EXCAVATION SAMPLING WORK PLAN

Chromium Plating Facility Air Pollution Control System Replacement

Watervliet Arsenal
Watervliet, New York

NYSDEC Site # 401034A

Contract: W912DS20D0002
WO: W911PT22F0399 – 22AE002

April 2022

EXCAVATION SAMPLING WORK PLAN

Chromium Plating Facility Air Pollution Control System Replacement

Watervliet Arsenal
Watervliet, NY

Prepared for:

Watervliet Arsenal
1 Buffington St.
Watervliet, NY 12189-4000

Prepared by:

Arcadis U.S., Inc.
855 Route 146
Suite 210
Clifton Park
New York 12065
Tel 518 250 7300

Date:

7 April 2022

Andrew R. Vitolins, PG
Vice President

Stefan Bagnato, PG
Principal Geologist

VERSION CONTROL

Revision No	Date Issued	Description
0	14 March 2022	Draft Work Plan
1	28 March 2022	Revised Draft Work Plan
2	7 April 2022	Final Work Plan

CONTENTS

FIGURES

APPENDICES

ACRONYMS AND ABBREVIATIONS

AMSL	Above Mean Sea Level
APP	Accident Prevention Plan
bgs	below ground surface
CAMP	Community Air Monitoring Plan
CSM	Conceptual Site Model
DER	Division of Environmental Remediation
DMP	Data Management Plan
DUSR	Data Usability Summary Report
ELAP	Environmental Laboratory Approval
IRP	Installation Restoration Program
mg/L	Milligrams per liter
MMA	Main Manufacturing Area
NMT	New Medium Tube
NYCRR	New York Codes, Rules, and Regulations
NYSDEC	New York State Department of Environmental Conservation
NYSDOH	New York State Department of Health
PID	Photoionization Detector
RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
QAPP	Quality Assurance Project Plan
SA	Siberia Area
SCO	Soil Cleanup Objective
SSHP	Site Safety and Health Plan
UFP	Uniform Federal Policy
USACE	US Army Corps of Engineers
USEPA	United States Environmental Protection Agency
WVA	Watervliet Arsenal

1 INTRODUCTION

The Watervliet Arsenal (WVA) in Watervliet, New York is performing an upgrade to its chromium plating operations at the 120-mm Gun Pit plating pit in WVA Building 35 (Figures 1-1 and 1-2). This upgrade will include the demolition of the existing air pollution control equipment, which is comprised of a wet air scrubber and associated utilities, and replacement with a new air scrubber and utilities. This work, which will involve excavation of buried utilities connected to the air scrubber equipment, will take place adjacent to an area that was excavated in 2018 upon the discovery of a release hexavalent chromium plating solution from subsurface air ductwork connecting the plating area inside Building 35 to the to the air scrubber. This area, and the surrounding areas downgradient (east) of the air scrubber were further investigation as part of a Site Investigation conducted in 2019, which concluded that the magnitude and extent of hexavalent chromium impacts to soil and groundwater were limited and that additional delineation and/or remediation was not warranted based on existing land use controls and ongoing monitoring of the site.

This Work Plan has been prepared to document the understanding of site conditions to-date and present the scope of soil sampling that will be conducted during the excavation activities associated with the air scrubber replacement to document site conditions. This Work Plan was prepared in accordance with the provisions of Chapter 4 of the NYSDEC DER-10 Technical Guidance for Site Investigation and Remediation (DER-10) guidance document. This Work Plan is supported by, and will be used in conjunction with the Uniform Federal Policy (UFP) Quality Assurance Project Plan (QAPP), Data Management Plan (DMP), and Accident Prevention Plan (APP) submitted as Appendix A, Appendix B, and Appendix C to the Installation Restoration Program (IRP) Work Plan (PIKA-MP, JV, 2016) at WVA. Laboratory SOPs that are specific to the soil sampling activities associated with the air scrubber replacement project that are not included in the IRP Work Plan are provided in **Appendix A** of this document.

2 SITE BACKGROUND

2.1 Facility Description

The WVA encompasses approximately 143 acres in and around the City of Watervliet, New York, approximately 3.5 miles northeast of the City of Albany (**Figures 1-1** and **1-2**). To the east of the WVA, Broadway Street and a six-lane interstate highway (I-787) separate the WVA from the Hudson River. To the west, the WVA extends beyond the limits of the City of Watervliet into the Town of Colonie. Residential areas border the WVA to the north and south.

Building 35, also known as the Heat Treat and Metal Processing Building, and was originally constructed in 1918, with several updates thereafter. Building 35 is located along the southern property boundary of the Main Manufacturing Area at WVA (**Figure 1-2**). It is bounded to the east by Buildings 20 and 25, to the south by residential property, to the west by Building 110, and to the north by the WVA fire house (Buildings 21 and 22).

As described in the Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) (Malcolm Pirnie, 2000), Building 35 is a single-story structure approximately 850 feet long and 600 feet wide at its widest point constructed in 1918. The building was subsequently expanded in 1942 and again in mid to late 1970s. There were two process pits at the south end of the building at the time of construction, formerly referred to as the West and East Pits. Extensions were added to the west, east, and north and two additional process pits were installed in 1978. A number of reconstructions/conversions have been made to the process pits since their installation.

Following is a chronology of events relating to the process pits based on available WVA drawings and information provided by WVA personnel:

- 1918 - Two pits installed during construction of Building 35.
- 1952 - West Pit converted to chrome plating of 155 mm guns.
- 1976 - East Pit converted to chrome plating of 8-inch guns.
- 1978 - New Medium Tube (NMT) Pit installed, as an extension to the 8-inch Gun Pit. This pit was used for chrome plating.
- 1979/1980 - 120mm Gun Pit constructed, but left idle.
- 1986/1987 - Chrome plating equipment installed in 120mm Gun Pit.
- 1990 - West pit converted to a furnace pit.

There are currently four process pits located at the south end of Building 35. From west to east these pits are called the 120-mm Gun Pit (a.k.a. West Pit), the Furnace Pit, the 8-inch Gun Pit (a.k.a East Pit and now the Commercial Pit), and the NMT Pit. Note that the 8-inch Gun Pit (Commercial Pit) and the NMT Pit are contiguous. The 120 pit and the Commercial pit are currently capable of conducting chromium plating operations. The NMT pit has been inoperable since the 1990s. Process pits are shown on **Figure 2-1**.

The Furnace Pit is 45 feet long, 20 feet wide and 30 feet deep with a sump located at the southwest corner. During conversion of this pit from chrome plating to heat treating operations in 1987, the acid resistant brick, waterproof membrane, and part of the concrete floor slab, were removed. At that time, oil was observed to be seeping through cracks in the concrete walls. A groundwater/oil collection channel is located around the walls of the pit, approximately 3 feet above the concrete floor slab, and directs groundwater/oil seepage towards the sump.

The New Medium Tube/8-inch Gun Pit is 60 feet long, 60 feet wide and approximately 40 feet deep. A small sump is located in the southwest corner which collects condensate blowdown and some groundwater seepage. The pits at Building 35 were constructed partially in overburden material and partially in bedrock. This is confirmed by a soil boring installed adjacent to the New Medium Tube Pit (East Pit) in 1978 by the USACE. Drilling logs for this boring shows the top of bedrock at 19.5 feet below shop floor level. Drawings for the 120mm Gun Pit were not available for review at the time of this Work Plan.

Current manufacturing operations at Building 35 include cannon tube chrome plating and heat treatment in the three process pits located at the southern end of the building. Cadmium-cyanide plating, previously conducted at Building 110, was relocated to Building 35 in 1985 and discontinued in 1994. In general, however, the manufacturing processes and equipment in Building 35 is believed to have changed very little since its construction. The remainder of the main floor is occupied by machining equipment used for finishing the cannon tubes and for conducting magnaflux testing operations.

2.2 Geology/Hydrogeology

The major overburden unit identified in the MMA is fill, consisting of brown or dark gray silty sand with angular gravel. The fill material is the only unit consistently found throughout the site, with the thickest amount of fill being in the eastern portion of the MMA. Underlying the fill are the following native overburden units: a fine-grained alluvium, a coarser alluvium, and glacial till. These units are not present in all areas of the site.

The bedrock underlying the site is a black, medium-hard laminated shale, showing some characteristics of minor metamorphism. This shale is part of the Snake Hill Formation. The bedrock can be described in three ways based on the degree of weathering observed. The first is an extremely weathered zone approximately four feet thick. This extremely weathered bedrock unit was encountered at depths ranging from near ground surface to approximately 20 feet below ground surface (bgs). Beneath this extremely weathered bedrock is a zone of less weathered shale showing minimal competency. Competent bedrock is generally encountered at depths ranging from approximately 1.5 feet bgs to 18 feet bgs.

The majority of the MMA is relatively impervious to rainfall except at the residential and recreational areas of the northeastern portion of the WVA. Due to the shallow depth of bedrock and the limited amount of overburden in several areas of the WVA, groundwater is encountered within different geologic units (overburden, weathered bedrock, or bedrock) depending on the location. For instance, groundwater is encountered in the bedrock at the western end of WVA (topographic high and local recharge area); progressing eastward toward the Hudson River, groundwater is encountered in the weathered bedrock and then in the overburden deposits.

Groundwater flow in bedrock in the MMA is primarily controlled by the degree of fracturing within the bedrock itself and in the local recharge area, which is coincident with a topographic high along a bedrock ridge in the central portion of the facility. The most prominent feature on the potentiometric surface is a groundwater divide trending approximately north to south through Buildings 135 and 125. This feature appears to mirror the bedrock ridge. The primary discharge area for groundwater from the Main Manufacturing Area is the Hudson River, which is located to the east of WVA. For the area surrounding Building 25, groundwater in each of the hydrostratigraphic units flows from west to east towards the Hudson River, with a component of flow to the northeast. In the Building 40 area, groundwater in the bedrock unit flows to the east-southeast. West of the groundwater divide, shallow groundwater flow discharges toward the Kromma Kill.

2.3 Previous Investigation and Remedial Action

In August 2018, the WVA discovered a subsurface release (NYSDEC Spill # 1804728) of chromic acid plating solution in the area next to the 120-mm Gun Pit plating pit in Building 35 (**Figure 2-1**). The release was associated with ventilation duct work that runs underground from the plating area to the air scrubber system. The WVA conducted initial source removal activities required to conduct the necessary repairs to their plating systems, which consisted of replacement of the subsurface ventilation duct work between the plating area and the above grade air scrubber. Source removal activities included soil excavation and focused groundwater dewatering. Arcadis competed an initial round of groundwater and sump water sampling. Observations of groundwater and initial sampling activities confirmed that groundwater was impacted with hexavalent chromium in the area of the release.

In August 2018, initial groundwater samples were collected from the four existing site monitoring wells closest to the release and from sumps in the 120 Pit and Commercial Pit (see **Figure 2-1**). None of the groundwater samples from existing monitoring wells or the 120 Pit contained hexavalent chromium at concentrations greater than the corresponding NYSDEC Class GA Groundwater Standard of 0.05 milligrams per liter (mg/L). The groundwater sample from the Commercial Pit contained hexavalent chromium at a concentration of 680 mg/L. Results of the sampling are further described in the Site Investigation Report (Arcadis, 2020).

In conjunction with the necessary repairs to their plating systems, consisting of replacement of the subsurface ventilation duct work between the plating area and the above grade air scrubber, the WVA excavated hexavalent chromium-impacted soil from the vicinity of the underground ventilation duct work in August 2018. The excavation area was dewatered during the excavation activities, with extracted water contained for shipment and disposal off-site. As shown on **Figure 2-1**, the excavation encompassed an area beneath Building 35 and the adjacent exterior soil around the ventilation duct work. Representative photographs of excavation activities were provided as Appendix C of the Plating Area Site Investigation Work Plan (Arcadis, July 2019). The excavation extended horizontally and vertically as far as was physically possible given constraints of building/duct work construction and bedrock. The northern sidewall was constrained by the wall of 120 mm Pit, while the eastern sidewall was constrained by the wall of the adjacent utility pit. The western and southern sidewalls were constrained by the ventilation duct work/scrubber infrastructure. The excavation extended vertically to the top of bedrock at approximately 13 feet below the Building 35 main floor level. Following excavation of impacted soil, sidewall and bottom soil samples were collected at the locations shown on **Figure 2-1**. The eastern interior sidewall sample, collected approximately one foot above the bedrock surface but below the bottom of the utility pit sidewall, contained hexavalent chromium at a concentration greater than the 6 New York Codes, Rules, and Regulations (NYCRR) Part 375 Industrial Soil Cleanup Objective (SCO). The southern exterior sidewall and exterior bottom samples contained hexavalent chromium at concentrations greater than the 6 NYCRR Part 375 Protection of Groundwater SCO. Results of the sampling are further described in the Site Investigation Report (Arcadis, 2020). Prior to backfill of the excavation, an interstitial monitoring/recovery well/sump was installed in the northwest corner of the excavation area utilizing slotted 8-inch steel pipe to allow for post-excavation monitoring of groundwater conditions and possible future use for groundwater extraction and/or in-situ treatment. Two post-excavation groundwater samples were collected from this excavation area sump, which contained hexavalent chromium at concentrations of 2.7 and 1.6 mg/L, both greater than the corresponding NYSDEC Class GA Groundwater Standard. Additionally, a post-excavation groundwater sample was collected from the Commercial Pit after the sump was purged for one week. This sample contained hexavalent chromium at a concentration of 11 mg/L, which while greater than the corresponding NYSDEC Class GA Groundwater Standard, was an order of magnitude lower than the pre-excavation sample from this sump. The excavation was backfilled with clean off-site fill material, compacted, and surface restoration completed to match pre-excavation conditions.

The 2019 Site Investigation (Arcadis, 2020) was designed to further characterize the magnitude and extent of groundwater impacts associated with the chromic acid release at Building 35. During the investigation, well installation, soil, groundwater, and sump/pit sampling were used to delineate hexavalent chromium impacts. Laboratory results indicated that hexavalent chromium was present in the NMT Pit and in overburden groundwater in the immediate down-gradient vicinity of the release area, however, the saturated overburden thickness in this area is very small and even absent in some areas. Hexavalent chromium was detected in the groundwater samples collected from the overburden well WVA-AW-35-MW-12 at concentrations greater than the Class GA Standard during both sampling events. However, based on the fact that this well is located cross-gradient from the chromium plating area, and that overburden well WVA-AW-35-MW-9 was dry, and that there were no hexavalent chromium exceedances in bedrock well WVA-AW-35-MW-5, the presence of hexavalent chromium at this well did not appear to be associated with the 120 Pit release that was the subject of the investigation.

The 2019 Site Investigation sampling documented a reduction in hexavalent chromium concentrations at the spill source since the 2018 release and excavation:

- Hexavalent chromium was no longer detected in samples from the Excavation Sump.
- Hexavalent chromium was not detected in the pre-excavation sample or the 2019 samples collected from the 120 Pit.
- Hexavalent chromium concentrations had dropped two orders of magnitude in the Commercial Pit; from 680 mg/L prior to the 2018 excavation, to 11 mg/L following the excavation, and to 1.2 mg/L during the 2019 sampling events.

Hexavalent chromium was not detected in any of the four bedrock wells during both the September and December 2019 events.

Sampling of overburden well WVA-AW-35-MW-12 for hexavalent chromium was subsequently added to the annual Long-Term Monitoring sampling program. Concentrations of hexavalent chromium in samples from this well have decreased since the 2019 investigation (0.2 and 0.4 mg/L) to 0.12 mg/L and 0.0004 mg/L during the 2020 and 2021 LTM events, respectively.

3 EXCAVATION AND SAMPLING

The scope of work for the chrome scrubber replacement/upgrade generally involves installation of new above grade air scrubber equipment, demolition of portions of the existing equipment subsurface piping, duct pipe support pedestals, fence posts, and pavement, and installation of new subsurface utilities (i.e., electrical conduit, water supply pipe, and water discharge pipe). New subsurface ventilation duct work that was installed during the 2018 emergency repairs will remain in place. Representative USACE contract drawings for the demolition and construction work are provided in **Appendix B**. Existing equipment concrete pads will be preserved and reused for the new scrubber equipment, with some expansion of the pads, as shown in **Appendix B**. Following demolition and excavation of the necessary components and areas, new subsurface piping will be installed. This section describes the activities and procedures that will be used to manage potentially impacted soil that could be encountered during the construction, to document conditions within the excavated area prior to backfill, and mitigate exposure to potentially impacted soil and groundwater, consistent with standard site management measures. The base scope of work includes oversight of excavation activities, documentation sampling, survey, waste characterization sampling, and placing a demarcation layer at the maximum extent of excavation prior to backfill and final construction.

