## Pirkey Power Plant West Bottom Ash Pond Alternate Source Demonstration

The Pirkey West Bottom Ash Pond initiated an assessment monitoring program in accordance with 40 CFR 257.95 on April 3, 2018. Groundwater protection standards (GWPS) were set in accordance with 257.95(d)(2) and a statistical evaluation of the assessment monitoring data was conducted. The statistical evaluation revealed an exceedance of the cobalt GWPS on July 10, 2019. A successful alternate source demonstration (ASD) was completed per 257.95(g)(3), therefore, the Pirkey West Bottom Ash Pond will remain in assessment monitoring. An alternate source demonstration is documentation that shows a source other than the CCR unit was responsible for causing the statistics to exceed the GWPS. The ASD document will explain the alternate cause of the GWPS exceedance. The successful ASD is attached.

### ALTERNATIVE SOURCE DEMONSTRATION REPORT FEDERAL CCR RULE

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

Submitted to



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#### LIST OF ACRONYMS

AEP American Electric Power

ASD Alternative Source Demonstration

CCR Coal Combustion Residuals

CFR Code of Federal Regulations

EDS Energy Dispersive Spectroscopic Analyzer

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

UTL Upper Tolerance Limit

USEPA United States Environmental Protection Agency

VAP Vertical Aquifer Profiling

WBAP West Bottom Ash Pond

XRD X-Ray Diffraction

#### INTRODUCTION AND SUMMARY

The H.W. Pirkey Plant, located in Hallsville, Texas, has four regulated coal combustion residuals (CCR) storage units, including the West Bottom Ash Pond (WBAP, Figure 1). In February 2019, a semi-annual assessment monitoring event was conducted at the WBAP in accordance with 40 CFR 257.95(d)(1). The monitoring data were submitted to Groundwater Stats Consulting, LLC (GSC) for statistical analysis. Groundwater protection standards (GWPSs) were previously established for each Appendix IV parameter in accordance with the statistical analysis plan developed for the facility (AEP, 2017) 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 the background concentration and the maximum contaminant level (MCL) or risk-based level specified in 40 CFR 257.95(h)(2). 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 calculated for Appendix IV parameters at the compliance wells to assess whether Appendix IV 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). At the WBAP, an SSL was identified for cobalt at AD-28, where the LCL of 0.0132 milligrams per liter (mg/L) was above the calculated GWPS of 0.009 mg/L (Geosyntec, 2019a). No other SSLs were identified.

#### 1.1 CCR Rule Requirements

United States Environmental Protection Agency (USEPA) regulations regarding assessment monitoring programs for coal combustion residuals (CCR) landfills and surface impoundments provide owners and operators with the option to make an alternative source demonstration when an SSL is identified (40 CFR 257.95(g)(3)(ii)). An owner or operator may:

Demonstrate that a source other than the CCR unit caused the contamination, or that the statistically significant increase resulted from error in sampling, analysis, statistical evaluation, or natural variation in groundwater quality. Any such demonstration must be supported by a report that includes the factual or evidentiary basis for any conclusions and must be certified to be accurate by a qualified professional engineer or approval from the Participating State Director or approval from EPA where EPA is the permitting authority. If a successful demonstration is made, the owner or operator must continue monitoring in accordance with the assessment monitoring program pursuant to this section....

Pursuant to 40 CFR 257.95(g)(3)(ii), Geosyntec Consultants, Inc. (Geosyntec) has prepared this Alternative Source Demonstration (ASD) report to document that the SSL identified for cobalt at AD-28 should not be attributed to 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.

#### ALTERNATIVE SOURCE DEMONSTRATION

The Federal CCR Rule 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 ASDs due to Type I (sampling), Type II (laboratory), or Type III (statistical evaluation) issues. As described below, the SSL has been attributed to natural variation associated with the underlying geology, which is a Type IV issue.

AD-28 is located at the southwest corner of the pond, as shown in Figure 1. In a previous ASD for cobalt at the WBAP, evidence was provided to show that cobalt is present in the aquifer media at the site and that the observed cobalt concentrations were due to natural variation (Geosyntec, 2019b). The previous ASD discussed how the WBAP itself 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. Because cobalt mobility is affected by pH, the SPLP test results are likely even more conservative than actual pond conditions. SPLP is run at a pH of 5 SU, whereas the operational pH of the pond varies between approximately 5.8 and 7.0 SU. Cobalt mobility increases under more acidic conditions, although even at a pH of approximately 5, only 2% of cobalt in fly ash is mobile (Izquierdo and Querol, 2012).

