ALTERNATIVE SOURCE DEMONSTRATION REPORT TEXAS STATE CCR RULE

H.W. Pirkey Power Plant West Bottom Ash Pond Hallsville, Texas

Submitted to



1 Riverside Plaza Columbus, Ohio 43215-2372

Submitted by



engineers | scientists | innovators

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December 2021

CHA8495

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LIST OF ACRONYMS

AEP American Electric Power

ASD Alternative Source Demonstration

CCR Coal Combustion Residuals

EBAP East Bottom Ash Pond

EDS Energy Dispersive Spectroscopy

EPRI Electric Power Research Institute

GSC Groundwater Stats Consulting, LLC

GWPS Groundwater Protection Standard

LCL Lower Confidence Limit

MCL Maximum Contaminant Level

QA Quality Assurance

QC Quality Control

SEM Scanning Electron Microscopy

SPLP Synthetic Precipitation Leaching Procedure

SSL Statistically Significant Level

TAC Texas Administrative Code

TCEQ Texas Commission on Environmental Quality

UTL Upper Tolerance Limit

USEPA United States Environmental Protection Agency

VAP Vertical Aquifer Profiling

WBAP West Bottom Ash Pond

XRD X-Ray Diffraction

SECTION 1

INTRODUCTION AND SUMMARY

This Alternative Source Demonstration (ASD) report has been prepared to address a statistically significant level (SSL) for cobalt in the groundwater monitoring network at the H.W. Pirkey Plant Western Bottom Ash Pond (WBAP), located in Hallsville, Texas, following the first semi-annual detection monitoring event of 2021. The WBAP is registered as a surface impoundment under Texas Commission on Environmental Quality (TCEQ) Industrial and Hazardous Waste Solid Waste Registration No. 33240.

The H.W. Pirkey Plant has four regulated coal combustion residuals (CCR) storage units, including the WBAP (**Figure 1**). In May 2021, a semi-annual assessment monitoring event was conducted at the WBAP in accordance with 30 TAC §352.951(a). The monitoring data were submitted to Groundwater Stats Consulting, LLC (GSC) for statistical analysis. Groundwater protection standards (GWPSs) were established for each Appendix IV parameter in accordance with the statistical analysis plan developed for the facility (Geosyntec, 2020a) and United States Environmental Protection Agency's (USEPA) *Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities – Unified Guidance* (Unified Guidance; USEPA, 2009). The GWPS for each parameter was established as the greater of either the background concentration or, for constituents with a maximum contaminant level (MCL), the MCL. To determine background concentrations, an upper tolerance limit (UTL) was calculated using pooled data from the background wells collected during the background monitoring and assessment monitoring events.

Confidence intervals were re-calculated for Appendix IV parameters at the compliance wells to assess whether these parameters were present at a statistically significant level (SSL) above the GWPSs. An SSL was concluded if the lower confidence limit (LCL) of a parameter exceeded the GWPS (i.e., if the entire confidence interval exceeded the GWPS). An SSL was identified for cobalt at AD-28 at the WBAP, where the LCL of 0.0136 milligrams per liter (mg/L) exceeded the calculated GWPS of 0.0090 mg/L (Geosyntec, 2021a). No other SSLs were identified.

1.1 CCR Rule Requirements

TCEQ regulations regarding assessment monitoring programs for CCR landfills and surface impoundments (TCEQ, 2020a) provide owners and operators with the option to make an ASD when an SSL is identified (30 TAC §352.951(e)):

... In making a demonstration under this subsection, the owner or operator must, within 90 days of detecting a statistically significant level above the groundwater protection standard of any constituent listed in Appendix IV adopted by reference in §352.1431 of this title, submit a report prepared and certified in accordance with §352.4 of this title (relating to Engineering and Geoscientific Information) to the executive director, and any local pollution

agency with jurisdiction that has requested to be notified, demonstrating that a source other than a CCR unit caused the exceedance or that the exceedance resulted from error in sampling, analysis, statistical evaluation, or natural variation in groundwater quality.

Pursuant to 30 TAC §352.951(e), Geosyntec Consultants, Inc. (Geosyntec) has prepared this ASD report to document that the SSL identified for cobalt at AD-28 is from a source other than the WBAP.

1.2 <u>Demonstration of Alternative Sources</u>

An evaluation was completed to assess possible alternative sources to which the identified SSL could be attributed. Alternative sources were identified amongst five types, based on methodology provided by EPRI (2017):

- ASD Type I: Sampling Causes;
- ASD Type II: Laboratory Causes;
- ASD Type III: Statistical Evaluation Causes;
- ASD Type IV: Natural Variation; and
- ASD Type V: Alternative Sources.

A demonstration was conducted to show that the SSL identified for cobalt at AD-28 was based on a Type IV cause and not by a release from the Pirkey WBAP.

SECTION 2

ALTERNATIVE SOURCE DEMONSTRATION

The TCEQ CCR rules allows the owner or operator 90 days from the determination of an SSL to demonstrate that a source other than the CCR unit caused the SSL. The methodology used to evaluate the SSL identified for cobalt and the proposed alternative source are described below.

2.1 Proposed Alternative Source

An initial review of site geochemistry, site historical data, and laboratory quality assurance/quality control (QA/QC) data did not identify alternative sources for cobalt due to Type I (sampling), Type II (laboratory), or Type III (statistical evaluation) issues. Groundwater sampling, laboratory analysis, and statistical evaluations were generally completed in accordance with 30 TAC §352.931 and the draft TCEQ guidance for groundwater monitoring (TCEQ, 2020b). As described below, the SSL has been attributed to natural variation associated with the underlying geology, which is a Type IV (natural variation) issue.