An analytical laboratory approved by the New York State Department of Health (NYSDOH) under the Environmental Laboratory Approval Program (ELAP) will analyze all samples collected during the excavation. A Data Usability Summary Report (DUSR) will be prepared upon the receipt of all analytical data to ensure that the quality of the data is sufficient to document existing conditions. Sample collection, handling activities, and QA/QC sampling will be conducted in accordance with the approved QAPP and supplemental information in **Appendix A**.

3.1 Excavation

The anticipated limits of construction-related excavation activities are approximately 250 square feet and are shown on **Figure 3-1** in relation to the 2018 excavation limits. The vertical extent of the excavation is expected to be no greater than five feet below ground surface (bgs), which is well above the elevation of the water table; therefore, dewatering of the excavation will not be necessary. Only the minimum amount of soil needed for demolition and construction will be excavated from the site. However, if visibly contaminated soil is identified during the work, it will be removed to the extent feasible at the time of work. None of the excavated soil from this project will be reused onsite. All excavated soil will be staged in roll off containers pending characterization sampling and transported to a permitted facility for disposal in accordance with applicable federal, state, and local regulations.

Monitoring for volatile vapors and airborne dust will be conducted by the demolition/construction contractor using a photoionization detector (PID) and a respirable airborne dust monitor (MIE Miniram or equivalent), respectively, during excavation activities. Monitored levels in excess of the action levels established by the Safety Officer shall require mitigative action to lower dust levels. Dust control methods will include the periodic application of potable water. A generic Community Air Monitoring Plan (CAMP) is provided in **Appendix C**.

Due to the time-critical operational constraints of the project, which involves the shutdown of the WVA manufacturing operations during the work, only documentation samples will be collected upon reaching the target depth (i.e., no further excavation or sampling will be conducted based on the results of the sampling). Documentation sampling will be conducted in accordance with DER-10 to document the concentrations of hexavalent chromium that may be present at the maximum extent of the disturbed area. Soil samples will be collected by the on-site Arcadis representative with the assistance of the demolition/construction contractor, if necessary. Per DER-10 guidelines, one sample will be collected from the bottom of each sidewall for every approximately 30 linear feet of sidewall, and one sample will be collected from the excavation bottom for every approximately 900 square feet of bottom area. Each soil sample will be placed into laboratory-supplied, pre-cleaned sample jars, and placed into a cooler chilled with ice. Soil samples will be sent under chain-of-custody to an analytical laboratory for analysis of hexavalent chromium by United States Environmental Protection Agency (USEPA) Method 7196 under standard turnaround time.

The maximum horizontal and vertical extents of excavation/disturbance will be surveyed by the demolition/construction contractor to the nearest 0.01-foot vertically and 0.1-foot horizontally and will be added to an AutoCAD base map for the site. A demarcation layer consisting of geotextile fabric will be placed within the excavation prior to backfilling. Backfill material will be tested to confirm that it does not contain contaminants at concentrations greater than the corresponding Part 375 Industrial SCOs before being placed in the excavation.

4 REPORTING

The results of the sampling activities will be provided to the NYSDEC in a data summary report. The report will include the following:

- Discussion of field activities.
- Presentation of analytical results for all media sampled.
- Comparison of analytical results applicable regulatory standards and objectives.
- Supporting data, including analytical data packages, field log forms, and project photographs.

5 SCHEDULE

The project schedule will be based on the overall project schedule as determined by the WVA manufacturing schedule and the construction contractor. To the extent possible given the construction schedule constraints, the NYSDEC will be notified of the start of excavation activities a minimum of 10 days prior to initiation. The current tentative schedule includes shutdown of manufacturing operations on 25 April 2022, with the work described herein to be conducted in May/June 2022.

6 REFERENCES

Arcadis, 2015. Site Management Plan, Watervliet Arsenal, Watervliet, New York. June 2015.

Arcadis, 2019, Plating Area Site Investigation Work Plan, Watervliet Arsenal, Watervliet, New York. July 2019

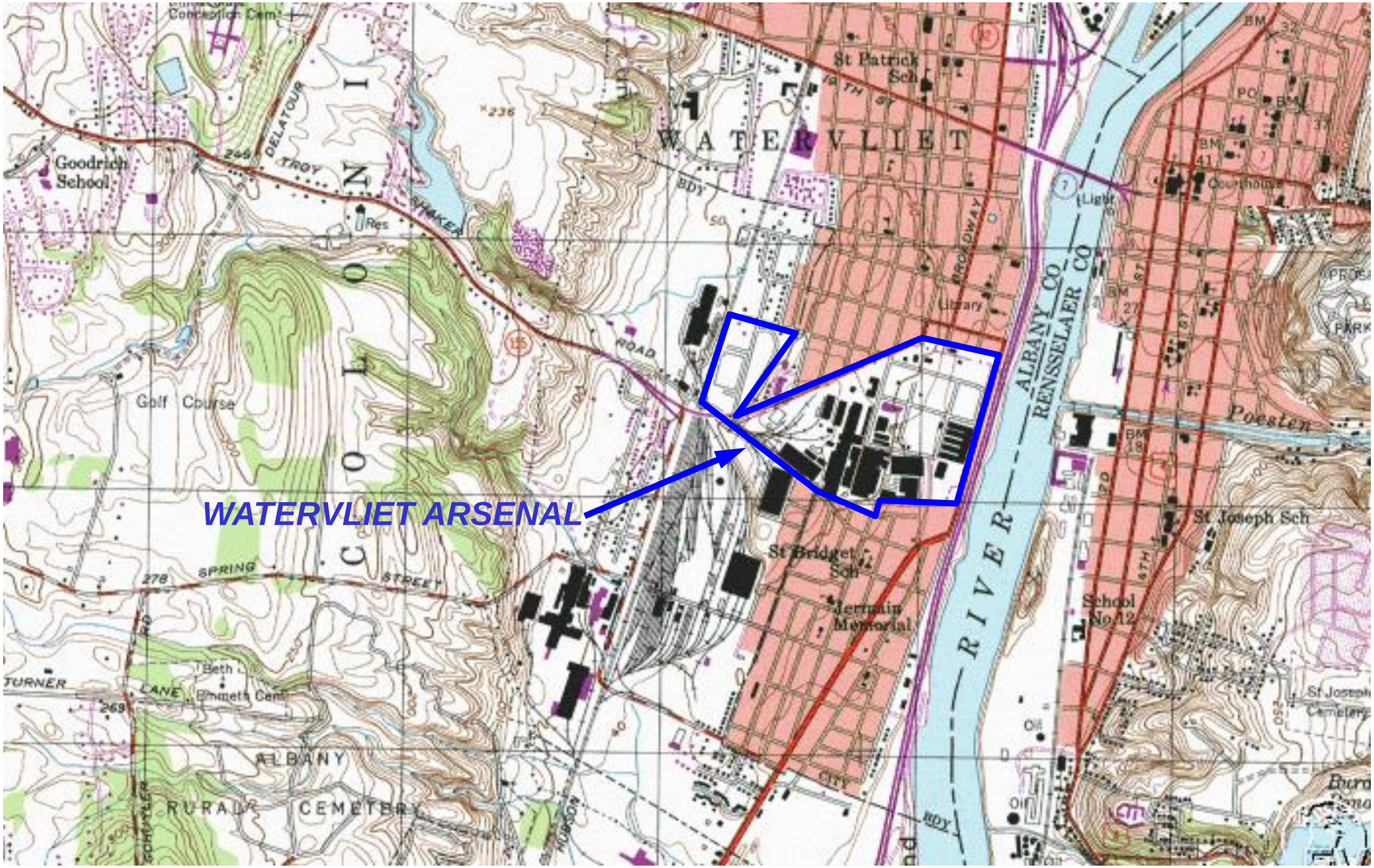
Arcadis, 2020, Plating Area Site Investigation Report, Watervliet Arsenal, Watervliet, New York. June 2020.

Malcolm Pirnie, 2000, Final RCRA Facility Investigation Report, Main Manufacturing Area, Watervliet Arsenal, Watervliet, New York.

New York State Department of Environmental Conservation, 2010, DER-10 Technical Guidance for Site Investigation and Remediation.

PIKA-MP JV, 2016, Installation Restoration Program Work Plan, Watervliet Arsenal, Watervliet, New York.

FIGURES



SOURCE: U.S.G.S 7.5 MIN. TROY SOUTH QUADRANGLE

US Army Corps of Engineers
Baltimore District

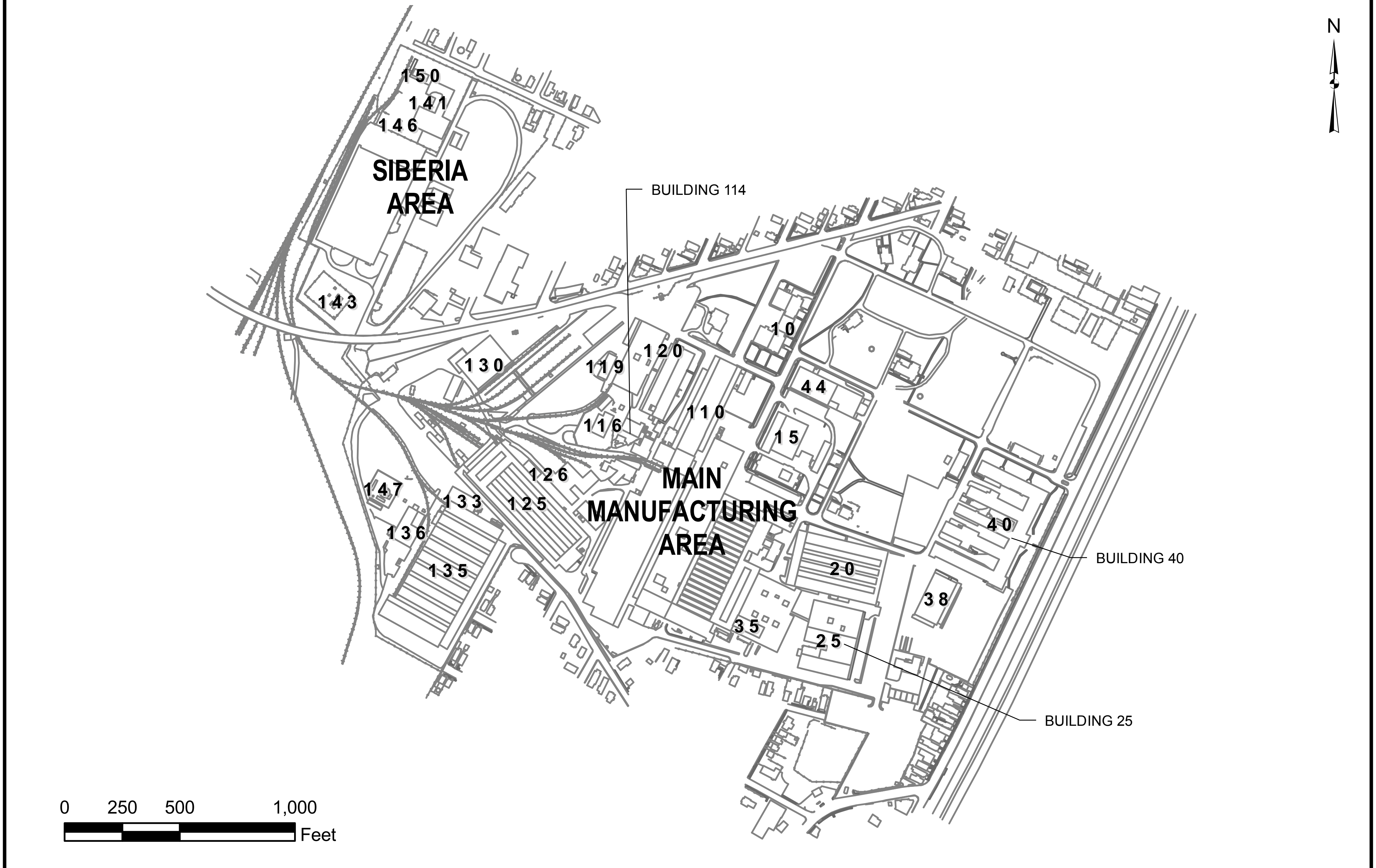
WATERVLIET ARSENAL
WATERVLIET, NEW YORK

PLATING AREA SITE INVESTIGATION

SITE LOCATION

FIGURE 1-1

G:\GISMOD\WatervlietArsenal\LTM\Figures\WVA Site Plan.mxd



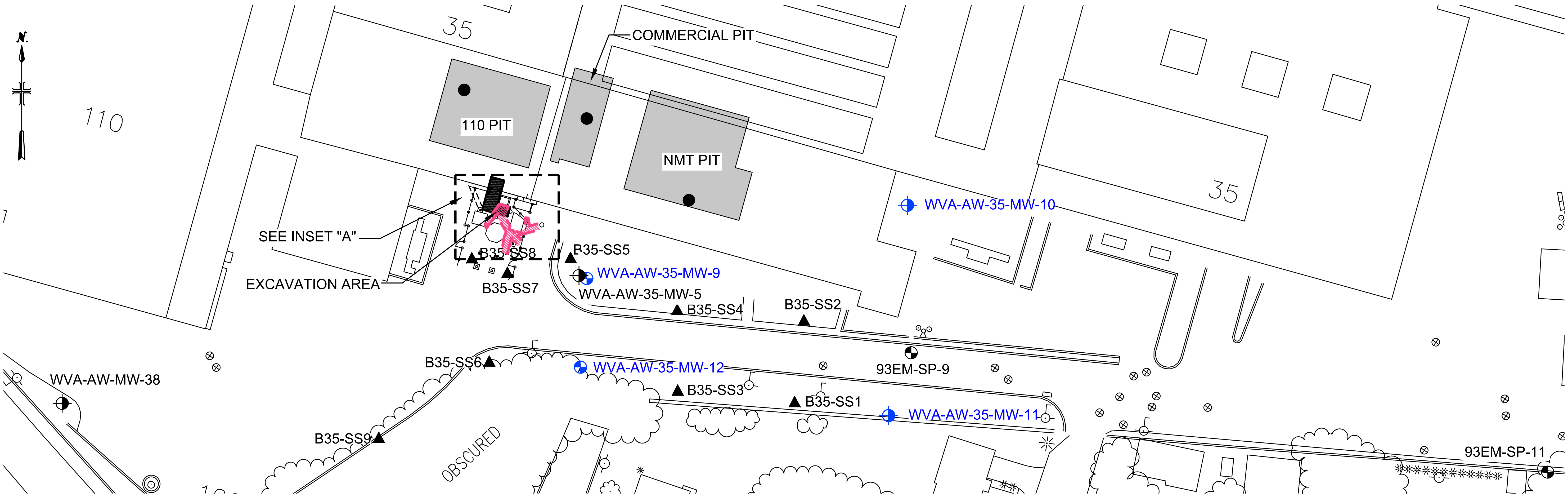
US Army Corps of Engineers

LONG-TERM MONITORING PROGRAM
WATERVLIET ARSENAL
WATERVLIET, NEW YORK

SITE MAP

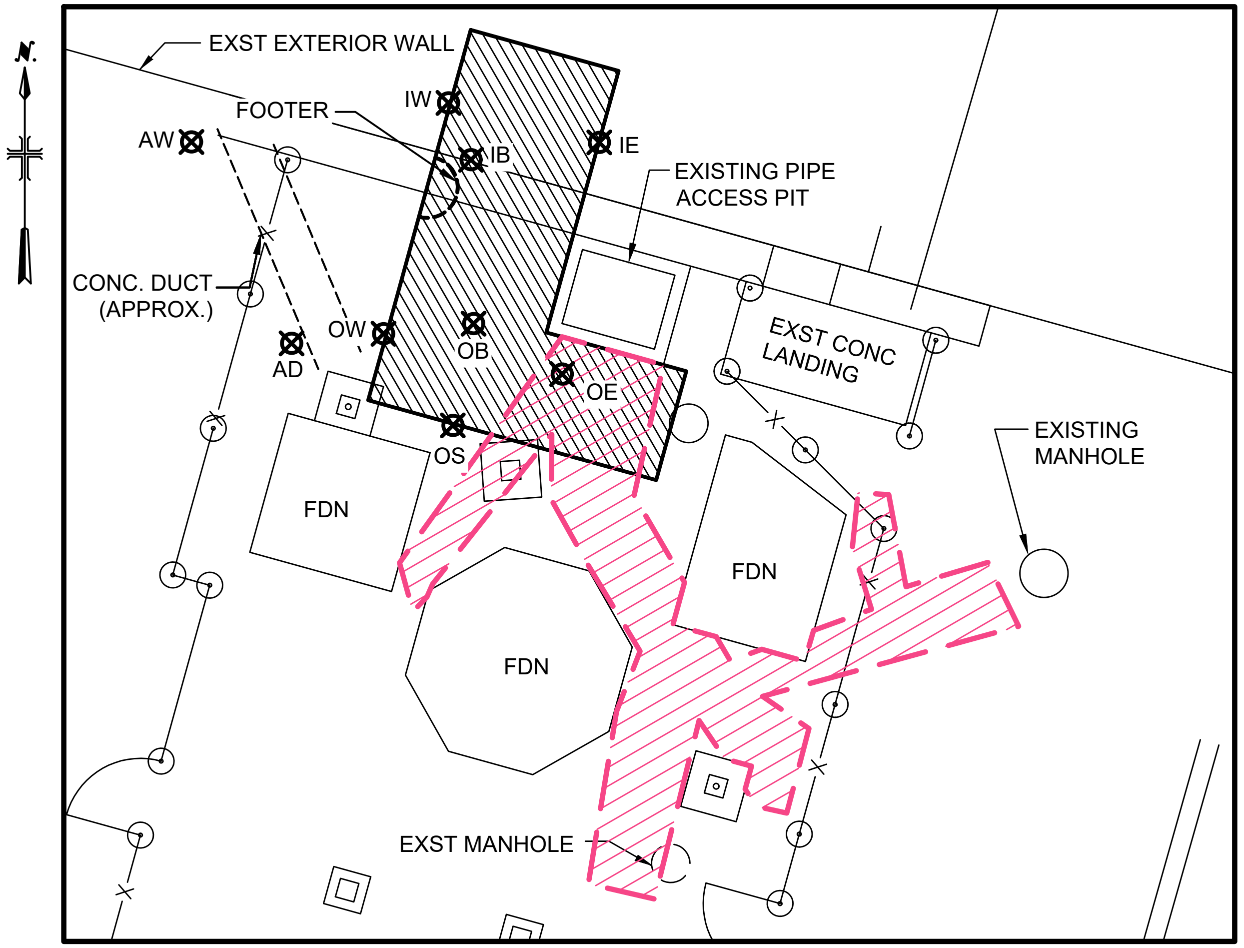
ARCADIS US INC

FIGURE 1-2



PLAN

0 30' 60' 120'