Cobalt was also not detected above the reporting limit of 0.005 mg/L in a grab sample of the pond water. As shown in Table 1, the reporting limits for the SPLP ash leachate test and pond water analysis are both below the average concentration of cobalt observed at AD-28 during the background and assessment monitoring periods (0.0147 mg/L). Since the previous ASD was prepared, there have been no notable changes in coal handling or sourcing at the plant that would have affected the composition of the ash or pond water.

Since completion of the prior ASD, four additional permanent wells (B-2, B-3, AD-40, and AD-41) have been installed upgradient of the WBAP. The most recent data available for select wells in the vicinity of the WBAP, including the new upgradient locations, are shown in Figure 2. Groundwater cobalt concentrations at upgradient locations vary from 0.0008 mg/L to 0.0345 mg/L at AD-40 and B-3, respectively. This wide range in cobalt concentrations provides further evidence for the natural variation of cobalt at the Site, particularly as the concentrations at B-3 exceed both the GWPS for the WBAP and the LCL calculated for cobalt at AD-28 (the well of interest).

As noted in the prior ASD, soil samples collected across the site, including from locations near the WBAP, identified cobalt in the aquifer solids at varying concentrations. Since completion of the prior ASD, additional soil samples have been collected from locations upgradient of the WBAP. Select soil sample data from the previous ASD and recently collected data are summarized in Table 2. Cobalt was identified in the aquifer solids at varying concentrations, with the highest value of 24 milligrams per kilogram (mg/kg) reported at AD-41, which is upgradient of the EBAP (Figure 3). Other testing included collection of aquifer solids to evaluate for the presence of cobalt-containing minerals. X-ray diffraction evidence identified pyrite and marcasite (both iron sulfides) at select locations at concentrations up to 3% by weight (Table 2). Cobalt is known to substitute for iron in crystalline iron minerals such as pyrite and marcasite due to their similar ionic radii (Krupka and Serne, 2002; Hitzman et al., 2019).

Groundwater samples were collected from upgradient location B-3 via vertical aquifer profiling (VAP), as described in an ASD previously generated for the EBAP (Geosyntec, 2019c). The VAP groundwater samples were centrifuged to separate solid and liquid phases, and the solid material was submitted for analysis of total metals and mineralogy by X-ray diffraction (XRD). The samples were also submitted for analysis of chemical composition and mineralogy by scanning electron microscopy (SEM) using an energy dispersive spectroscopic analyzer (EDS). Following installation of permanent monitoring wells at B-2 and B-3, groundwater samples were collected by purging groundwater through the filter pack using a submersible pump. An additional groundwater sample was collected at AD-30. These permanent well groundwater samples were filtered through a 1.5-micron filter, and the solid material retained on the filter was submitted for analysis of total metals and by SEM/EDS.

Based on total metals analysis, cobalt was identified both in the centrifuged solid material collected from upgradient location B-3 [VAP-B3-(40-45)] and in the material retained on the filter after processing groundwater from B-2 and B-3 (Table 2). Cobalt was detected in the AD-30 solid material at estimated value of 9.3 mg/kg, which is comparable to the concentration observed in bulk soil collected at the same location at the screened interval (15 mg/kg). These results provide further evidence that cobalt concentrations reported during groundwater sampling are naturally occurring and associated with the solid phase in the aquifer.

According to XRD results of the centrifuged solid sample [VAP-B3-(40-45)], pyrite was present as approximately 3% of the solid phase, with hematite (an iron(III) oxide) present at 2% (Table 3). 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 framboid pattern (Harris, 1981; Sawlowicz, 2000). Major peaks involving iron and sulfur were identified in the EDS spectrum, which further support the identification of pyrite (Attachment A). While cobalt was not identified in the EDS spectrum, it is likely present at concentrations below the detection limit. Pyrite was also identified during SEM/EDS analysis of lignite which is mined immediately adjacent to the site.

While soil analytical and mineralogical data are not available for AD-28, the wide distribution of pyrite across the site suggests that naturally occurring cobalt, which may substitute for iron in pyrite, may also be present in the aquifer solids near AD-28. The presence of lignite in the area is well-documented, including at upgradient and downgradient locations relative to the WBAP (Broom and Myers, 1966; ETTL, 2010). Additionally, the pond was not identified as the source of cobalt at AD-28 in the previous ASD based on the documented low mobility of cobalt under the pond conditions and lack of detectable cobalt in the pond itself.

#### 2.2 <u>Sampling Requirements</u>

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.