Monitoring well AD-28 is located near the southwest corner of the WBAP, as shown in **Figure 1**. Previous ASDs for cobalt at the WBAP provided evidence that cobalt is present in the aquifer media at the site and that the observed cobalt concentrations were due to natural variation (Geosyntec, 2019a; Geosyntec, 2019b; Geosyntec, 2020b; Geosyntec, 2020c; Geosyntec, 2021b). The previous ASDs discussed how the WBAP did not appear to be a source for cobalt in downgradient groundwater, based on observed concentrations of cobalt both in the ash material and in leachate from Synthetic Precipitation Leaching Procedure (SPLP) analysis (SW-864 Test Method 1312, [USEPA, 1994]) of the ash material. Cobalt was not detected in the SPLP leachate above the reporting limit of 0.01 mg/L, which is lower than the average concentration at AD-28 (**Table 1**).

Surface water samples were previously collected from the East Bottom Ash Pond (EBAP) and WBAP to characterize the total cobalt concentrations. The EBAP and WBAP receive the same process water, with the use of each pond dependent on available freeboard and cleaning schedule; thus, there is a basis for the equivalency between these two surface water samples. Cobalt was detected at a concentration of 0.000501 mg/L in a sample collected from the WBAP on November 4, 2020. Cobalt was detected in a surface water sample collected on June 2, 2020 from the EBAP at an estimated concentration of 0.00008 mg/L (**Table 1**). These concentrations are lower than all reported cobalt concentrations for in-network wells from the most recent sampling event, and over an order of magnitude lower than the average concentration observed at AD-28 (**Figure 2**; **Table 1**). Thus, the WBAP is not the likely source of cobalt at AD-28.

As noted in the previous ASDs, soil samples collected across the site, including from locations near the WBAP, identified cobalt in the aquifer solids at varying concentrations. SB-28 was advanced in the vicinity of AD-28 in April 2020 to re-log the geology at AD-28 and collect samples

for laboratory analysis of total metals and mineralogy. The SB-28 field boring log, which was generated by Auckland Consulting LLC, is provided as **Attachment A**. Cobalt was identified at SB-28 at concentrations of 4.53 milligrams per kilogram (mg/kg) at 15.5-16 feet below ground surface (bgs) and 8.70 mg/kg at 40-41 feet bgs (**Table 2**). The 15.5-16 feet bgs interval at SB-28 correlates to the depth of the monitoring well screen of AD-28 (15-35 feet bgs), indicating that cobalt is present in aquifer solids within the AD-28 screened interval. Cobalt was also identified in the aquifer solids at varying concentrations at other locations throughout the site, with the highest value of 23.5 mg/kg reported at AD-41, which is upgradient of the WBAP (**Figure 3**).

In addition to total cobalt, soil samples were submitted for mineralogical analysis to evaluate the presence of cobalt-containing minerals. X-ray diffraction (XRD) analysis of soils from SB-28 identified pyrite (an iron sulfide mineral) in samples collected at 25-30 feet bgs and 40-41 feet bgs at concentrations up to 3% by weight (**Table 3**). Cobalt is known to undergo isomorphic substitution for iron in crystalline iron minerals such as pyrite due to their similar ionic radii of approximately 1.56 angstrom (Å) for iron vs. 1.52 Å for cobalt (Clementi and Raimondi, 1963; Krupka and Serne, 2002; Hitzman et al., 2017).

The aquifer solids at SB-28 are distinctly red in color at shallow depths, as illustrated in the photolog of soil cores provided in **Attachment B.** Red color in soils is often associated with the presence of oxidized iron-bearing minerals such as hematite and goethite. Goethite, an iron oxide mineral (FeOOH), was present at depths up to 16 ft bgs at SB-28 at up to 37% of the total aquifer solids (**Table 3**). The weathering of pyrite to goethite under oxidizing conditions is also a well-understood phenomenon, including in formations in east Texas (Senkayi et al., 1986; Dixon et al., 1982). It is likely that the pyrite weathering process is resulting in the release of isomorphically substituted cobalt from the pyrite crystal structure as it undergoes oxidative weathering to iron oxide minerals.

As described in an ASD previously generated for the EBAP, vertical aquifer profiling (VAP) was used to collect groundwater samples from upgradient locations B-2 and B-3 during the soil boring and sample collection process (Geosyntec, 2019b). A groundwater sample was also collected from AD-30, an existing well within the WBAP groundwater monitoring network. Solid phases within these groundwater samples were separated and submitted for analysis of chemical composition and mineralogy. For the VAP samples, separation was completed using a centrifuge due to the high abundance of solids. For the groundwater sample at AD-30, the sample was filtered using a 1.5-micron filter. Based on total metals analysis, cobalt was identified both in the centrifuged solid material collected from upgradient VAP location B-3 [VAP-B3-(40-45)] and in the material retained on the filter after processing groundwater from permanent monitoring wells AD-30, B-2, and B-3 (**Table 2**). The concentrations of cobalt in the solid material retained after filtration were comparable to the bulk soil samples collected from the same locations.

The solid sample [VAP-B3-(40-45)] was submitted for mineralogical analysis via XRD and scanning electron microscopy (SEM) using an energy dispersive spectroscopic analyzer (EDS). The XRD results identified pyrite as approximately 3% of the solid phase (**Table 4**). Pyrite was

identified during SEM/EDS analysis of lignite which is mined immediately adjacent to the site. Logging completed while the VAP boring was advanced identified coal at several intervals, including 45 and 48 ft bgs (**Figure 4**). Furthermore, SEM/EDS of both centrifuged solid samples [VAP-B3-(40-45) and VAP-B3-(50-55)] identified pyrite in backscattered electron micrographs by the distinctive framboidal morphology (Harris et al., 1981; Sawlowicz, 2000). Major peaks involving iron and sulfur were identified in the EDS spectrum, which further support the identification of pyrite (**Attachment C**). While cobalt was not identified in the EDS spectrum, it is likely present at concentrations below the detection limit.

Naturally occurring cobalt is known to substitute for iron in pyrite, which is then known to weather to iron oxides. The presence of pyrite and iron oxides has been confirmed at AD-28 and across the Site. The presence of these aquifer minerals suggests that weathering of pyritic minerals may be providing a source for aqueous cobalt in groundwater. Additionally, the pond was not identified as the source of cobalt at AD-28 based on the low concentrations of cobalt in the pond itself.