INSET "A"

LEGEND

⊗	MANHOLE
ጸ	HYDRANT
○	BOLLARD
-⊙-	UTILITY POLE
-⊙-	UTILITY/LIGHT POLE
—×—×—	FENCE
◐	OVERBURDEN MONITORING WELL LOCATIONS
⊕	BEDROCK MONITORING WELL LOCATIONS
◐	OVERBURDEN MONITORING WELL LOCATIONS (INSTALLED 2019)
⊕	BEDROCK MONITORING WELL LOCATIONS (INSTALLED 2019)
●	GROUNDWATER SUMP LOCATIONS (APPROX.)
▲	SURFACE SOIL SAMPLE LOCATIONS (2019)
AD ⊠	2018 EXCAVATION SAMPLE LOCATION
▨	2018 EXCAVATION
▨	ANTICIPATED LIMITS OF EXCAVATION ACTIVITIES

0 5' 10' 20'

SOIL SAMPLE NOTES:

- IW - 3' OFF BOTTOM, 5' FROM NORTH PIT WALL
- IE - 2' OFF BOTTOM, BELOW CONC., 5' FROM NORTH PIT WALL
- OW - 4' BELOW CONC.
- OE - 6" OUT FROM UTILITY PIT, BELOW CONDUIT
- AW - ADJACENT TO EXISTING WALL ON WEST SIDE OF FENCE POST
- AD - ADJACENT TO EXISTING DUCT

WATERVLIET ARSENAL
MANUFACTURING AREA
CHROME SCRUBBER EXCAVATION WORK PLAN

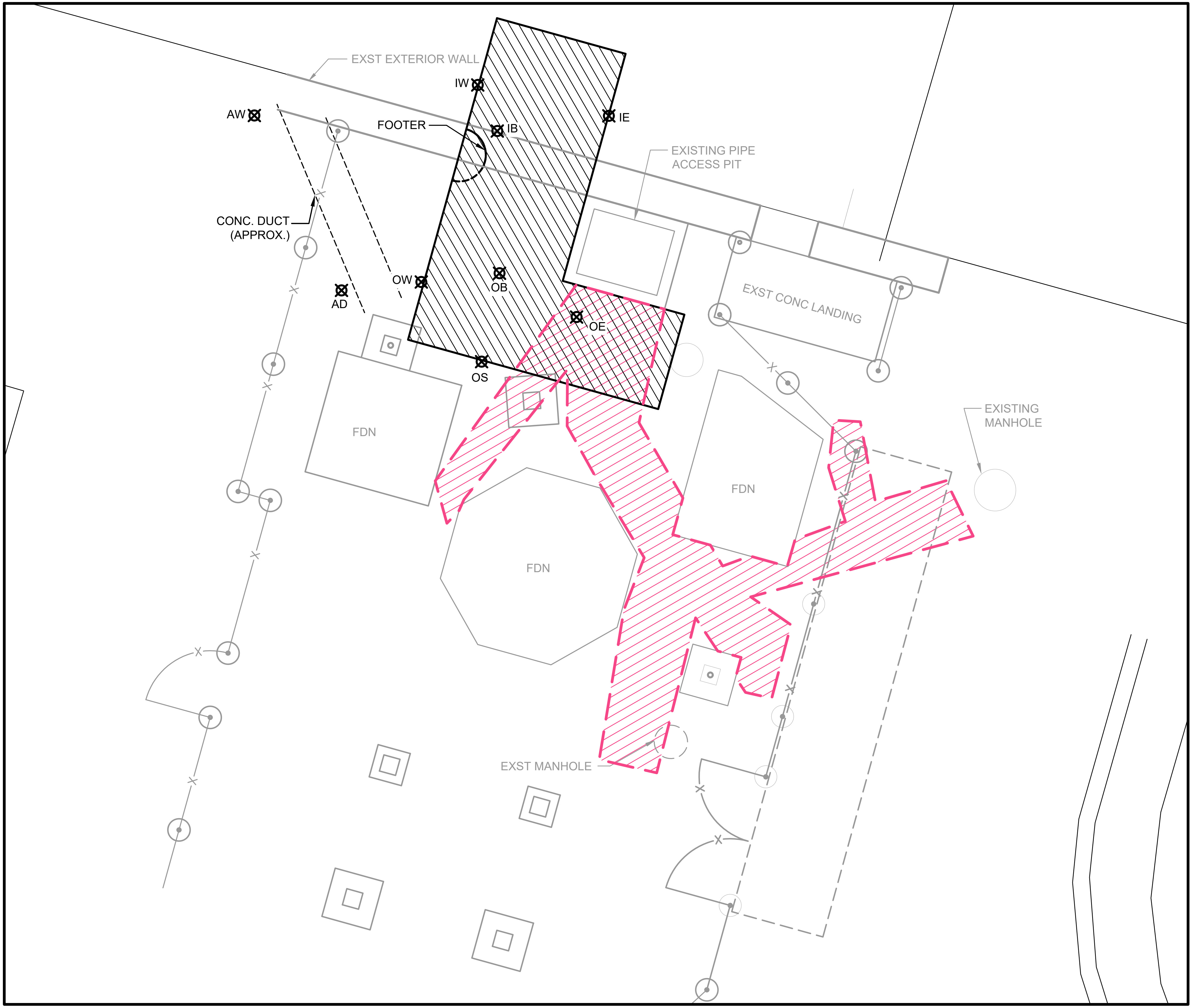
2018 EXCAVATION AND ASSOCIATED SAMPLING LOCATIONS

ARCADIS

FIGURE
2-1

C:\Users\mwasilewski\OneDrive - ARCADIS\BIM360 - OneDrive Sync Location\AUS-USACE-WATERVLIET ARSENAL-WATERVLIET New York\2022\01-In Progress\01-DWG\CSEWP FIG_3-1 EXCAVTION LIMITS.dwg LAYOUT: 3-1 SAVED: 3/24/2022 9:29 AM ACADVER: 23.1S (LMS TECH) PAGESETUP: ----
PLOTSTYLETABLE: PLTFULL.CTB PLOTTED: 3/24/2022 9:30 AM BY: WASILEWSKI, MATT

XREFS: IMAGES: PROJECTNAME: ----
XREF-WVA-BASEMAP Chrome SD-0401, S-0401, MP-0127_3.tif



LEGEND

▨ ANTICIPATED LIMITS OF EXCAVATION ACTIVITIES

▨ 2018 EXCAVATION

AD ☒ 2018 EXCAVATION SAMPLE LOCATION

—x—x— FENCE

NOTE:

1. TOTAL ANTICIPATED EXCAVATION AREA APPROXIMATELY 234 SQUARE FEET. DEPTH OF EXCAVATION NOT TO EXCEED 5 FEET BELOW GROUND SURFACE.

0 6' 12'
GRAPHIC SCALE

WATERVLIET ARSENAL
MANUFACTURING AREA
CHROME SCRUBBER EXCAVATION WORK PLAN

ANTICIPATED LIMITS OF EXCAVATION ACTIVITY

ARCADIS

FIGURE
3-1

APPENDIX A

Standard Operating Procedures / Relevant Guidance

METHOD 3060A

ALKALINE DIGESTION FOR HEXAVALENT CHROMIUM

1.0 SCOPE AND APPLICATION

1.1 Any reference in this method to “Method 3060" refers to this version of that method, and does not refer to previously published versions (e.g., in the Second Edition of this manual). When published as a new method to SW-846, a method’s number does not include a letter suffix. Each time a method is revised and made a part of SW-846 update, it receives a suffix. However, a method reference found within the text of SW-846 methods always refers to the latest version of that method published in SW-846, even if the method number at that location does not include the appropriate letter suffix.

1.2 Method 3060 is an alkaline digestion procedure for extracting hexavalent chromium [Cr(VI)] from soluble, adsorbed, and precipitated forms of chromium compounds in soils, sludges, sediments, and similar waste materials. To quantify total Cr(VI) in a solid matrix, three criteria must be satisfied: (1) the extracting solution must solubilize all forms of Cr(VI), (2) the conditions of the extraction must not induce reduction of native Cr(VI) to Cr(III), and (3) the method must not cause oxidation of native Cr(III) contained in the sample to Cr(VI). Method 3060 meets these criteria for a wide spectrum of solid matrices. Under the alkaline conditions of the extraction, minimal reduction of Cr(VI) or oxidation of native Cr(III) occurs. The addition of Mg^{2+} in a phosphate buffer to the alkaline solution has been shown to suppress oxidation, if observed. The accuracy of the extraction procedure is assessed using spike recovery data for soluble and insoluble forms of Cr(VI) (e.g., $K_2Cr_2O_7$ and $PbCrO_4$), coupled with measurement of ancillary soil properties, indicative of the potential for the soil to maintain a Cr(VI) spike during digestion, such as oxidation reduction potential (ORP), pH, organic matter content, ferrous iron, and sulfides. Recovery of an insoluble Cr(VI) spike can be used to assess the first two criteria, and method-induced oxidation is usually not observed except in soils high in Mn and amended with soluble Cr(III) salts or freshly precipitated $Cr(OH)_3$.

1.3 The quantification of Cr(VI) in Method 3060 digests should be performed using a suitable technique with appropriate accuracy and precision, for example Method 7196 (colorimetrically by UV-VIS spectrophotometry) or Method 7199 (colorimetrically by ion chromatography (IC)). Analytical techniques such as IC with inductively coupled plasma - mass spectrometric (ICP-MS) detection, high performance liquid chromatography (HPLC) with ICP-MS detection, capillary electrophoresis (CE) with ICP-MS detection, etc. may be utilized once performance effectiveness has been validated.

2.0 SUMMARY OF METHOD

2.1 This method uses an alkaline digestion to solubilize both water-insoluble (with the exception of partial solubility of barium chromate in some soil matrices, see Reference 10.9) and water soluble Cr(VI) compounds in solid waste samples. The pH of the digestate must be carefully adjusted during the digestion procedure. Failure to meet the pH specifications will necessitate redigestion of the samples.

2.2 The sample is digested using 0.28M Na_2CO_3/0.5M NaOH solution and heating at 90-95°C for 60 minutes to dissolve the Cr(VI) and stabilize it against reduction to Cr(III).

2.3 The Cr(VI) reaction with diphenylcarbazide is the most common and reliable method for analysis of Cr(VI) solubilized in the alkaline digestate. The use of diphenylcarbazide has been well established in the colorimetric procedure (Method 7196), in rapid-test field kits, and in the ion chromatographic method for Cr(VI) (Method 7199). It is highly selective for Cr(VI) and few interferences are encountered when it is used on alkaline digestates.

2.4 For additional information on health and safety issues relating to chromium, refer to References 10.7 and 10.10.

3.0 INTERFERENCES

3.1 When analyzing a sample digest for total Cr(VI), it is appropriate to determine the reducing/oxidizing tendency of each sample matrix. This can be accomplished by characterization of each sample for additional analytical parameters, such as pH (Method 9045), ferrous iron (ASTM Method D3872-86), sulfides (Method 9030), and Oxidation Reduction Potential (ORP) (ASTM Method D 1498-93 - aqueous samples). Method 9045 (Section 7.2 of Method 9045) is referenced as the preparatory method for soil samples. The ORP and temperature probes are inserted directly into the soil slurry. The displayed ORP value is allowed to equilibrate and the resulting measurement is recorded. Other indirect indicators of reducing/oxidizing tendency include Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD). Analysis of these additional parameters establishes the tendency of Cr(VI) to exist or not exist in the unspiked sample(s) and assists in the interpretation of QC data for matrix spike recoveries outside conventionally accepted criteria for total metals.

3.2 Certain substances, not typically found in the alkaline digests of soils, may interfere in the analytical methods for Cr(VI) following alkaline extraction if the concentrations of these interfering substances are high and the Cr(VI) concentration is low. Refer to Methods 7196 and 7199 for a discussion of the specific agents that may interfere with Cr(VI) quantification. Analytical techniques that reduce bias caused by co-extracted matrix components may be applicable in correcting these biases after validation of their performance effectiveness.

3.3 For waste materials or soils containing soluble Cr(III) concentrations greater than four times the laboratory Cr(VI) reporting limit, Cr(VI) results obtained using this method may be biased high due to method-induced oxidation. The addition of Mg^{2+} in a phosphate buffer to the alkaline extraction solution has been shown to suppress this oxidation. If an analytical method for Cr(VI) is used that can correct for possible method induced oxidation/reduction, then the Mg^{2+} addition is optional. The presence of soluble Cr(III) can be approximated by extracting the sample with deionized water (ASTM methods D4646-87, D5233-92, or D3987-85) and analyzing the resultant leachate for both Cr(VI) and total Cr. The difference between the two values approximates soluble Cr(III).

4.0 APPARATUS AND MATERIALS

4.1 Digestion vessel: borosilicate glass or quartz with a volume of 250 mL.

4.2 Graduated Cylinder: 100-mL or equivalent.

4.3 Volumetric Flasks: Class A glassware, 1000-mL and 100-mL, with stoppers or equivalent.

4.4 Vacuum Filtration Apparatus.

4.5 Filter membranes (0.45 µm). Preferably cellulosic or polycarbonate membranes. When vacuum filtration is performed, operation should be performed with recognition of the filter membrane breakthrough pressure.

4.6 Heating Device - capable of maintaining the digestion solution at 90-95°C with continuous auto stirring capability or equivalent.

4.7 Volumetric pipettes: Class A glassware, assorted sizes, as necessary.

4.8 Calibrated pH meter.

4.9 Calibrated balance.

4.10 Temperature measurement device (with NIST traceable calibration) capable of measuring up to 100°C (e.g. thermometer, thermistor, IR sensor, etc.).

4.11 An automated continuous stirring device (e.g. magnetic stirrer, motorized stirring rod, etc.), one for each digestion being performed.

5.0 REAGENTS

5.1 Nitric acid: 5.0 M HNO_3, analytical reagent grade or spectrograde quality. Store at 20-25°C in the dark. Do not use concentrated HNO_3 to make up 5.0 M solution if it has a yellow tinge; this is indicative of photoreduction of NO_3^- to NO_2, a reducing agent for Cr(VI).

5.2 Sodium carbonate: Na_2CO_3, anhydrous, analytical reagent grade. Store at 20-25°C in a tightly sealed container.

5.3 Sodium hydroxide: NaOH, analytical reagent grade. Store at 20-25°C in a tightly sealed container.

5.4 Magnesium Chloride: $MgCl_2$ (anhydrous), analytical reagent grade. A mass of 400 mg $MgCl_2$ is approximately equivalent to 100 mg Mg^{2+}. Store at 20-25°C in a tightly sealed container.

5.5 Phosphate Buffer:

5.5.1 K_2HPO_4: analytical reagent grade.

5.5.2 KH_2PO_4: analytical reagent grade.

5.5.3 0.5M K_2HPO_4/0.5M KH_2PO_4 buffer at pH 7: Dissolve 87.09 K_2HPO_4 and 68.04 g KH_2PO_4 into 700 mL of reagent water. Transfer to a 1L volumetric flask and dilute to volume.

