	27.72	126.46	76.33

Note: BDL = below XRPD detection limit (~1 wt%); based on corrected data shown in Table 3.

cerussite ($PbCO_3$), hydrocerussite [$Pb_3(CO_3)_2(OH)_2$], and lead oxide (Pb_2O_3) (Dermatas et al. 2004c, 2006; Moon et al. 2006; Grubb et al. 2008). No cerussite or hydrocerussite phases were observed in the study in this paper in contrast to firing-range soils. This could be due to the high pH of the SSF media where $Pb(OH)_2$ and $CaCO_3$ formation are favored (Jing et al. 2004). Cerussite and hydrocerussite phases present in highly alkaline systems are not expected to persist (David and Allison 1999). In the SSF media, CO_2 uptake seemed to be linked to the formation of $CaCO_3$ and its polymorphs. However, with ongoing carbonation of the SSF media and its associated drift toward pH of about 8–9, cerrusite/hydrocerrusite formation would become favored based on the K_{sp} considerations (Suer et al. 2009; Diener et al. 2010) in the absence of phosphate. In the presence of phosphate, Pb-hydroxypyromorphite formation is extremely favored, as reflected by (1) its low $K_{sp}(10^{-62.79})$ (David and Allison 1999); (2) as evidenced by the decreased extractability of Pb in the presence of PO_4 during TCLP testing; and (3) with increasing PO_4 dose during SPLP testing (Figs. 1 and 2). The amount of Pb immobilized in crystalline phases was between approximately 18 and 57% of the Pb mass in the Pb-containing suites. The remaining Pb was therefore likely associated with amorphous content or adsorbed on the metal oxide surfaces (Jing et al. 2004; Rietra et al. 2001).

W exists almost exclusively in the form of oxytungstate minerals either as $CaWO_4$ or wolframite [$(Fe/Mn)WO_4$] in terrestrial systems (Koutsospyros et al. 2006). In the SSF media, despite the moderate K_{sp} value ($10^{-8.72}$) of $CaWO_4$, it appears to control the solubility of W under a wide pH regime (Osseo-Asare 1982), as evidenced by the TCLP/SPLP leaching behavior (Table 2), and XRPD (Table 3) and ANC (Fig. 9) results. For perspective, 100% association of W with $CaWO_4$ would consume only approximately 0.2% of the total Ca content (26%) in the SSF media.

The PO_4 concentrations were also reduced significantly by the slag media in all suites. The common minerals observed during immobilization of PO_4 are calcium phosphate, brushite, and hydroxyapatite (Bowden et al. 2009) or amorphous phosphates (Hedström and Rastas 2006). No such PO_4-containing crystalline phases were observed. With Pb in the system, $Pb_5(PO_4)_3(OH)$ consumed between 35% and 76% of the total PO_4 mass. It appears that the formation of Ca-hydroxypyromorphite [$Ca_5(PO_4)_3(OH)$] was less favored than the formation of $Pb_5(PO_4)_3(OH)$, even though they have comparable K_{sp} values. The remaining phosphate mass could have been associated with mineral phases occurring below the detection limit of the XRPD device (approximately 1 wt%) or in the amorphous content. Phosphate also may have adsorbed onto the metal oxide surfaces in the SSF media or the newly formed calcite (Moon et al. 2006; Karageorgiou et al. 2007).

In summary, the highest immobilization of P, Pb, and W simultaneously occurred in the P-Pb-W suite. These results may reflect the general trend that Pb and PO_4 should selectively pair over other combinations of Pb, PO_4, Ca, WO_4, and CO_3 based on K_{sp} comparisons between Pb and Ca phosphates, tungstates, and carbonates (Nriagu 1974). Overall, Pb-hydroxypyromorphite has the lowest K_{sp} for all pairings considered. Since $CaWO_4$ has a lower K_{sp} than stolzite ($PbWO_4$; $K_{sp} = 10^{-6.34}$) (Speight 2004) and Ca was greatly in excess, $CaWO_4$ emerged as the dominant W-containing phase. These observations are supported by the results for the P-Pb-W suite (simultaneously highest % masses of each compound in crystalline phases) as shown in Table 4, and the fact that no cerrusites, stolzite, or calcium apatites were detected in any of the thresholding suites (Table 3), despite explicit searches for said crystalline phases.

Conclusions

This evaluation of beneficial use illustrated the rapid and strong potential for SSF media to immobilize Pb and W at very high dosing levels, consistent with conditions encountered in firing-range soils. On its own, the SSF media immobilized 100,000 mg/kg Pb and passed the TCLP-Pb criteria (5.0 mg/L), and immobilized W at rates greater than 99% to 3.5 mg/L (as opposed to a 500 mg/L spike). At these dosing levels, natural soils and other media used for firing range backstop berms would likely require hazardous waste disposal or treatment by stabilization/solidification or other expensive reagents. Contrary to what occurs in sandy soils, the presence of PO_4 tended to enhance both Pb and W removal under TCLP and SPLP conditions, except for W when Pb was not present (very unlikely in firing ranges). Phosphate concentrations were almost always <0.5 mg/L (up to 500 mg/L spike) for both TCLP and SPLP conditions (90%–99.9% removal).

These performance metrics bode well for the potential application of SSF media to firing-range soils simultaneously affected by all three metals or for use as a backstop berm media. Weathering of the SSF media due to acidification and/or carbonation suggests that the SSF media will require change-out based on potential rerelease of immobilized Pb and PO_4 as the system trends below pH values of about 7. This allows pH measurement (alone) to be a key screening tool for firing range environmental management. Finally, while Pb removal at high pH (approximately 12) was not effective, removal of Pb increased with simulated weathering (to approximate pH levels of 7) whereas removal of phosphate and tungsten in the range of $7 \leq pH \leq 12$ remained very high. The blending of SSF media with contaminated firing range soils also would likely promote pH buffering toward $7 \leq pH \leq 9$ where the removal of all three metals is optimal.

Pragmatically, the use of SSF media offers significant sustainability, technical, and cost advantages over the current U.S. EPA BMP methods for the environmental management of firing ranges. The high environmental quality of steel slags and the fact that they compare well to the composition of natural soils offer a very real opportunity to conduct recycling-based remediation at thousands of locations in the United States alone.

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