2.2 Sampling Requirements

As the ASD presented above supports the position that the identified SSL is not due to a release from the Pirkey WBAP, the unit will remain in the assessment monitoring program. Groundwater at the unit will continue to be sampled for Appendix IV parameters on a semi-annual basis.

SECTION 3

CONCLUSIONS AND RECOMMENDATIONS

The preceding information serves as the ASD prepared in accordance with 30 TAC §352.951(e) and supports the position that the SSL for cobalt identified at AD-28 during assessment monitoring in May 2021 was not due to a release from the WBAP. The identified SSL was, instead, attributed to natural variation in the underlying geology, including the presence of pyrite and goethite in the solid aquifer material. Therefore, no further action is warranted, and the Pirkey WBAP will remain in the assessment monitoring program. Certification of this ASD by a qualified professional engineer is provided in **Attachment D**.

SECTION 4

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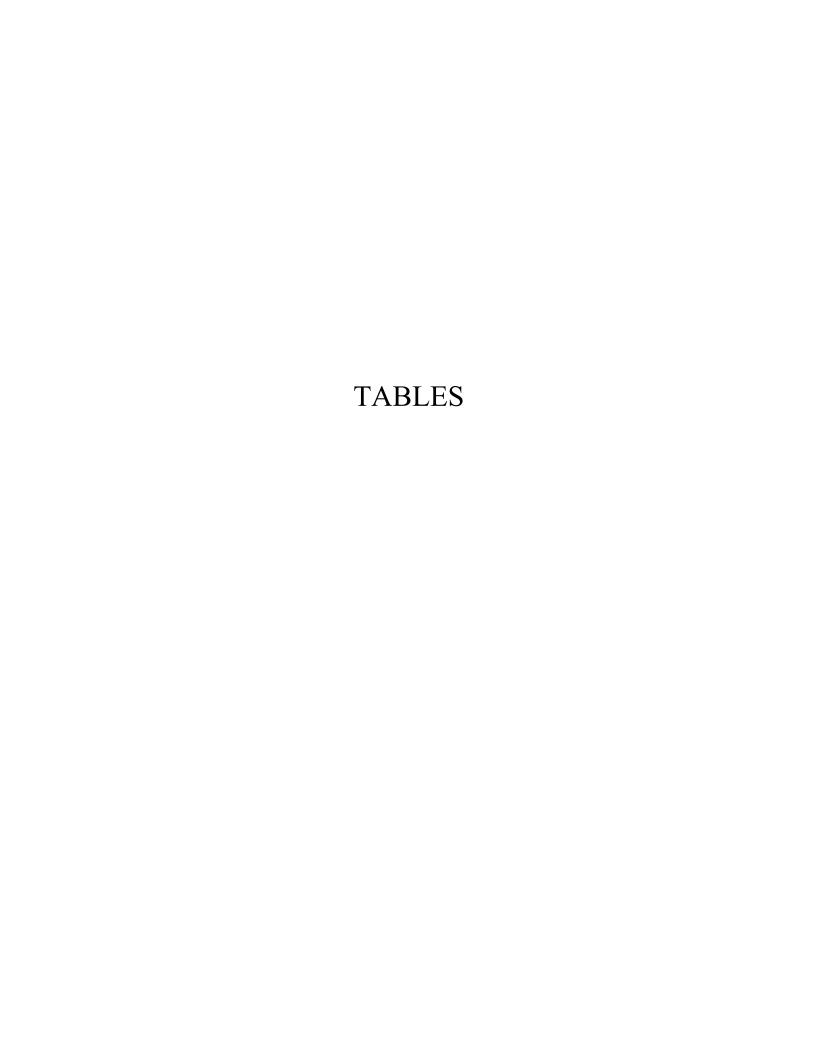


Table 1: Summary of Key Analytical Data West Bottom Ash Pond - H.W. Pirkey Plant

Sample	Sample Date	Unit	Cobalt Concentration
Bottom Ash (Solid Material)	2/11/2019	mg/kg	5.8
SPLP Leachate of Bottom Ash	2/11/2019	mg/L	< 0.01
WBAP Pond Water	11/4/2020	mg/L	0.000501
AD-28 - Average	May 2016 - May 2021	mg/L	0.0146

Notes:

mg/kg - milligram per kilogram

mg/L - milligram per liter

AD-28 - Average value was calculated using all cobalt data collected under 40 CFR 257 Subpart D.

Table 2: Soil Cobalt and Mineralogy Data West Bottom Ash Pond - H.W. Pirkey Plant

Location ID	Location	Sample Depth (ft bgs)	Cobalt (mg/kg)
	Bulk	Soil Samples	(mg/kg)
		6-6.5	< 2.38
AD 20	WBAP Network	15.5-16	4.53
AD-28	WBAP Network	25-30	< 2.50
		40-41	8.70
AD-30	WBAP Network	7	1.00
AD-30	W DAP Network	23	15.0
		10	2.36
		16	3.62
B-2	Upgradient	71	10.30
		82	7.21
		87	3.11
		10	1.30
B-3	Upgradient	20	0.59
		97	1.11
		15	<1.0
AD-41	Upgradient	35	23.5
		95	1.90
		Retained After Filtration	
AD-30	WBAP Network	15-25	9.3 J
B-2	Upgradient	38-48	4.3 J
B-3	Upgradient	29-34	12.0
D -3	Opgradient	VAP 40-45	18.0

Notes:

mg/kg- milligram per kilogram

ft bgs - feet below ground surface

J = estimated value

For AD-28 and AD-30, samples were collected from additional boreholes advanced in the immediate area of the location identified by the well ID. Samples were not collected from the cuttings of the borings advanced for well installation. Samples at B-2, B-3, and AD-41 were collected from cores removed from the borehole during well lithology logging.

Depths for samples collected after filtration represent the screened interval for the permanent well where the sample was collected.