5.6 Lead Chromate: $PbCrO_4$, analytical reagent grade. The insoluble matrix spike is prepared by adding 10-20 mg of $PbCrO_4$ to a separate sample aliquot. Store under dry conditions at 20-25°C in a tightly sealed container.

5.7 Digestion solution: Dissolve 20.0 ± 0.05 g NaOH and 30.0 ± 0.05 g Na_2CO_3 in reagent water in a one-liter volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle at 20-25°C and prepare fresh monthly. The pH of the digestion solution must be checked before using. The pH must be 11.5 or greater, if not, discard.

5.8 Potassium dichromate, $K_2Cr_2O_7$, spiking solution (1000 mg/L Cr(VI)): Dissolve 2.829 g of dried (105°C) $K_2Cr_2O_7$ in reagent water in a one-liter volumetric flask and dilute to the mark. Alternatively, a 1000 mg/L Cr(VI) certified primary standard solution can be used (Fisher AAS standard or equivalent). Store at 20-25°C in a tightly sealed container for use up to six months.

5.8.1 Matrix spiking solution (100 mg/L Cr(VI)): Add 10.0 mL of the 1000 mg Cr(VI)/L made from $K_2Cr_2O_7$ spiking solution (Section 5.8) to a 100 mL volumetric flask and dilute to volume with reagent water. Mix well.

5.9 Reagent Water - Reagent water will be free of interferences. Refer to Chapter One for a definition of reagent water.

6.0. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be collected using devices and placed in containers that do not contain stainless steel (e.g., plastic or glass).

6.3 Samples should be stored field-moist at 4 ± 2°C until analysis.

6.4 Hexavalent chromium has been shown to be quantitatively stable in field-moist soil samples for 30 days from sample collection. In addition, Cr(VI) has also been shown to be stable in the alkaline digestate for up to 168 hours after extraction from soil.

6.5 Hexavalent chromium solutions or waste material that are generated should be disposed of properly. One approach is to treat all Cr(VI) waste materials with ascorbic acid or other reducing agent to reduce the Cr(VI) to Cr(III). For additional information on health and safety issues relating to chromium, the user is referred to References 10.7 and 10.10.

7.0 PROCEDURE

7.1 Adjust the temperature setting of each heating device used in the alkaline digestion by preparing and monitoring a temperature blank [a 250 mL vessel filled with 50 mLs digestion solution (Section 5.7)]. Maintain a digestion solution temperature of 90-95°C as measured with a NIST-traceable thermometer or equivalent.

7.2 Place 2.5 ± 0.10 g of the field-moist sample into a clean and labeled 250 mL digestion vessel. The sample should have been mixed thoroughly before the aliquot is removed.

For the specific sample aliquot that is being spiked (Section 8.5), the spike material should be added directly to the sample aliquot at this point. (Percent solids determination, U.S. EPA CLP SOW for Organic Analysis, OLM03.1, 8/94 Rev.) should be performed on a separate aliquot in order to calculate the final result on a dry-weight basis).

7.3 Add 50 mL ± 1 mL of digestion solution (Section 5.7) to each sample using a graduated cylinder, and also add approximately 400 mg of $MgCl_2$ (Section 5.4) and 0.5 mL of 1.0M phosphate buffer (Section 5.5.3). For analytical techniques that can correct for oxidation/reduction of Cr, the addition of Mg^{2+} is optional. Cover all samples with watch glasses.

7.4 Stir the samples continuously (unheated) for at least five minutes using an appropriate stirring device.

7.5 Heat the samples to 90-95°C, then maintain the samples at 90-95°C for at least 60 minutes with continuous stirring.

7.6 Gradually cool, with continued agitation, each solution to room temperature. Transfer the contents quantitatively to the filtration apparatus; rinsing the digestion vessel with 3 successive portions of reagent water. Transfer the rinsates to the filtration apparatus. Filter through a 0.45µm membrane filter. Rinse the inside of the filter flask and filter pad with reagent water and transfer the filtrate and the rinses to a clean 250-mL vessel.

> NOTE: The remaining solids and filter paper resulting from filtration of the matrix spike in Section 7.6 should be saved for possible use in assessing low Cr(VI) matrix spike recoveries. See Section 8.5.2. for additional details. Store the filtered solid at 4 ± 2°C.

7.7 Place an appropriate stirring device into the sample digest beaker, place the vessel on a stirrer, and, with constant stirring, slowly add 5.0 M nitric acid solution to the beaker dropwise. Adjust the pH of the solution to 7.5 ± 0.5 if the sample is to be analyzed using Method 7196 (adjust the pH accordingly if an alternate analytical method is to be used; i.e. 9.0 ± 0.5 if Method 7199 is to be used) and monitor the pH with a pH meter. If the pH of the digest should deviate from the desired range, discard the solution and redigest. If overshooting the desired pH range occurs repeatedly, prepare diluted nitric acid solution and repeat digestion procedure. If a flocculent precipitate should form, the sample should be filtered through a 0.45 µm membrane filter. If the filter becomes clogged using the 0.45 µm filter paper, a larger size filter paper (Whatman GFB or GFF) may be used to prefilter the samples.

> CAUTION: CO_2 will be evolved. This step should be performed in a fume hood.

7.8 Remove the stirring device and rinse, collecting the rinsate in the beaker. Transfer quantitatively the contents of the vessel to a 100 mL volumetric flask and adjust the sample volume to 100 mL (to the mark for the volumetric flask) with reagent water. Mix well.

7.9 The sample digestates are now ready to be analyzed. Determine the Cr(VI) concentration in mg/kg by a suitable technique with appropriate accuracy and precision, for example Method 7196 (colorimetrically by UV-VIS spectrophotometry) or Method 7199 (colorimetrically by ion chromatography (IC)). Another analytical technique such as IC with inductively coupled plasma - mass spectrometric (ICP-MS) detection, high performance liquid chromatography (HPLC) with ICP-

MS detection, capillary electrophoresis (CE) with ICP-MS detection, etc. may be utilized once performance effectiveness has been validated.

7.10 CALCULATIONS

7.10.1 Sample Concentration

$$\text{Concentration} = \frac{A \times D \times E}{B \times C}$$

where: A = Concentration observed in the digest (µg/mL)
B = Initial moist sample weight (g)
C = % Solids/100
D = Dilution Factor
E = Final digest volume (mL)

7.10.2 Relative Percent Difference

$$\text{RPD} = \frac{(S - D)}{[(S + D)/2]}$$

where: S = Initial sample result
D = Duplicate sample result

7.10.3 Spike Recovery

$$\text{Percent Recovery} = \frac{(SSR - SR)}{SA} \times 100$$

where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

8.0 QUALITY CONTROL

8.1 The following Quality Control (QC) analyses must be performed per digestion batch as discussed in Chapter One.

8.2 A preparation blank must be prepared and analyzed with each digestion batch, as discussed in Chapter One and detected Cr(VI) concentrations must be less than the method detection limit or one-tenth the regulatory limit or action level, whichever is greater or the entire batch must be redigested.

8.3 Laboratory Control Sample (LCS): As an additional determination of method performance, utilize the matrix spike solution prepared in Section 5.8.1 or the solid matrix spiking agent $PbCrO_4$ (Section 5.6) to spike into 50 mL of digestion solution (Section 5.7). Alternatively, the use of a certified solid reference material (if available) is recommended. Recovery must be within the certified acceptance range or a recovery range of 80% to 120% or the sample batch must be reanalyzed.

8.4 A separately prepared duplicate soil sample must be analyzed at a frequency of one per batch as discussed in Chapter One. Duplicate samples must have a Relative Percent Difference (RPD) of $\leq$ 20%, if both the original and the duplicate are $\geq$ four times the laboratory reporting limit. A control limit of ± the laboratory reporting limit is used when either the original or the duplicate sample is < four times the laboratory reporting limit.

8.5 Both soluble and insoluble pre-digestion matrix spikes must be analyzed at a frequency of one each per batch of $\leq$ 20 field samples. The soluble matrix spike sample is spiked with 1.0 mL of the spiking solution prepared in Section 5.8.1 (equivalent to 40 mg Cr(VI)/Kg)) or at twice the sample concentration, whichever is greater. The insoluble matrix spike is prepared by adding 10-20 mg of $PbCrO_4$ (Section 5.6) to a separate sample aliquot. It is used to evaluate the dissolution during the digestion process. Both matrix spikes are then carried through the digestion process described in Section 7.0. More frequent matrix spikes must be analyzed if the soil characteristics within the analytical batch appear to have significant variability based on visual observation. An acceptance range for matrix spike recoveries is 75-125%. If the matrix spike recoveries are not within these recovery limits, the entire batch must be rehomogenized/redigested/reanalyzed. If upon reanalysis, the matrix spike is not within the recovery limits, but the LCS is within criteria specified in Section 8.3, information such as that specified on Figures 1 and 2 and in Section 3.1 should be carefully evaluated . The Cr(VI) data may be valid for use despite the perceived "QC failure." The information shown on Figure 1 and discussed below is provided to interpret ancillary parameter data in conjunction with data on spike recoveries.

8.5.1 First measure the pH (Method 9045) and Oxidation Reduction Potential (ORP) (ASTM Method D 1498-93 - aqueous samples, Method 9045 preparatory for soil samples), in the field if possible. If not possible, the measurements are to be made in the laboratory prior to the determination of the spike recovery data. When and where the measurements are taken must be noted by the analyst. Adjust the ORP measurement based on reference electrode correction factor to yield Eh values. The pH and Eh values should be plotted on Figure 2 in order to give an initial indication of the sample's reducing/oxidizing nature. Upon completion of the analysis of the analytical batch, the LCS should be evaluated. If the LCS is not within 80 - 120% recovery or the certified acceptance range, then the entire analytical batch (plus the QC samples) should be redigested and reanalyzed. If the LCS was within acceptance criteria and the pre-digestion matrix spike recoveries for Cr(VI) were less than the acceptance range minimum (75%), this indicates that the soil samples reduced Cr(VI) (e.g., anoxic sediments), and no measurable native Cr(VI) existed in the unspiked sample (assuming the criteria in Section 8.3 are met). Such a result indicates that the combined and interacting influences of ORP, pH and reducing agents (e.g., organic acids, Fe^{2+} and sulfides) caused reduction of Cr(VI) spikes. Characterize each matrix spike sample for additional analytical parameters, such as ferrous iron (ASTM Method D3872-86), and sulfides (Method 9030). Laboratory measurements of pH and ORP should also be performed to confirm the field measurements. Other indirect indicators of reducing/oxidizing tendency include Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD). Analysis of these additional parameters assists in evaluating the tendency of Cr(VI) to exist or not exist in the unspiked sample(s) and assists in the interpretation of QC data for matrix spike recoveries outside conventionally accepted criteria for total metals.

A value of Eh-pH below the bold diagonal line on Fig. 2 indicates a reducing soil for Cr(VI). The downward slope to the right indicates that the Eh value, at which Cr(VI) is expected to be reduced, decreases with increasing pH. The solubility and quantity of organic constituents influence reduction of Cr(VI). The presence of H_2S or other strong odors indicates a reducing environment for Cr(VI). In general, acidic conditions accelerate reduction of Cr(VI) in soils, and alkaline conditions tend to stabilize Cr(VI) against reduction. If pre-digestion matrix spike recovery is not within the recovery limits, the reductive nature of the sample must be documented. This is done by plotting the Eh and pH data on the Eh-pH diagram (Fig. 2) to see if spike recovery is or is not expected in the soil. If the data point falls below the Cr(VI)-Cr(III) line on the diagram, then the data is not qualified or rejected. The sample is reducing for Cr(VI). If the data point falls above the line, then the sample is capable of supporting Cr(VI). In this case, technical error may be responsible for the poor spike recovery, and the extraction should be repeated, along with the Eh and pH measurements. If re-extraction results in a poor spike recovery again, then the data is qualified. At this point, review of other soil characteristics, such as levels of pH, Eh, TOC, sulfides, Fe(II), is appropriate to understand why poor spike recovery occurred. This extra review of these soil properties is only necessary if the unspiked sample contains detectable Cr(VI).

8.5.2 If a low or zero percent pre-digestion matrix spike recovery is obtained, an alternate approach can be used to determine the potential contribution of the sample matrix to Cr(VI) reduction. This approach consists of performing a mass balance, whereby total chromium is analyzed (Method 3052) for two samples: (1) a separate unspiked aliquot of the sample previously used for spiking, and (2) the digested solids remaining after the alkaline digestion and filtration of the matrix spike (i.e., the filtered solids from the matrix spike in Section 7.6).

The difference between the total chromium measurements should be approximately equal to the amount of the spike added to the matrix spike. If the LCS (Section 8.3) met the acceptance criteria and the Cr(VI) spike is accounted for in the filtered solids as total chromium, it is likely that the reduction of the Cr(VI) to insoluble Cr(III) resulted from the reducing matrix of the original sample subjected to Cr(VI) spiking.

8.6 A post-digestion Cr(VI) matrix spike must be analyzed per batch as discussed in Chapter One. The post-digestion matrix spike concentration should be equivalent to 40 mg/kg or twice the sample concentration observed in the unspiked aliquot of the test sample, whichever is greater.

8.6.1 Dilute the sample aliquot to a minimum extent, if necessary, so that the absorbance reading for both the unspiked sample aliquot and spiked aliquot are within the initial calibration curve.

8.6.2 A guideline for the post-digestion matrix spike recovery is 85-115%. If not achieved, consider the corrective actions/guidance on data use specified in Section 8.5 or the Method of Standard Additions (MSA) as specified in Section 8.0 of Method 7000. If the MSA technique is applied post digestion and no spike is observed from the MSA, these results indicate that the matrix is incompatible with Cr(VI) and no further effort on the part of the laboratory is required. These digestates may contain soluble reducing agents for Cr(VI), such as fulvic acids.

9.0 METHOD PERFORMANCE

9.1 A commercial laboratory analyzed soil/sediment samples containing Cr(VI) with the results found in Table 1.

10.0 REFERENCES

10.1 United States Environmental Protection Agency, 1982. Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods. SW-846, Second Edition. Office of Solid Waste and Emergency Response, Washington, D.C.

10.2 New Jersey Department of Environmental Protection and Energy (NJDEPE). NJDEPE Modified Methods 3060/7196. 1992.

10.3 Vitale, R., G. Mussoline, J. Petura, B. James, 1993. A Method Evaluation Study of an Alkaline Digestion (Modified Method 3060) Followed by Colorimetric Determination (Method 7196) for the Analysis for Hexavalent Chromium in Solid Matrices. Environmental Standards, Inc. Valley Forge, PA 19482.

10.4 Zatka, V.J., 1985. Speciation of Hexavalent Chromium in Welding Fumes Interference by Air Oxidation of Chromium. J. Ray Gordon Research Laboratory, INCO Limited, Sheridan Park, Mississauga, Ontario L5K 1Z9, Am. Ind. Hyg. Assoc. J., 46(6) : 327-331.

10.5 ASTM (American Society for Testing and Materials), 1981. Standard Practice for Oxidation Reduction Potential of Water. ASTM Designation:D1498-93.

10.6 Vitale, R.J., Mussoline, G.R., Petura, J.C. and James, B.R. 1994. Hexavalent Chromium Extraction from Soils: Evaluation of an Alkaline Digestion Method. J. Environ. Qual. 23:1249-1256.

10.7 U.S. Department of Health and Human Services - Agency for Toxic Substances and Disease Registry. Toxicological Profile for Chromium. April, 1993.

10.8 Vitale, R.J., Mussoline, G.R., Petura, J.C. and James, B.R. 1995. Hexavalent Chromium Quantification in Soils: An Effective and Reliable Procedure. Am. Env. Lab., April Ed.

10.9 James, B.R., Petura, J.C., Vitale, R.J., and Mussoline, G.R. 1995. Hexavalent Chromium Extraction form Soils: A Comparison of Five Methods. Environ. Sci. Technol. 29:2377-2381.

10.10 U.S. Environmental Protection Agency. 1993. IRIS: A continuously updated electronic database maintained by the U.S. Environmental Protection Agency. National Library of Medicine, Bethesda, MD.

10.11 ASTM (American Society for Testing and Materials), 1981. Standard Test Method for Ferrous Iron in Iron Oxides. ASTM Designation:D3872-86.

10.12 ASTM (American Society for Testing and Materials), 1981. Standard Test Method for 24-h Batch-Type Measurement of Contaminant Sorption by Soil and Sediments. ASTM Designation:D4646-87.

10.13 ASTM (American Society for Testing and Materials), 1981. Standard Test Method for Single Batch Extraction Method for Waters. ASTM Designation:D5233-92.

10.14 ASTM (American Society for Testing and Materials), 1981. Standard Test Method for Shake Extraction of Solid Waste with Water. ASTM Designation:D3987-85.

10.15 U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Multimedia Multiconcentration Document, OLM03.1, 8/94 Rev.

TABLE 1
SINGLE LABORATORY METHOD EVALUATION DATA

Sample Type	Eh (mV)[b]	pH[d]	S^{2-} (ppm)[c]	Mean Native Cr(VI) Conc. (mg/kg)	Mean Cr(VI) Spike Conc. (mg/kg)	Matrix Spike Recovery Range,%
COPR[a]/Soil Blends	550	7.4	<10.0	4.1	42.0	89.8-116
Loam	620	6.4	<10.0	ND	62.5	65.0-70.3
Clay	840	3.0	<10.0	ND	63.1	37.8-71.1
COPR[a]	460	7.4	<10.0	759	813	85.5-94.8
Anoxic Sediment	-189	7.2	25.0	ND	381	0
Quartz Sand	710	5.3	<10.0	ND	9.8	75.5-86.3

Source: Reference 10.3

Notes:

ND - Not detected
a - COPR - chromite ore processing residue
b - Corrected for the reference electrode, laboratory field moist measurement
c - Field measurement
d - Laboratory field moist measurement

FIGURE 1
QUALITY CONTROL FLOW CHART

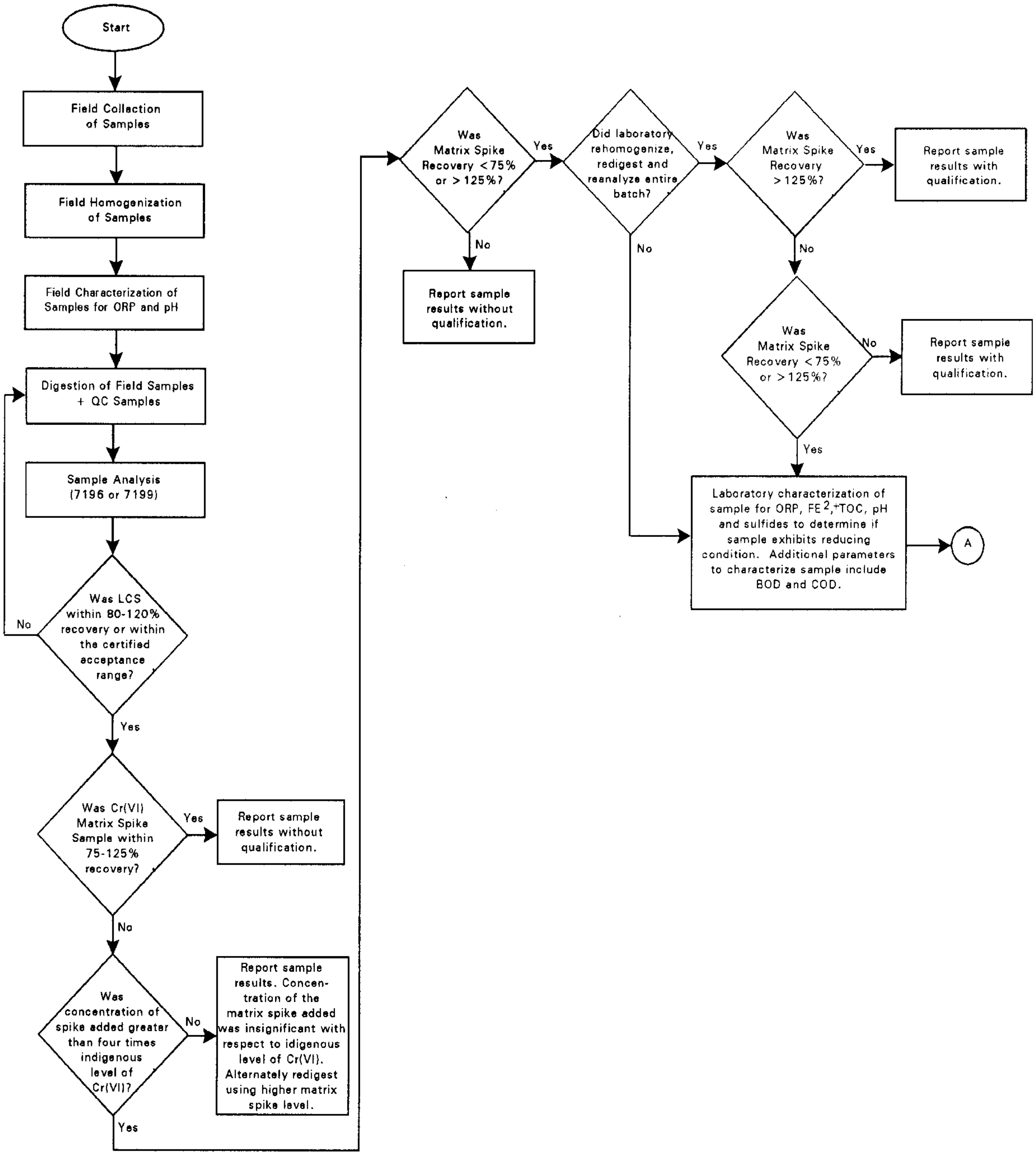


FIGURE 1
QUALITY CONTROL FLOW CHART (Continued)

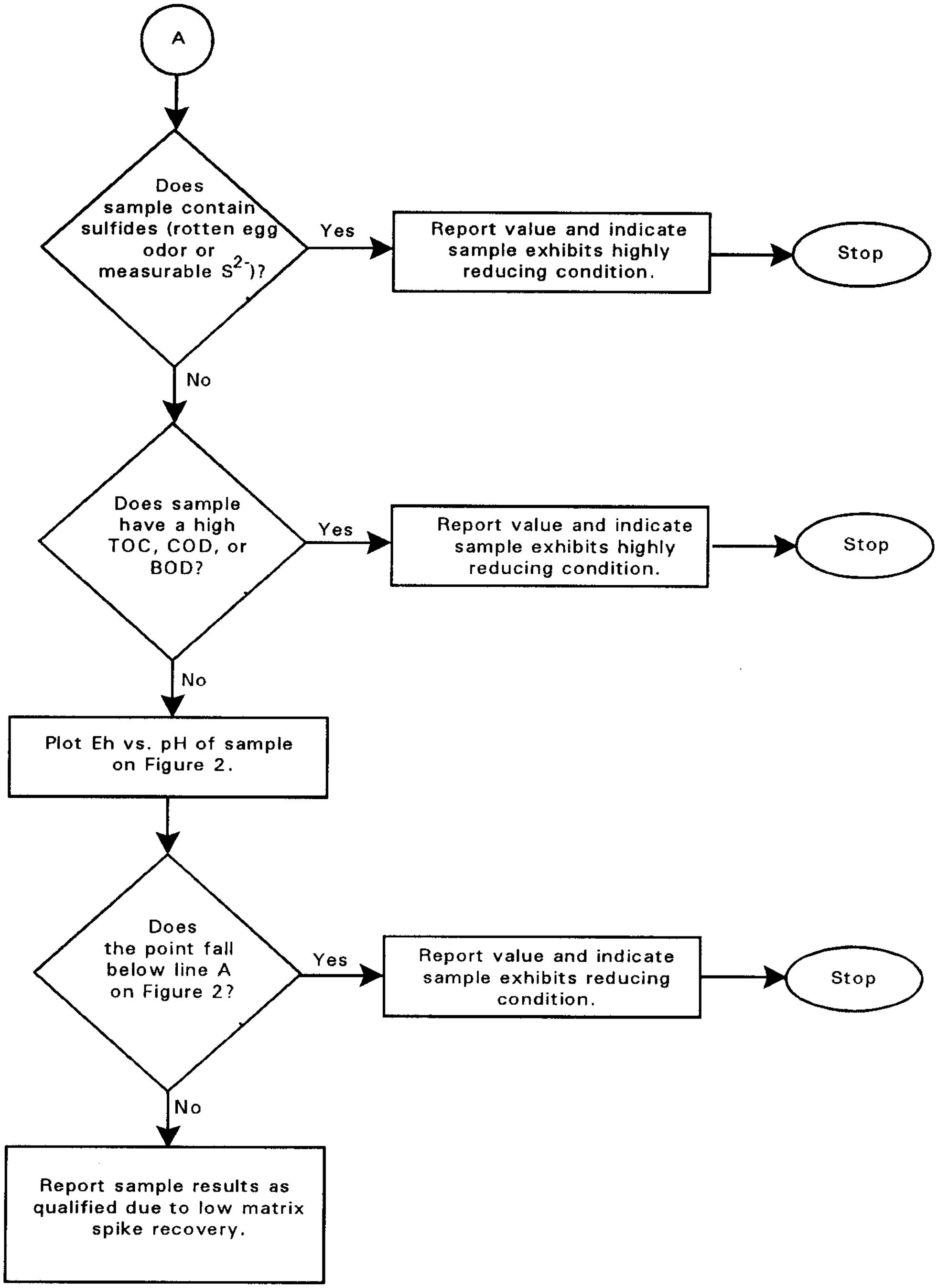
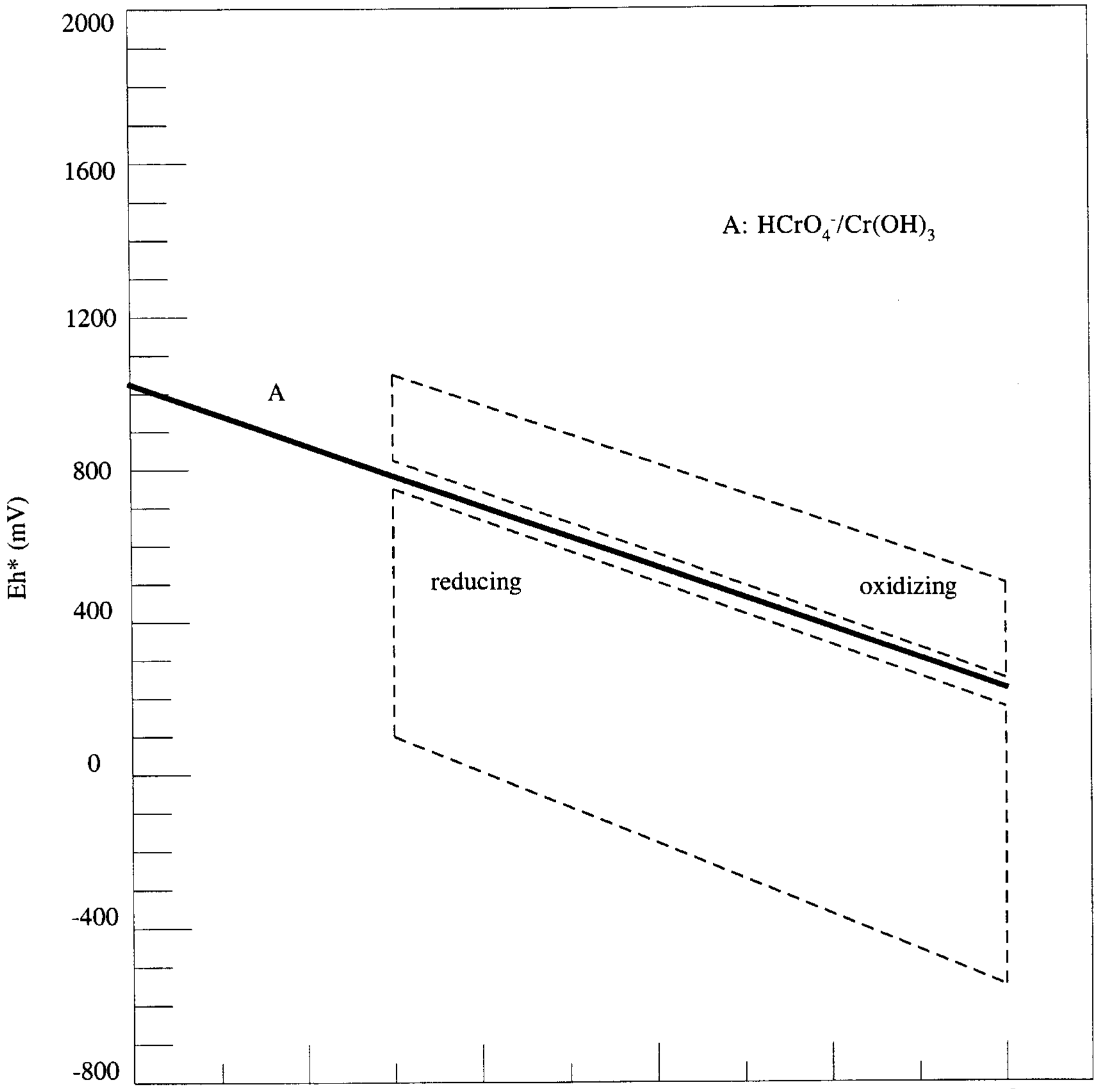


FIGURE 2
Eh/pH PHASE DIAGRAM

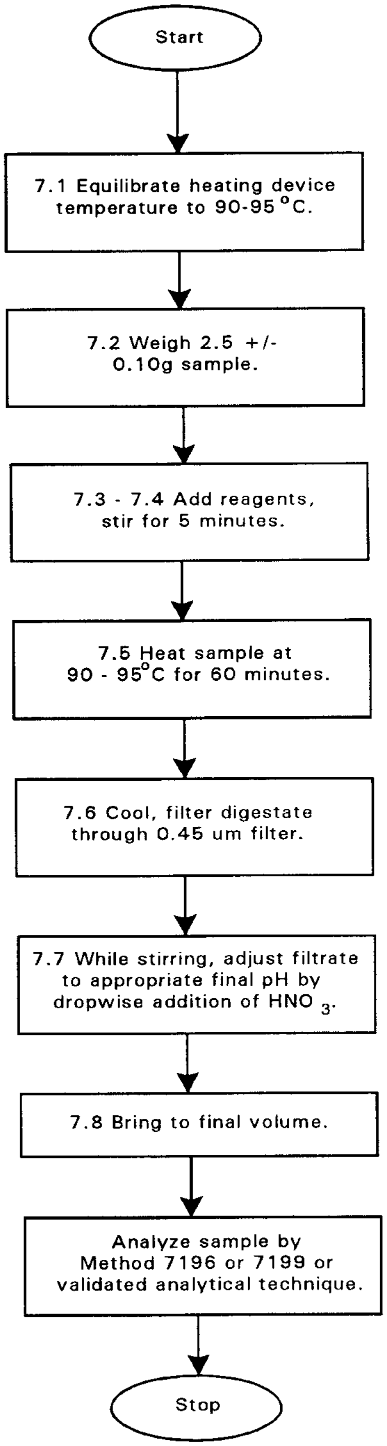
The dashed lines define Eh-pH boundaries commonly encountered in soils and sediments.



* Note the Eh values plotted on this diagram are corrected for the reference electrode voltage: 244 mV units must be added to the measured value when a separate calomel electrode is used, or 199 mV units must be added if a combination platinum electrode is used.

METHOD 3060A

ALKALINE DIGESTION FOR HEXAVALENT CHROMIUM



METHOD 7196A

CHROMIUM, HEXAVALENT (COLORIMETRIC)

1.0 SCOPE AND APPLICATION

1.1 Method 7196 is used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in EP/TCLP characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1 below).

1.2 Method 7196 may be used to analyze samples containing from 0.5 to 50 mg of Cr(VI) per liter.

2.0 SUMMARY OF METHOD

2.1 Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product, and its absorbance is measured photometrically at 540 nm.

3.0 INTERFERENCES

3.1 The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

3.2 Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and difficulty is not normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

4.0 APPARATUS AND MATERIALS

4.1 Colorimetric equipment: One of the following is required: Either a spectrophotometer, for use at 540 nm, providing a light path of 1 cm or longer, or a filter photometer, providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.

5.0 REAGENTS

5.1 Reagent water: Reagent water should be monitored for impurities.

5.2 Potassium dichromate stock solution: Dissolve 141.4 mg of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in reagent water and dilute to 1 liter (1 mL = 50 ug Cr).

5.3 Potassium dichromate standard solution: Dilute 10.00 mL potassium dichromate stock solution to 100 mL (1 mL = 5 ug Cr).

5.4 Sulfuric acid, 10% (v/v): Dilute 10 mL of distilled reagent grade or spectrograde quality sulfuric acid, H_2SO_4, to 100 mL with reagent water.

5.5 Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide in 50 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.

5.6 Acetone (analytical reagent grade): Avoid or redistill material that comes in containers with metal or metal-lined caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Since the stability of Cr(VI) in extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4°C until analyzed. The maximum holding time prior to analysis of the samples or extracts is 24 hr. The 24 hr holding time begins after extraction.

7.0 PROCEDURE

7.1 Color development and measurement: Transfer 95 mL of the extract to be tested to a 100-mL volumetric flask. Add 2.0 mL diphenylcarbazide solution and mix. Add H_2SO_4 solution to give a pH of 2 ± 0.5, dilute to 100 mL with reagent water, and let stand 5 to 10 min for full color development. Transfer an appropriate portion of the solution to a 1-cm absorption cell and measure its absorbance at 540 nm. Use reagent water as a reference. Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the method (see Note below). An aliquot of the sample containing all reagents except diphenylcarbazide should be prepared and used to correct the sample for turbidity (i.e., a turbidity blank). From the corrected absorbance, determine the mg/L of chromium present by reference to the calibration curve.