Table 3 - AD-28 Mineralogy Results West Bottom Ash Pond - H. W. Pirkey Plant

Boring ID		SB-28 ((AD-28)	
Sample Depth Interval	6-6.5	15.5-16	25-30	40-41
Sample Location	Above Screened Interval	Within Scree	ened Interval	Below Screened Interval
Color	Red-brown to yellow-brown	Light gray, light red-brown	Brown, light red- brown	Gray to dark gray
Mineralogy				
Quartz	58%	46%	73%	34%
Pyrite		-	3%	3%
K-Feldspar		1%	1%	1%
Siderite		-	2%	52%
Goethite	37%	15%		
Anhydrite				2%
Clay/Mica	5%	38%	21%	8%

Notes:

Sample depths are shown in feet below ground surface (bgs)

Well AD-28 is screened from 15-35 ft. below ground surface.

Mineralogical components are shown in relative abundance.

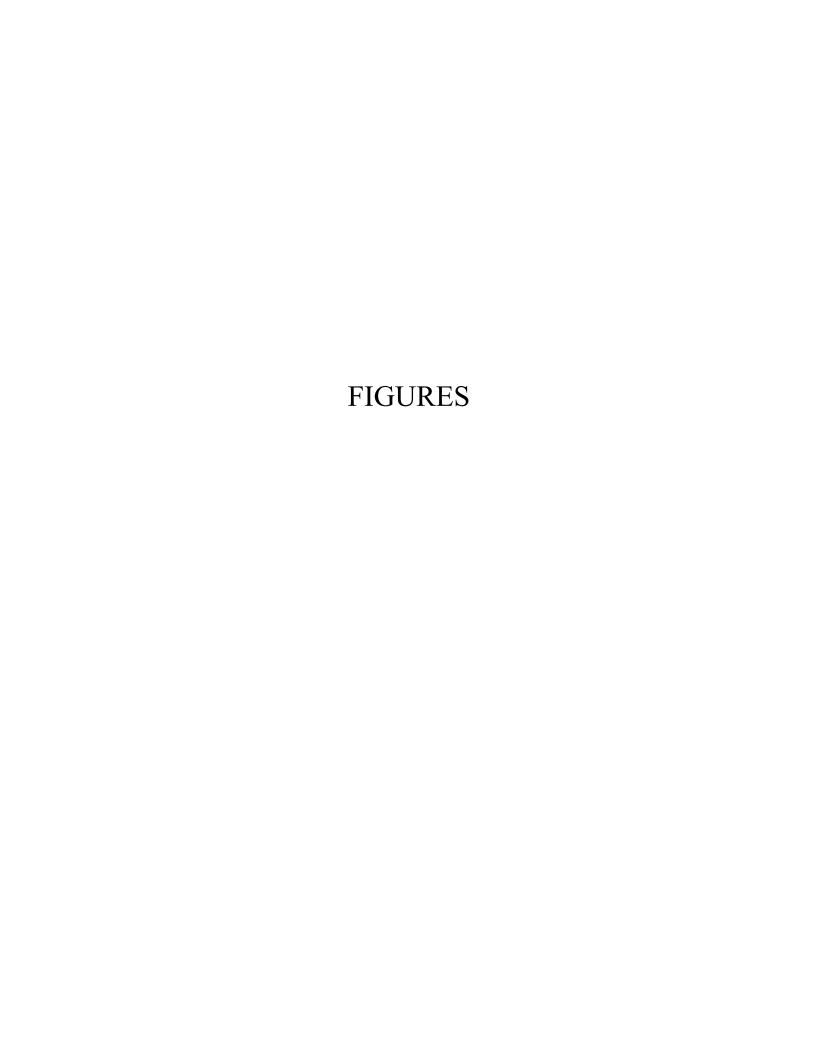
Table 4: B-3 X-Ray Diffraction Results West Bottom Ash Pond - H. W. Pirkey Plant

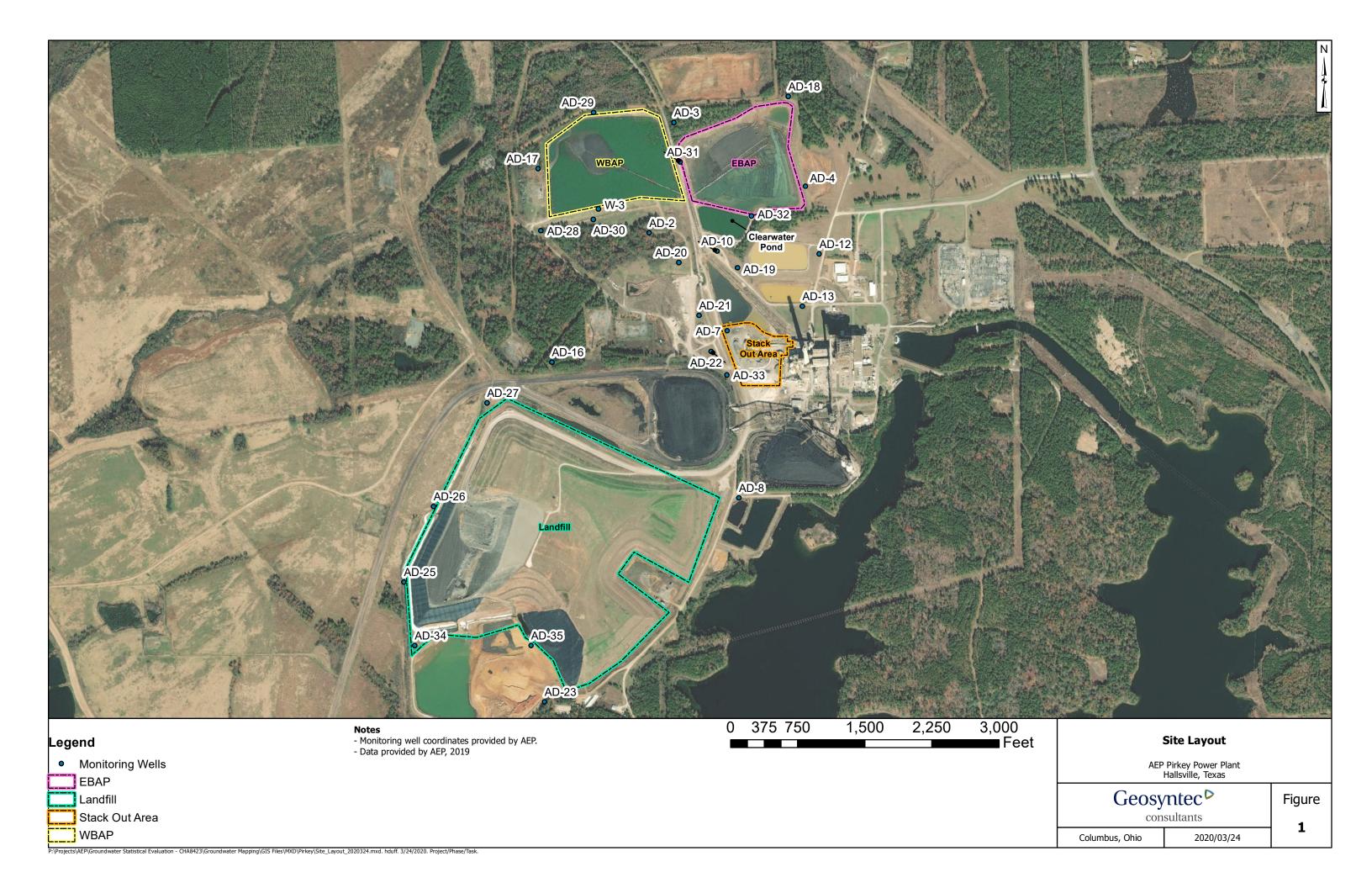
Constituent	VAP-B3-(40-45)
Quartz	15
Plagioclase Feldspar	0.5
Orthoclase	ND
Calcite	ND
Dolomite	ND
Siderite	0.5
Goethite	ND
Hematite	2
Pyrite	3
Kaolinte	42
Chlorite	4
Illite/Mica	6
Smectite	12
Amorphous	15