NOTE: If the solution is turbid after dilution to 100 mL in Step 7.1, above, take an absorbance reading before adding the carbazide reagent and correct the absorbance reading of the final colored solution by subtracting the absorbance measured previously.

7.2 Preparation of calibration curve:

7.2.1 To compensate for possible slight losses of chromium during digestion or other operations of the analysis, treat the chromium standards by the same procedure as the sample. Accordingly, pipet a chromium standard solution in measured volumes into 250-mL beakers or conical flasks to generate standard concentrations ranging from 0.5 to 5 mg/L Cr(VI) when diluted to the appropriate volume.

7.2.2 Develop the color of the standards as for the samples. Transfer a suitable portion of each colored solution to a 1-cm absorption cell and measure the absorbance at 540 nm. As reference, use reagent water. Correct the absorbance readings of the standards by subtracting the absorbance of a reagent blank carried through the method. Construct a calibration curve by plotting corrected absorbance values against mg/L of Cr(VI).

7.3 Verification:

7.3.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting color development. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstances should the increase be less than 30 µg Cr(VI)/liter. To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.3.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.3.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.3.4 If the interference persists after sample dilution, an alternative method (Method 7195, Coprecipitation, or Method 7197, Chelation/Extraction) should be used.

7.4 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

7.5 Analyze all extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions (see Method 7000, Section 8.7).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for more information.

8.2 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.3 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.4 Verify calibration with an independently prepared check standard every 15 samples.

8.5 Run one matrix spike replicate or one replicate sample for every ten samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process. Refer to Chapter One for more information concerning matrix spikes and matrix spike duplicates.

8.6 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

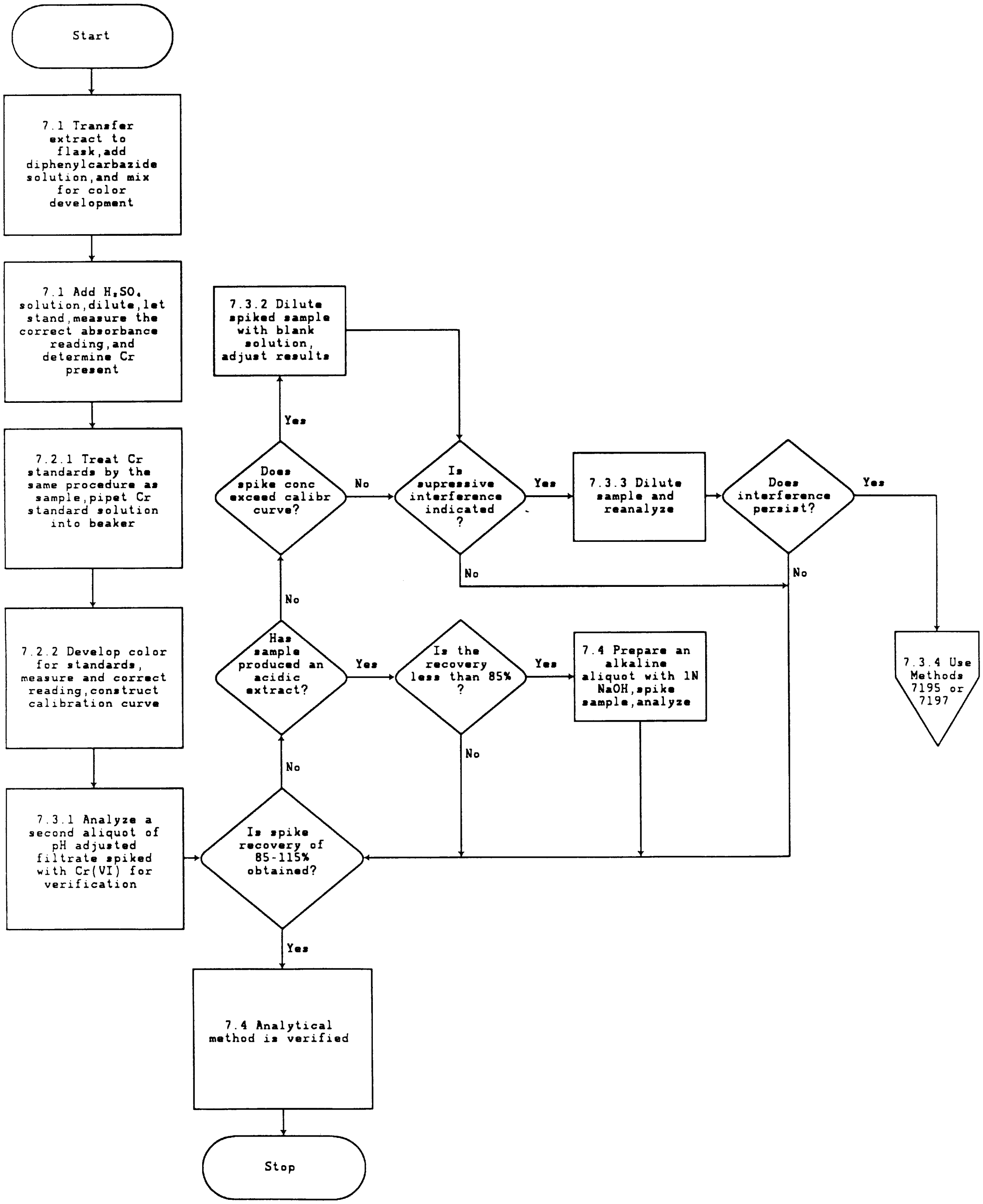
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Methods 218.4 and 218.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	Not known	0.096, 0.107 ug/g
Sediment from chemical storage area	3060	115, 117 ug/g

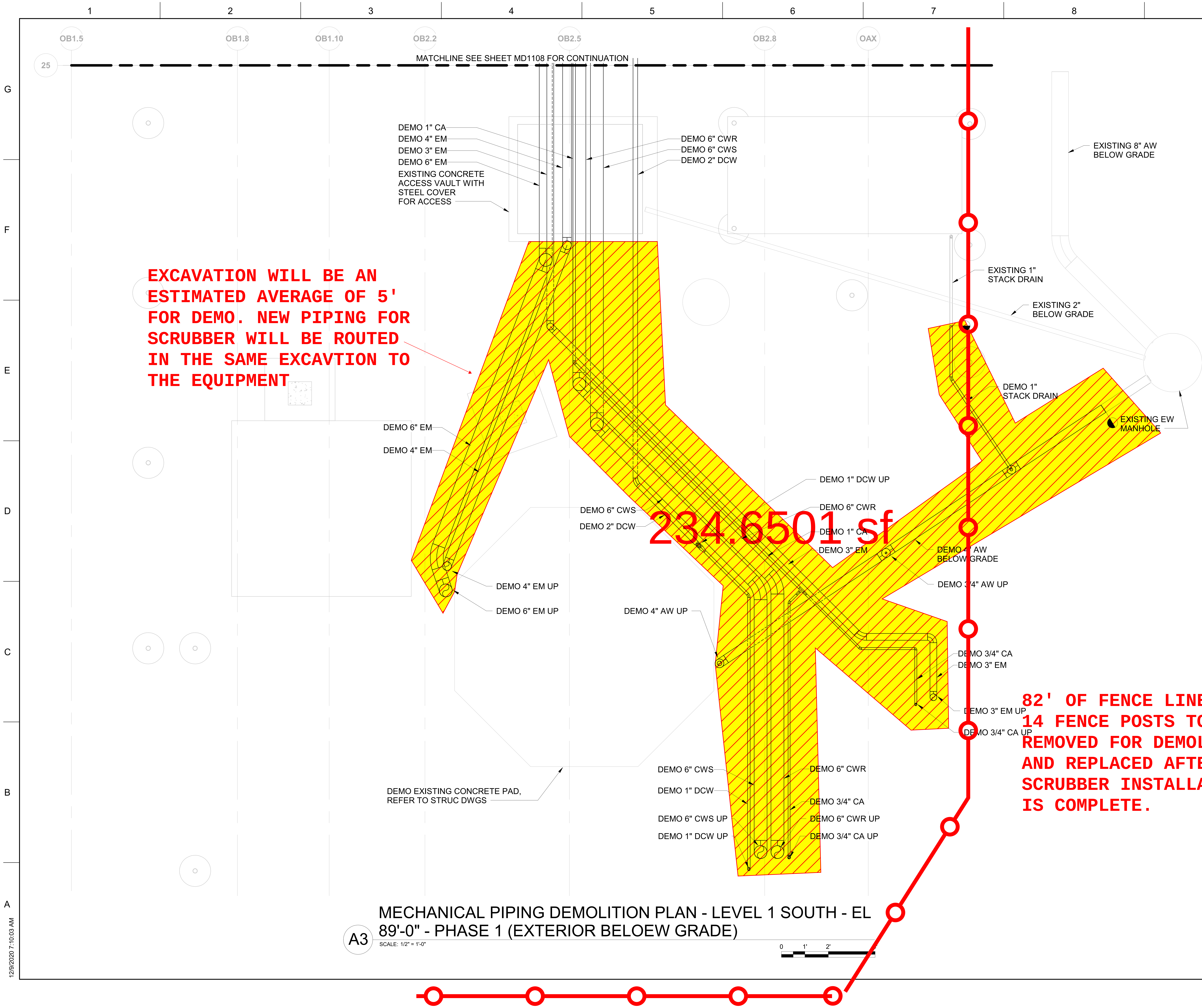
METHOD 7196A
CHROMIUM, HEXAVALENT (COLORIMETRIC)



Revision 1

APPENDIX B

Representative USACE Air Scrubber Demolition and Construction Drawings



EXCAVATION WILL BE AN ESTIMATED AVERAGE OF 5' FOR DEMO. NEW PIPING FOR SCRUBBER WILL BE ROUTED IN THE SAME EXCAVTION TO THE EQUIPMENT

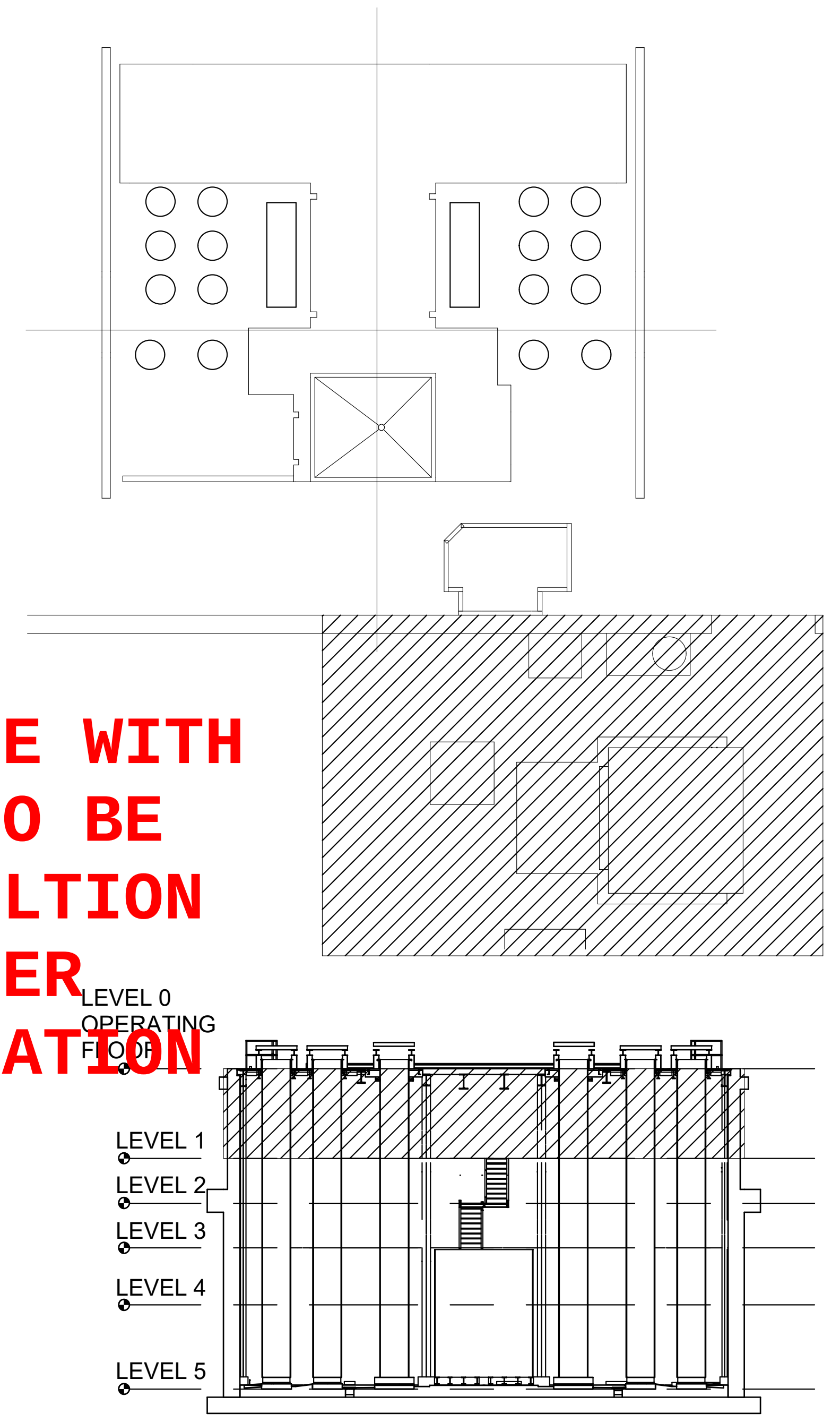
82' OF FENCE LINE WITH 14 FENCE POSTS TO BE REMOVED FOR DEMOLTION AND REPLACED AFTER SCRUBBER INSTALLATION IS COMPLETE.

A3 MECHANICAL PIPING DEMOLITION PLAN - LEVEL 1 SOUTH - EL 89'-0" - PHASE 1 (EXTERIOR BELOEW GRADE)

SCALE: 1/2" = 1'-0"

GENERAL NOTES:

1. DARKENED LINES DEPICT PIPE / EQUIPMENT TO BE REMOVED. ALL LIGHT PIPE / EQUIPMENT TO REMAIN DURING THIS PHASE.
2. DEMOLISH EXISTING PIPING AS IDENTIFIED. PREPARE REMAINING PIPING FOR CONNECTION TO NEW WORK. CAP / BLIND FLANGE ALL OPEN PIPES / VALVES.
3. COORDINATE REMOVAL OF DUCTWORK AND HOODS WITH TANK, PIPING, AND EQUIPMENT REMOVAL. DUCT IS ROUTED ABOVE AND BELOW OTHER EQUIPMENT AND PIPING. COORDINATE WITH OTHER CONTRACTORS, WORKERS, AND GOVERNMENT.
4. ALL PIPING AND DUCT TO REMAIN AFTER DEMOLITION SHALL BE PREPARED FOR FUTURE CONNECTION AND CLOSED OFF TO PREVENT CONSTRUCTION DEBRIS FROM ENTERING SYSTEM.
5. EXISTING EM, CWR, CWS, DCW AND DRAIN PIPING INCLUDES HEAT TRACE, INSULATION AND JACKETING TO APPROXIMATELY 4'-6" BELOW GRADE. COORDINATE REUSE OF EXISTING HEAT TRACE CIRCUITS WITH NEW HEAT TRACE REQUIREMENTS.



US ARMY CORPS OF ENGINEERS
New York District

SYM.	DESCRIPTION	DATE	APPR.