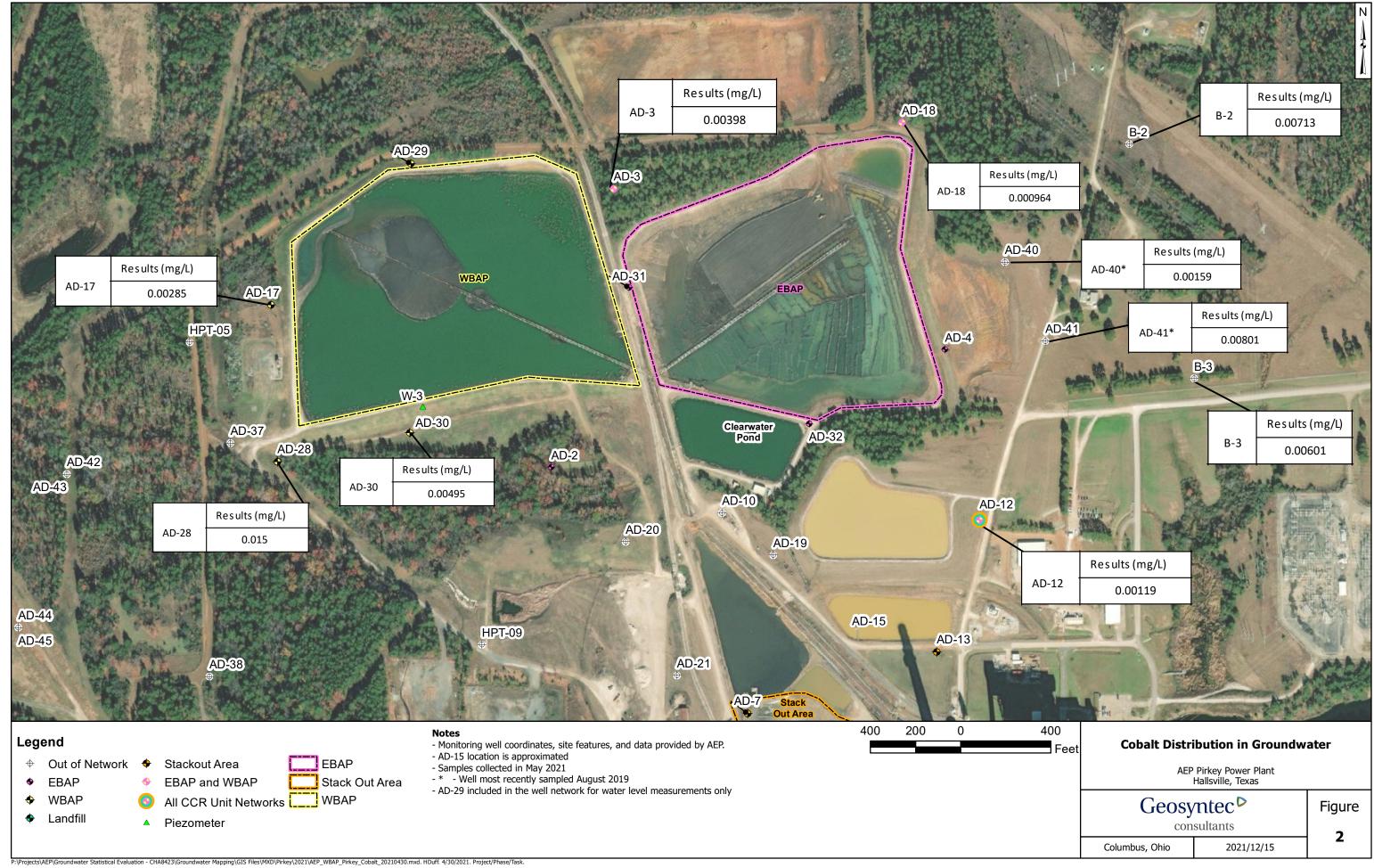
Notes:

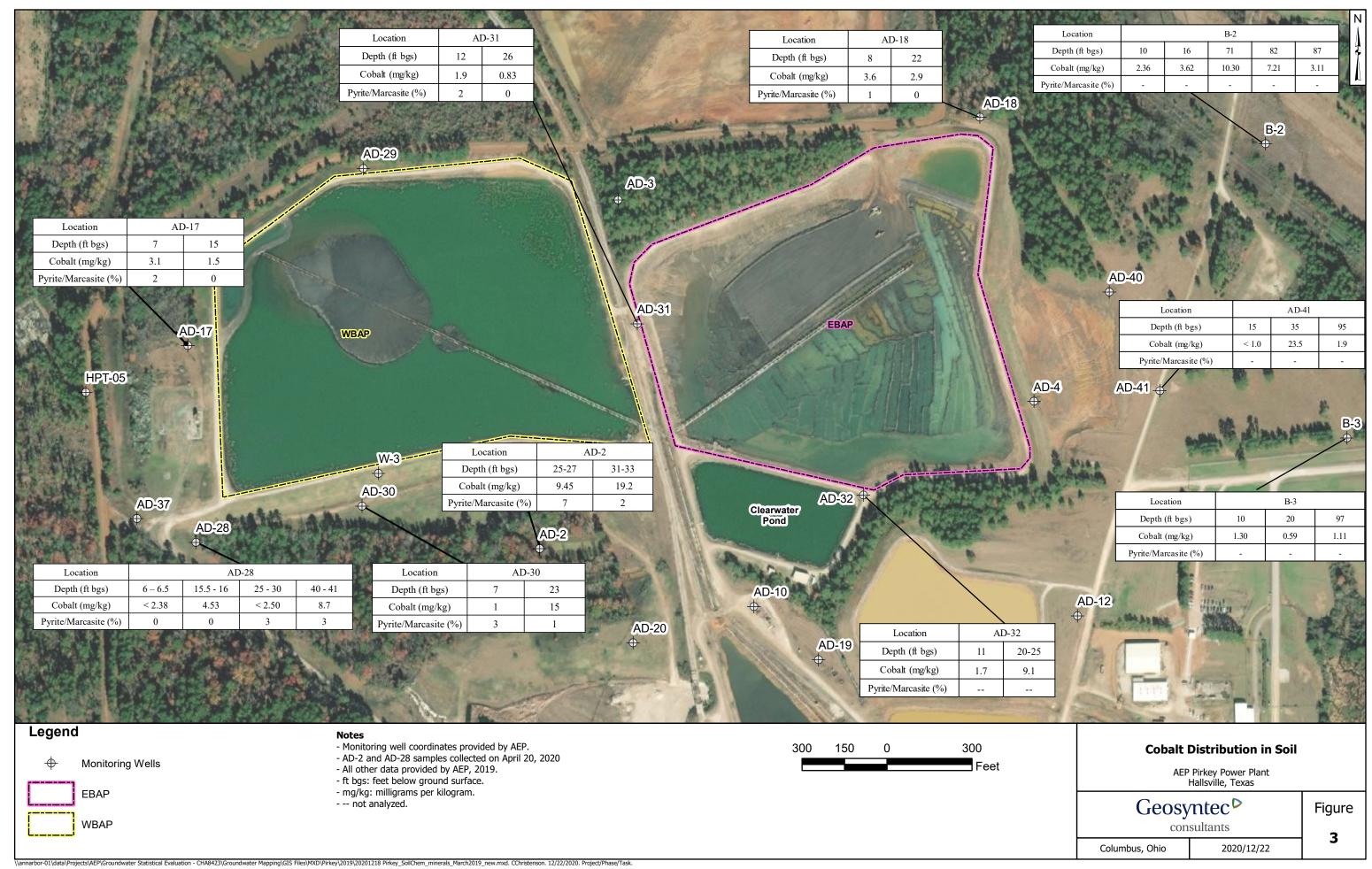
ND: Not detected

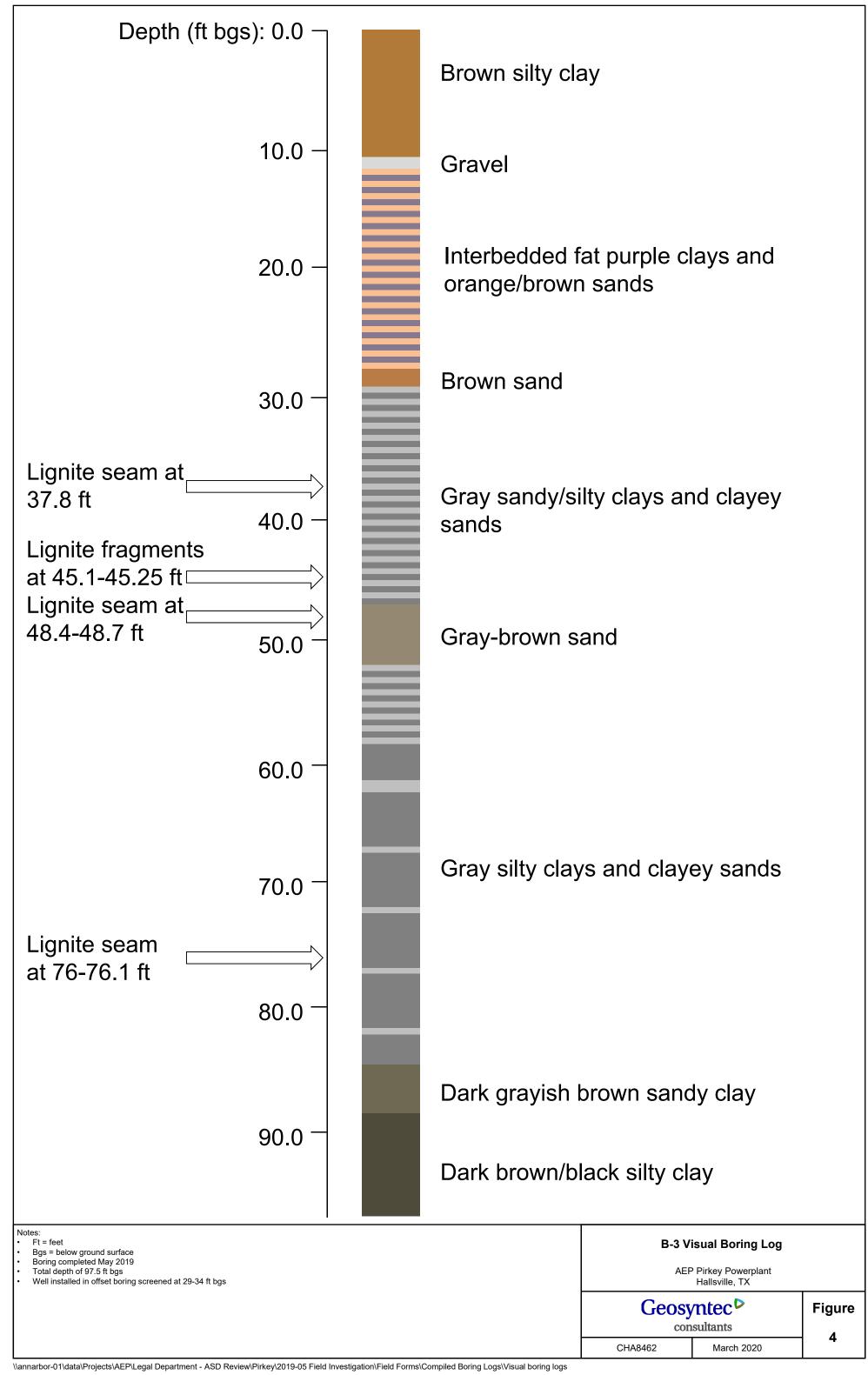
VAP-B3-(40-45) is the centrifuged solid material from the groundwater sample collected at that interval.











ATTACHMENT A SB-28 Boring Log

SILTS	& SANDS ONDITION ery Loose oose ded. Dense ense	_	Vso So Mst St VSt		0 - 0.25 0.25 - 0.5 0.5 - 1.0 1.0 - 2.0	CLAYS ER N - VA	4 8 15 15 15 15 16 16 16 16 16 16 16 16 16 16 16 16 16	ELEV. COLORS i Light Br Brown k Dark Bk Black Grey Bl Blue Tan Gr Grenn Red Y Yellow dish.Reddish.Wh White	MATERIALS CI Clay, Clayer Si Silt, Silty Sa Sand, Sandy Ls Limestone Gr Gravel SiS Siltstone SS Sandstone Sh Shale, Shale		<u>SAN</u> FI MN	D ADJ.	Calc C Lig L Org O Lam L	ignite rganic aminate lickensided ightly cam (s)
ASSIGNMENT	RELOVENY	BPTH FT.	SAMPLES	CONDITION OR CONSISTENCY	OLOR	MATERIALS OR ADJECTIVES	PREDOMINATE MY MATERIAL D	CHARACTE OR MODIFICA			TANDA ETRON	ARD METER	UNIFIED SOIL CLASSIFICATION	N - VALUE OR HAND PENETROMETER
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		-					in the	DIE CONGO	Hons	PI			moist	15-10
5-10	1,5'						16.6	- some v.f.		ne				
			H	1			4.00	Jayer @ 6-6.	5'					
			H					0	to f					
10-15	1'	10		10'-	RLBC.	SICI	Sa	Salty Sand I	ith day in				Y. Mais	110-10
				16-	4.67			they lences.	trace conevo	2			1777-10	-
15 m	11-1			200		1		dayey sand						
15-20	1.5'		H		4.6nd 4.R	Br		- clay lenge					vindist	(15-16
		•					1,0100	- irons to re lay						
20-25	13"			16-	Br. U.Rd	Si	Sa	Silver Sand-		ne en			Satura	cdell
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25-30	2/1		H		Gray			- gray@ 20'	1-1 -1	-	,	,		
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*GPS: 32.465448, -94.49432 (18'W-NW) of AD-28/MW-28

ATTACHMENT B SB-28 Boring Photographic Log

GEOSYNTEC CONSULTANTS Photographic Record

Geosyntec consultants

Client: American Electric Power Project Number: CHA8495/12A/02

Site Name: H.W. Pirkey Plant WBAP Site Location: Hallsville, Texas

Photograph 1

Date: 4/21/2020

Direction: N/A

Comments:

Multiple sections of core from soil boring SB-28 advanced near downgradient monitoring well AD-28 within the Western Bottom Ash Pond (WBAP) CCR unit. 5-foot pushes were used. Note the reddish color indicating the presence of oxidized iron-bearing minerals.



Photograph 2

Date: 4/21/2020

Direction: N/A

Comments:

0-5 foot interval of SB-

28.



Photograph 3

Date: 4/21/2020

Direction: N/A

Comments:

5-10 foot interval of SB-28. Recovery of this interval was limited. A sample was collected from this interval from 6-6.5 ft. below ground surface (bgs).



Photograph 4

Date: 4/21/2020

Direction: N/A

Comments:

10-15 foot interval of SB-28. Recovery of this interval was limited.



Photograph 5

Date: 4/21/2020

Direction: N/A

Comments:

15-20 foot interval of SB-28. Recovery of this interval was limited. A sample was collected from this interval from 15.5-16 ft. bgs.



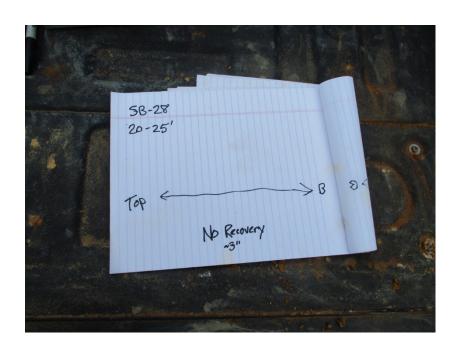
Photograph 6

Date: 4/21/2020

Direction: N/A

Comments:

Field geologist's note indicating that very little of the 20-25 foot interval of SB-28 was recovered.