DATE: DEC 2020
SOLICITATION NO.: W912DS21R0002
CONTRACT NO.:
AF DRAWING CODE:
PLOT DATE:
DESIGNED BY: J. MCCLUSKY
DWN BY: B. POOLE
CKD BY: G. REWALD
PROJECT NO:
FILE NAME:
SIZE: 34X22
PLOT SCALE: 1/2" = 1'-0"

U.S. ARMY CORPS OF ENGINEERS
NEW YORK DISTRICT
26 FEDERAL PLAZA
NEW YORK, NY 10278

BURNS McDONNELL
9400 WARD PARKWAY, KANSAS CITY, MO 64114

CHROME PLATING FACILITY RENOVATIONS
WATERVLIET ARSENAL, NEW YORK

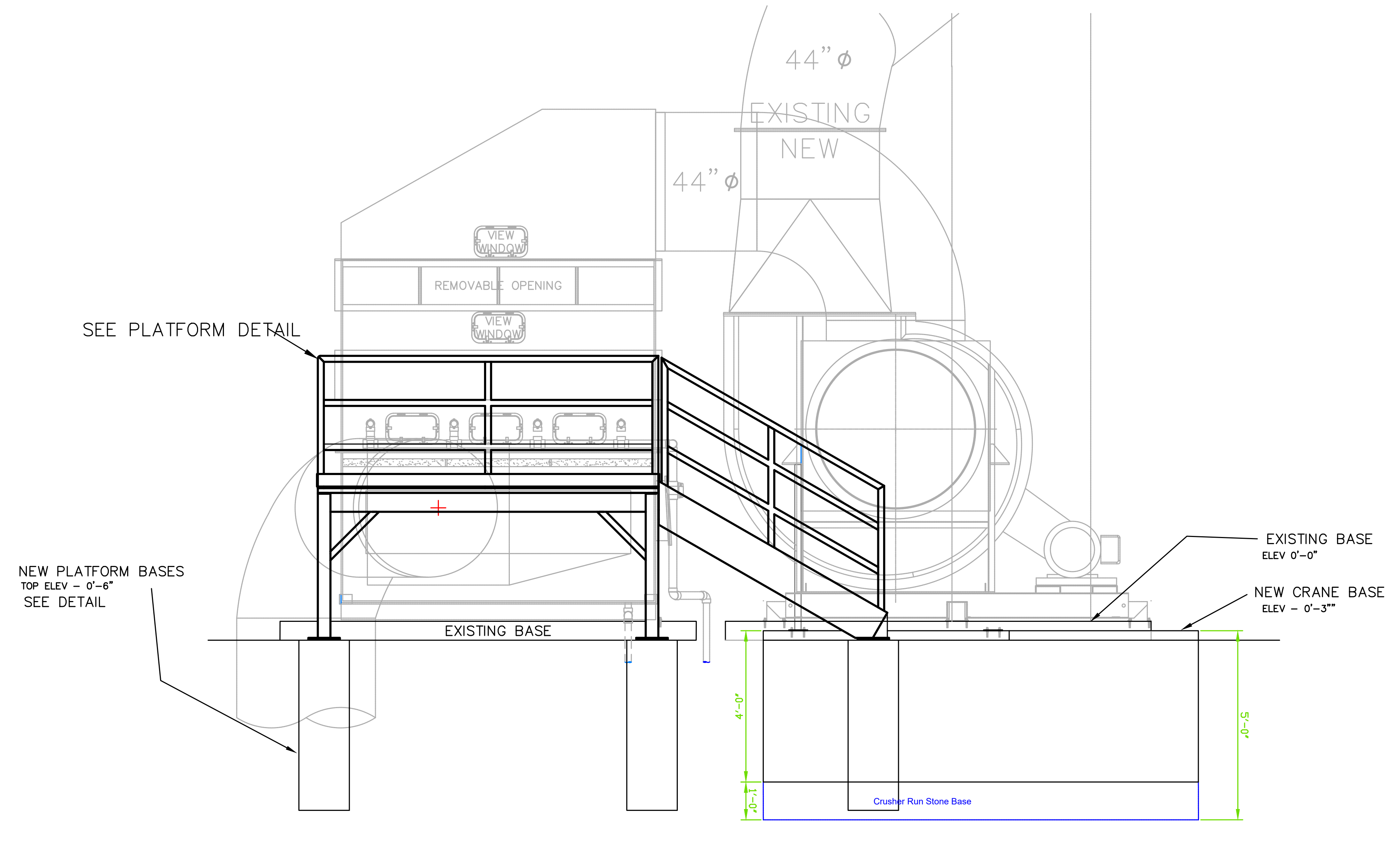
MECHANICAL PIPING DEMOLITION PLAN - LEVEL 1 SOUTH - EL 100'-0" - PHASE 1

JARED A. KLENOWSKI
NUMBER PE-2019017843
12/09/2020

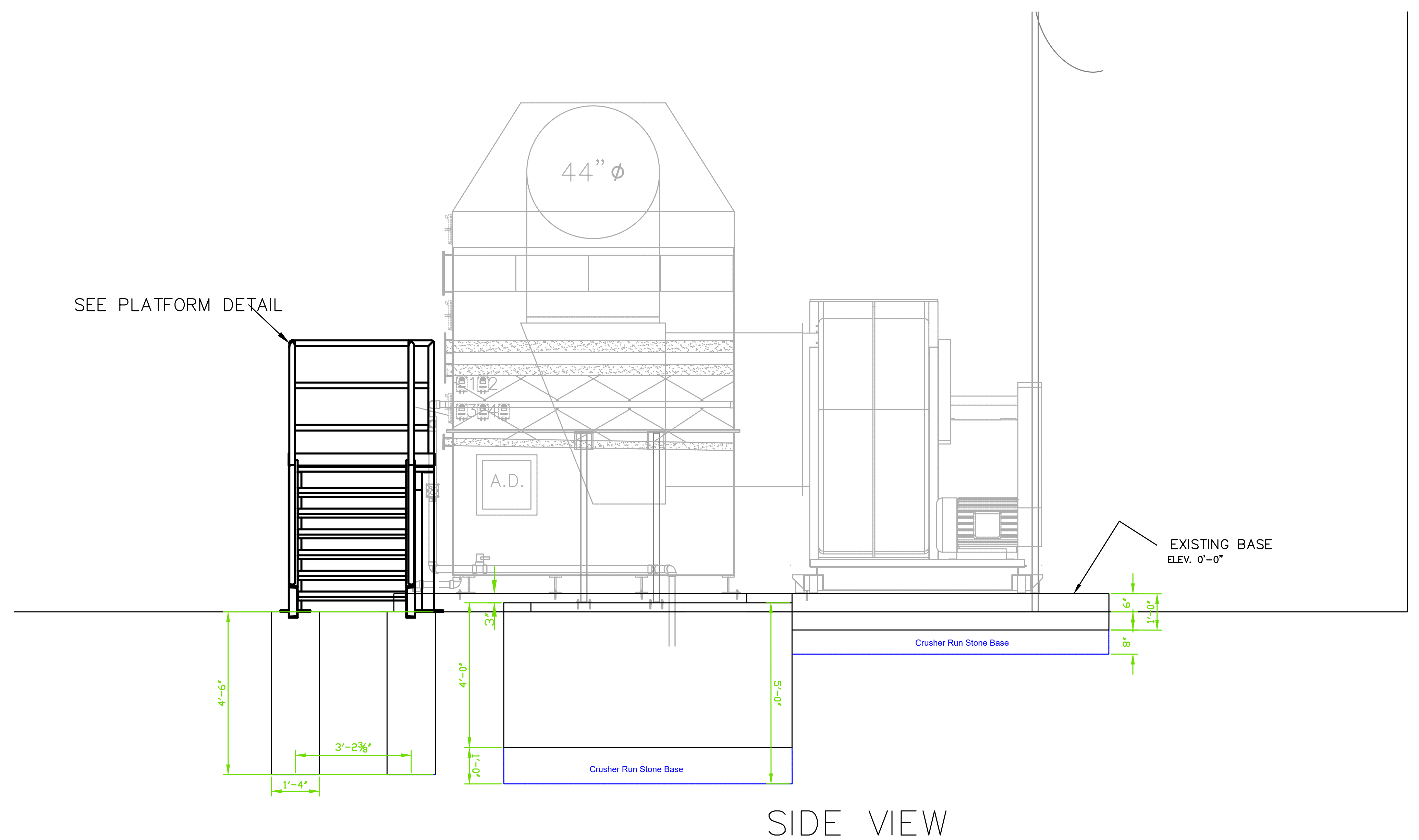
SHEET ID
MD1134

12/9/2020 7:10:03 AM

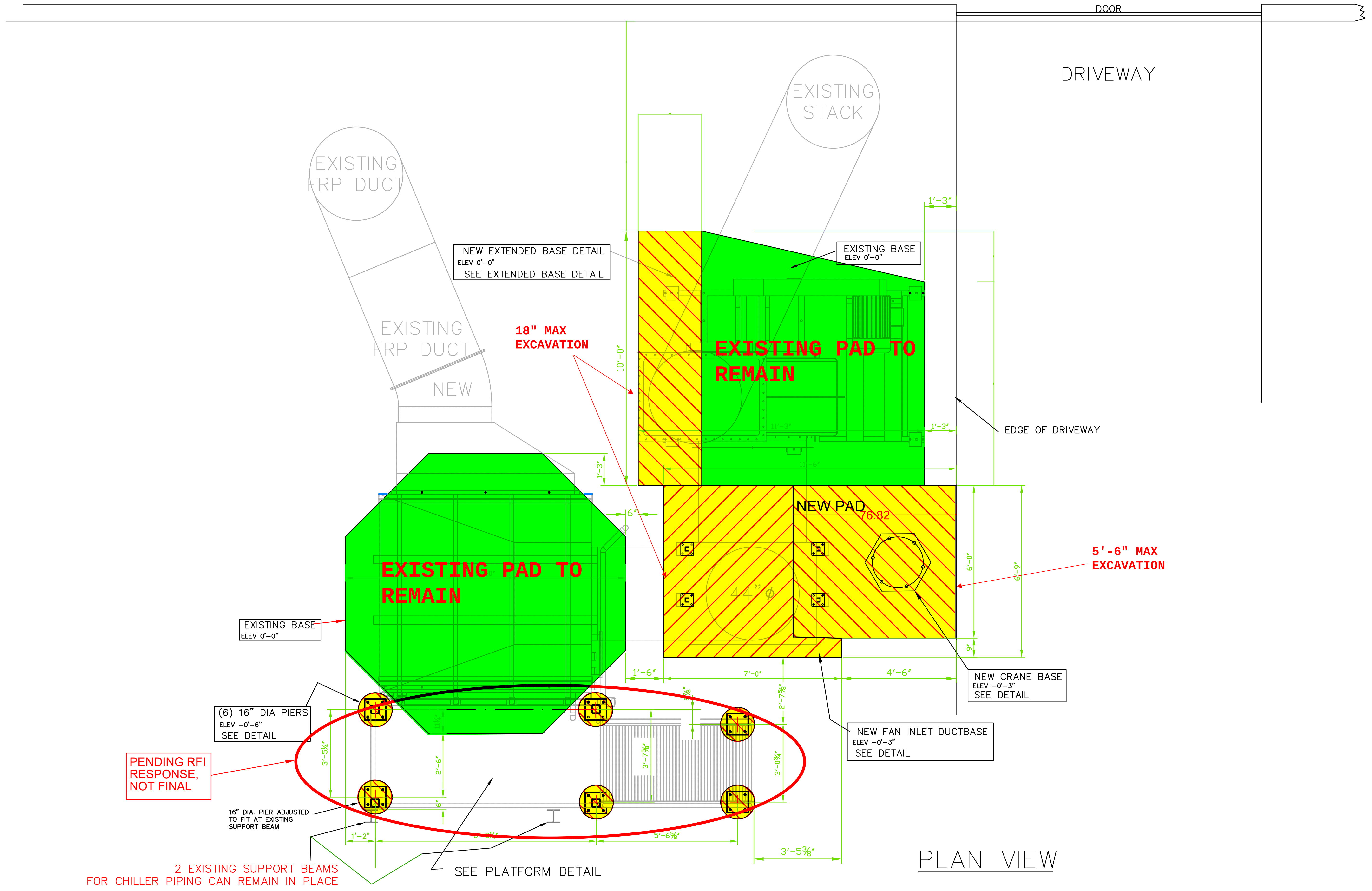
RTA SUBMISSION



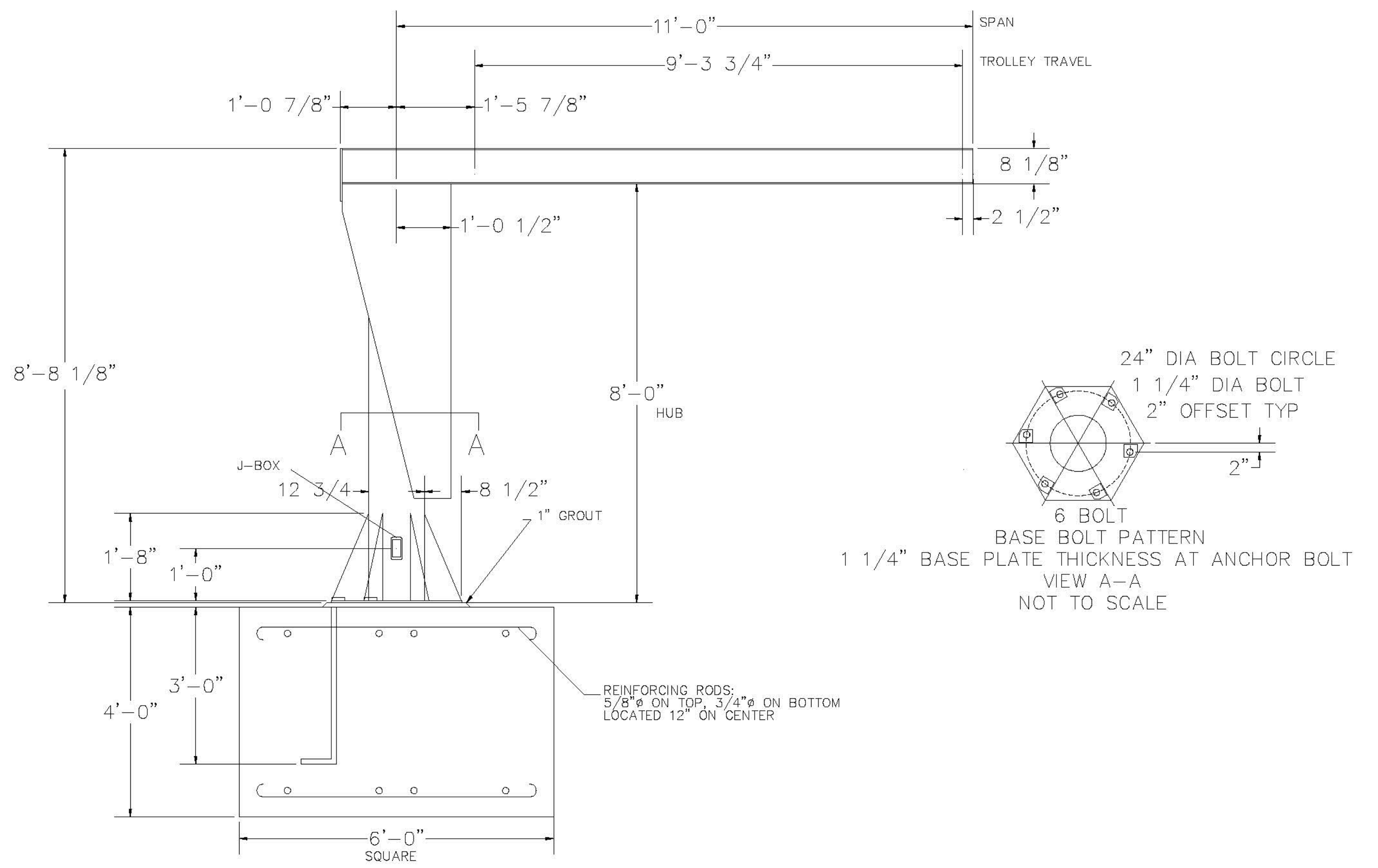
FRONT VIEW



SIDE VIEW
FROM DRIVEWAY



PLAN VIEW



1) JIB CRANE FOUNDATION REQUIREMENTS ARE BASED ON A SOIL PRESSURE OF 2500 LBS PER SQUARE FOOT. CONCRETE RECOMMENDED FOR JIB CRANE FOUNDATION IS 3000 LBS PER SQUARE INCH OF COMPRESSIVE FORCE.
2) DO NOT SCALE FROM THIS DRAWING.
3) OVERALL HEIGHT = 8.675 FT

W8 @ 18 #/FT

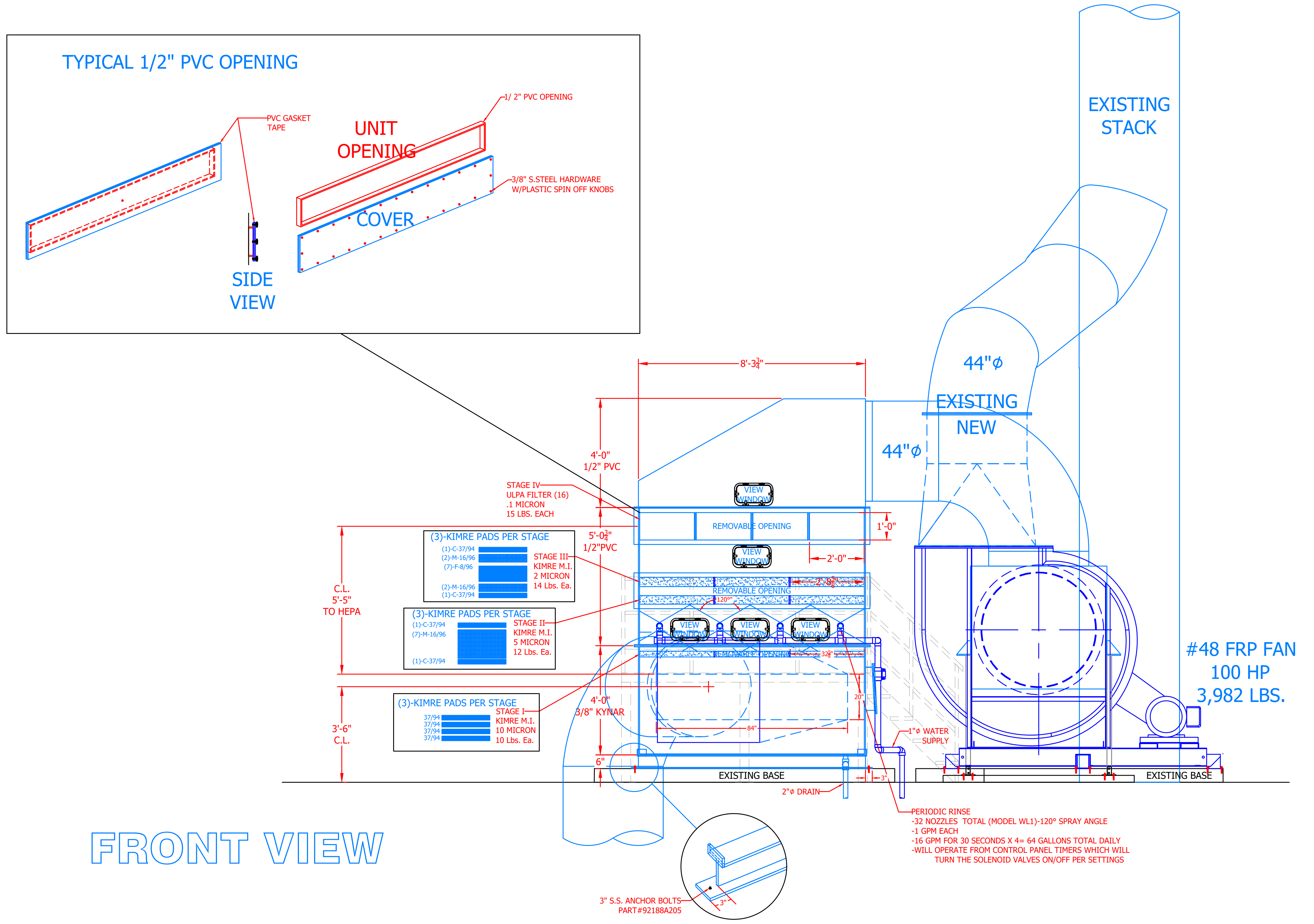
Notes:
- Repair existing pads.
- New pad for jib crane and and pipe support.
- New pad doweled into existing pad, 2" embedment, 12" maximum spacing.
- Pad extension doweled into existing pad, 2" embedment, 12" maximum spacing.
- #4 grade 60 rebar to be used for all new pads and pad extensions.
- Estimated 10 yards^3 to be excavated, including mecanical and electrical excavation support.
- Waiting on RFI clarification on scrubber platform.

THREE D RIGGING & CONSTRUCTION, Inc.
542 RT 9W, GLENMONT, NY 12077
518–729–3977

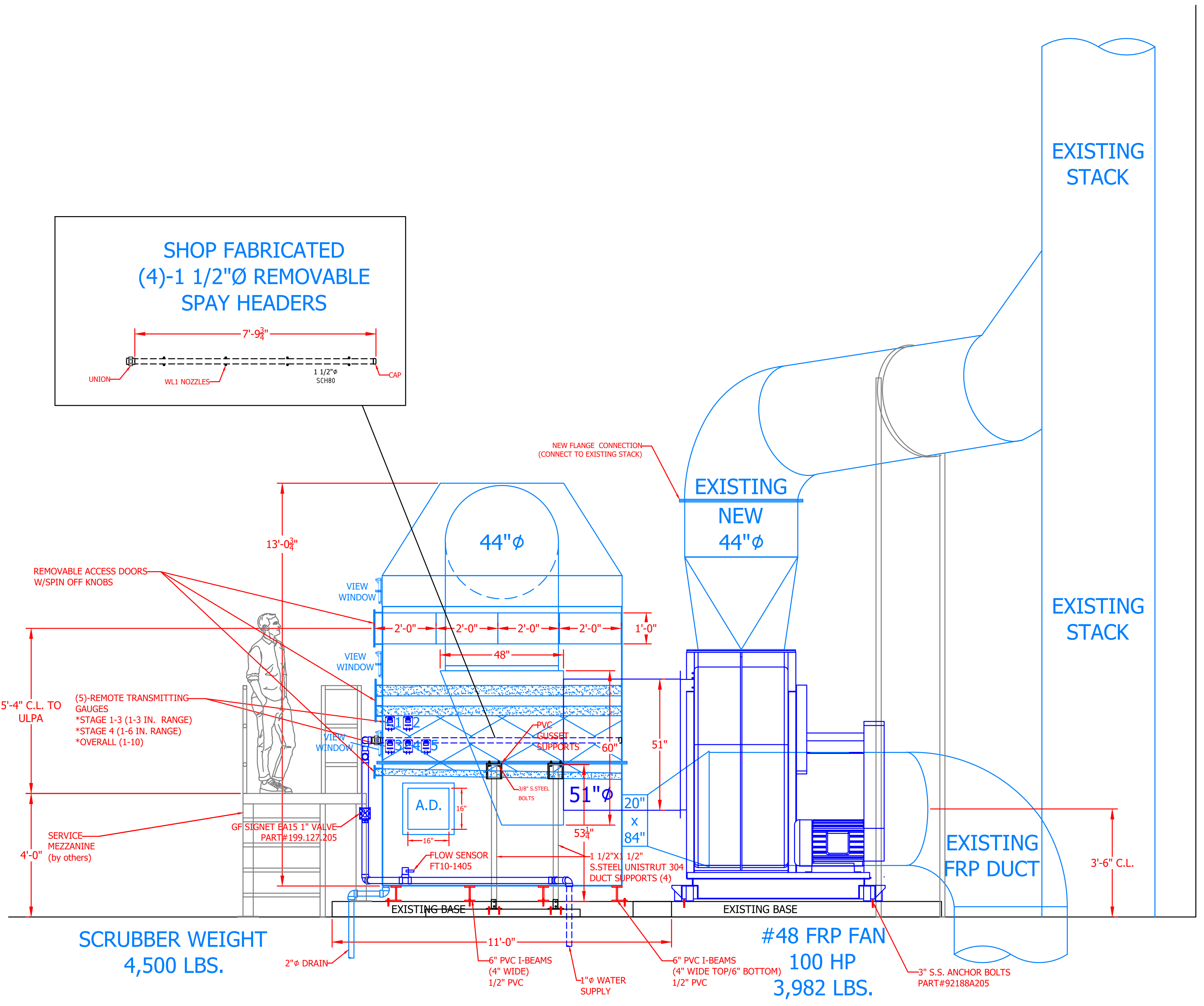
REVISIONS	
No	REMARKS

WATERVLIET ARSENAL
CHROME VENTILATION
LAYOUT

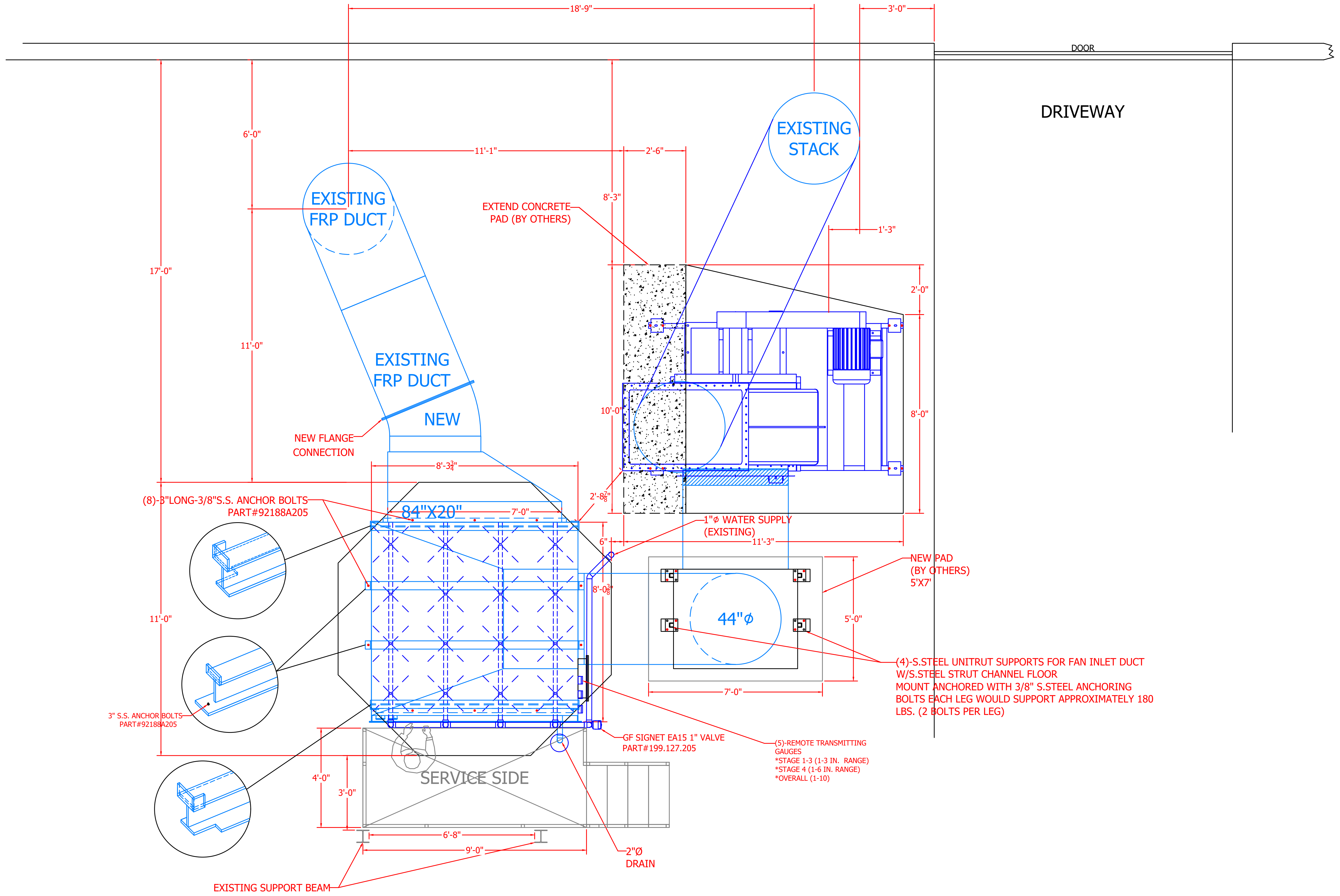
DWG 2
DATE 1/22/2022
JOB No.
OF X



FRONT VIEW



SIDE VIEW



PLAN VIEW

MODEL SSQV 36,000 CFM VERTIVAL CHROME SEPARATOR/FAN

-3 STAGES OF COMPOSITE MESH PAD FILTERS WITH
4th STAGE ULPA FILTERS (16 TOTAL)
-4FT. BOTTOM SECTION (INCLUDING INLET) UP PAST THE FIRST STAGE MIST ELIMINATOR
FABRICATED FROM 3/8" THICK RE-ENFORCED "KYNAR"
-9FT. TOP SECTION FABRICATED FROM 1/2" THICK WHITE HIGH IMPACT PVC
-PERIODIC RINSE
-REMOVAL EFFICIENCY .1 MICRON PARTICLE SIZE AT 99.99% REMOVAL (BEST AVAILABLE TECHNOLOGY)
(4)-FOUR FILTER HOUSING
- -Stage I -(10 MICRON REMOVAL) WITH (3) "KIMRE" COMPOSITE MIST ELIMINATOR PADS EACH (32.5"X95.625") 10 lbs. per pad
- -Stage II -(5 MICRON REMOVAL) WITH (3) "KIMRE" COMPOSITE MIST ELIMINATOR PADS EACH (32.5"X95.625") 12 lbs. per pad
- -Stage III -(2 MICRON REMOVAL) WITH (3) "KIMRE" COMPOSITE MIST ELIMINATOR PADS EACH (32.5"X95.625") 14 lbs. per pad
- -Stage IV -(16 ULPA FILTERS) 24"Wx24"Dx12"H, 15 lbs. each.

#48 FRP FAN (100 HP)
*DESIGNED FOR 36,200 CFM @ 10" S.P.
*3,892 lbs.

ScrubAir
ScrubAir Systems, Inc.
1200 Ensell Road
Lake Zurich, IL 60047

36,000 CFM CHROME VENTILATION/FILTER SYSTEM

MACHINE TOLERANCES
UNLESS OTHERS SPECIFIED

4ScrubAir–J2726_Greenland

Fractional....................±1/4

SIZE
D

Drawn By M.CHAVOYA

Checked By

SCALE:NTS

SHEET 1 OF 1 SHEETS

APPENDIX C

CAMP

COMMUNITY AIR MONITORING PLAN
B35 CHROME SCRUBBER EXCAVATION
WATERVLIET ARSENAL
WATERVLIET, NEW YORK

To provide a measure of protection for any potential downwind receptors, and to confirm that work activities do not generate airborne contaminants, the excavation contractor will conduct continuous monitoring for volatile organic compounds (VOCs) and particulate matter (dust) during all ground intrusive activities at the site. Monitoring will be conducted at the upwind and downwind perimeter of each work area.

VOC MONITORING, RESPONSE LEVELS, AND ACTIONS

Volatile organic compounds (VOCs) will be monitored on a continuous basis during all ground intrusive activities. Upwind concentrations will be measured at the start of each workday and periodically thereafter to establish background conditions. VOC monitoring will be conducted using a MiniRae 3000 photoionization detector (PID), or equivalent. The PID will be calibrated at least daily using the span calibration gas recommended by the manufacturer. The PID will calculate 15-minute running average concentrations. These averages will be compared to the action levels specified below.

Action Levels

- If the ambient air concentration of total organic vapors at the downwind perimeter of the work area or exclusion zone exceeds 5 parts per million (ppm) above background for the 15-minute average, work activities will be temporarily halted and monitoring continued. If the total organic vapor level readily decreases (per instantaneous readings) below 5 ppm over background, work activities will resume with continued monitoring.

- If total organic vapor levels at the downwind perimeter of the work area or exclusion zone persist at levels in excess of 5 ppm over background but less than 25 ppm, work activities will be halted, the source of vapors identified, corrective actions taken to abate emissions, and monitoring continued. After these steps, work activities will resume provided that the total organic vapor level 200 feet downwind of the exclusion zone or half the distance to the nearest potential receptor or residential/commercial structure, whichever is less - but in no case less than 20 feet, is below 5 ppm over background for the 15-minute average.

- If the organic vapor level is above 25 ppm at the perimeter of the work area, all work activities will be stopped.

All 15-minute average readings will be recorded and be available for review by the New York State Department of Environmental Conservation (NYSDEC) or the NYS Department of Health (DOH). Instantaneous readings, if any, used for decision purposes will also be recorded.

PARTICULATE MONITORING, RESPONSE LEVELS, AND ACTIONS

Particulate concentrations will be monitored continuously at the downwind perimeter of the each work area during all ground intrusive activities. Real-time monitoring equipment capable of measuring particulate matter less than 10 micrometers in size (PM-10) and capable of integrating over a period of 15 minutes (or less) will be used for the particulate monitoring. The equipment will be equipped with an audible alarm to indicate exceedance of the action levels summarized below. Any fugitive dust migration will also be visually assessed during all work activities.

Action Levels

- If the downwind PM-10 particulate level is 0.1 milligrams per cubic meter (mg/m3) greater than background (upwind perimeter) for the 15-minute period or if airborne dust is observed leaving the work area, then dust suppression techniques will be employed. Work will continue with dust suppression techniques provided that downwind PM-10 particulate levels do not exceed 0.15 mg/m3 above the upwind level and provided that no visible dust is migrating from the work area.

- If, after implementation of dust suppression techniques, downwind PM-10 particulate levels are greater than 0.15 mg/m3 above the upwind level, work will be stopped and a re-evaluation of activities initiated. Work will resume provided that dust suppression measures and other controls are successful in reducing the downwind PM-10 particulate concentration to within 0.15 mg/m^3 of the upwind level and in preventing visible dust migration.

All particulate monitoring measurements readings will be recorded and made available for NYSDEC and NYSDOH review.

ARCADIS Design & Consultancy for natural and built assets

Arcadis U.S., Inc.

855 Route 146

Suite 210

Clifton Park, New York 12065

Tel 518 250 7300

Fax 518 250 7301

www.arcadis.com