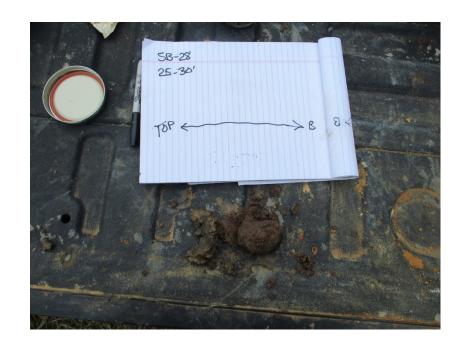
Photograph 7

Date: 4/21/2020

Direction: N/A

Comments:

25-30 foot interval of SB-28. Very little of this interval was recovered. Note the color change of the soil from red to dark brown/black. A sample was collected from this interval.



Photograph 8

Date: 4/21/2020

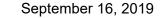
Direction: N/A

Comments:

Bottom of SB-28. The boring log indicates no recovery of soil from the 30-40 foot interval. A sample was collected from this interval.



ATTACHMENT C SEM/EDS Analysis



via Email: BSass@geosyntec.com

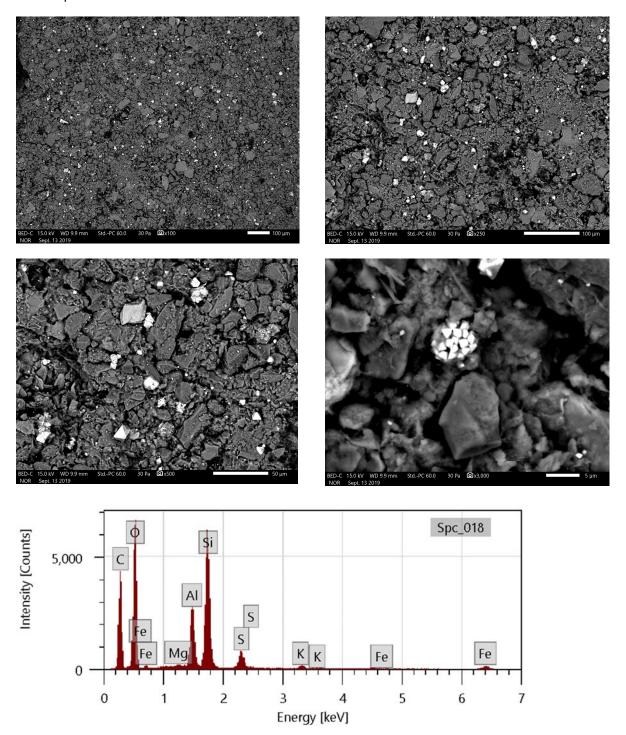


Dr. Bruce Sass 941 Chatham Lane, Suite 103, Columbus, OH 43221

Spc_004 Intensity [Counts] 1,500 Αl 1,000 500 Fe

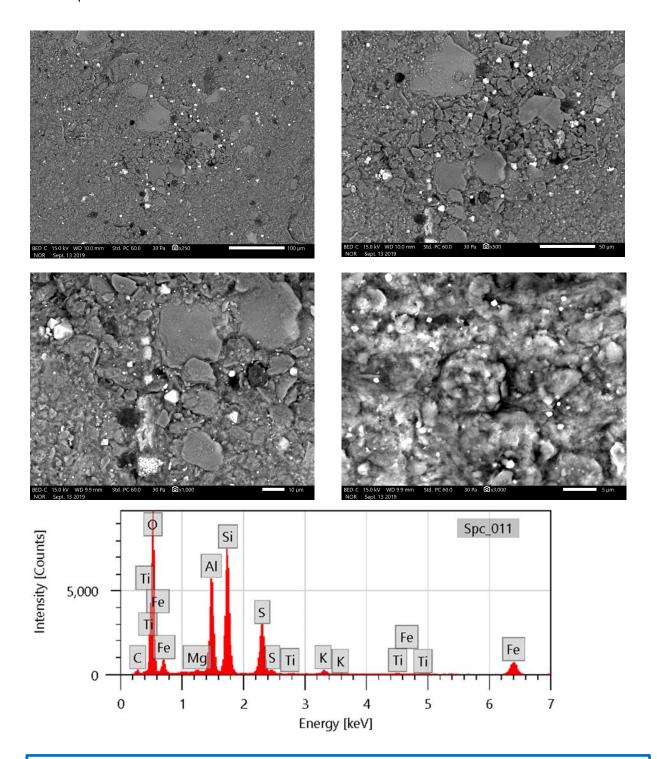
Lignite. Backscattered electron micrographs show the sample at 100X, 1,100X, and 1,500X. EDS spectrum at bottom is an area scan of the region shown in top right micrograph. Bright particles are mostly quartz and feldspar. Major peaks for carbon, oxygen, silicon, and aluminum suggest coal and clay.

Energy [keV]



Sample VAP B3 40-45. Backscattered electron micrographs show the sample at 100X, 250X, 500X, and 3000X. EDS spectrum at bottom is an area scan of the region shown at 500X. Bright particles are pyrite (framboid in bottom right micrograph). Major peaks for carbon, oxygen, silicon, and aluminum suggest coal and clay.





Sample VAP B3 50-55. Backscattered electron micrographs show the sample at 250X, 500X, 1000X, and 3000X. EDS spectrum at bottom is an area scan of the region shown at 3000X. Bright particles are mostly pyrite (framboid in bottom left micrograph); occasional particles of Fe-Ti oxide are detected. Major peaks for oxygen, silicon, and aluminum suggest clay. Large blocky particles are mostly quartz, feldspar, and clay.



ATTACHMENT D Certification by Qualified Professional Engineer

CERTIFICATION BY A QUALIFIED PROFESSIONAL ENGINEER

I certify that the selected and above described alternative source demonstration is appropriate for evaluating the groundwater monitoring data for the Pirkey West Bottom Ash Pond CCR management area and that the requirements of 30 TAC §352.951(e) have been met.

<u>Beth</u>	Ann	Gross

Printed Name of Licensed Professional Engineer

Signature



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License Number

Texas

Licensing State

12/22/2021

Date