#### CONCLUSIONS AND RECOMMENDATIONS

The preceding information serves as the ASD prepared in accordance with 40 CFR 257.95(g)(3)(ii) and supports the position that the SSL of cobalt for AD-28 identified during assessment monitoring in . February 2019 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 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 B.

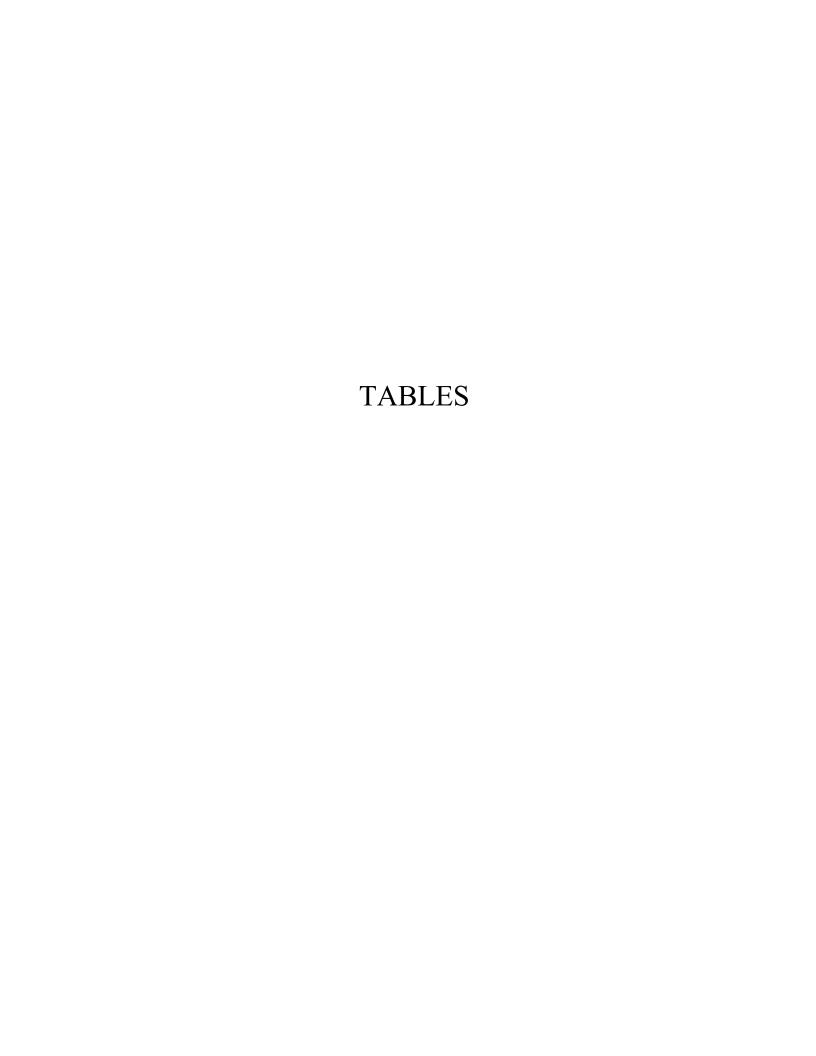
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USEPA, 2009. Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities – Unified Guidance. EPA 530/R-09/007. March.



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

Sample	Unit	Cobalt Concentration
Bottom Ash	mg/kg	5.8
SPLP Leachate	mg/L	< 0.01
WBAP Pond Water	mg/L	< 0.005
AD-28 - Average	mg/L	0.0147

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	Sample Depth (ft bgs)	Cobalt (mg/kg)	Pyrite/Marcasite (%)				
	Bulk Soil Samples						
AD 17	7	3.10	2				
AD-17	15	1.50	0				
AD 10	8	3.60	1				
AD-18	22	2.90	0				
AD 20	7	1.00	3				
AD-30	23	15.0	1				
AD-31	12	1.90	2				
AD-31	26	0.83	0				
AD-32	11	1.70					
AD-32	20-25	9.10					
	15	< 1.0					
AD-41	35	23.5					
	95	1.90					
	10	2.36					
	16	3.62					
B-2	71	10.30					
	82	7.21					
	87	3.11					
	10	1.30					
B-3	20	0.59					
	97	1.11					
Solid Material Retained After Filtration							
AD-30	15-25	9.3 J					
B-2	38-48	4.3 J					
B-3	29-34	12.0					
D-3	VAP 40-45	18.0	3				

#### Notes:

'--' - analysis not completed

mg/kg- milligram per kilogram

ft bgs - feet below ground surface

J = estimated value

For AD-XX locations, 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 for B-X locations 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.

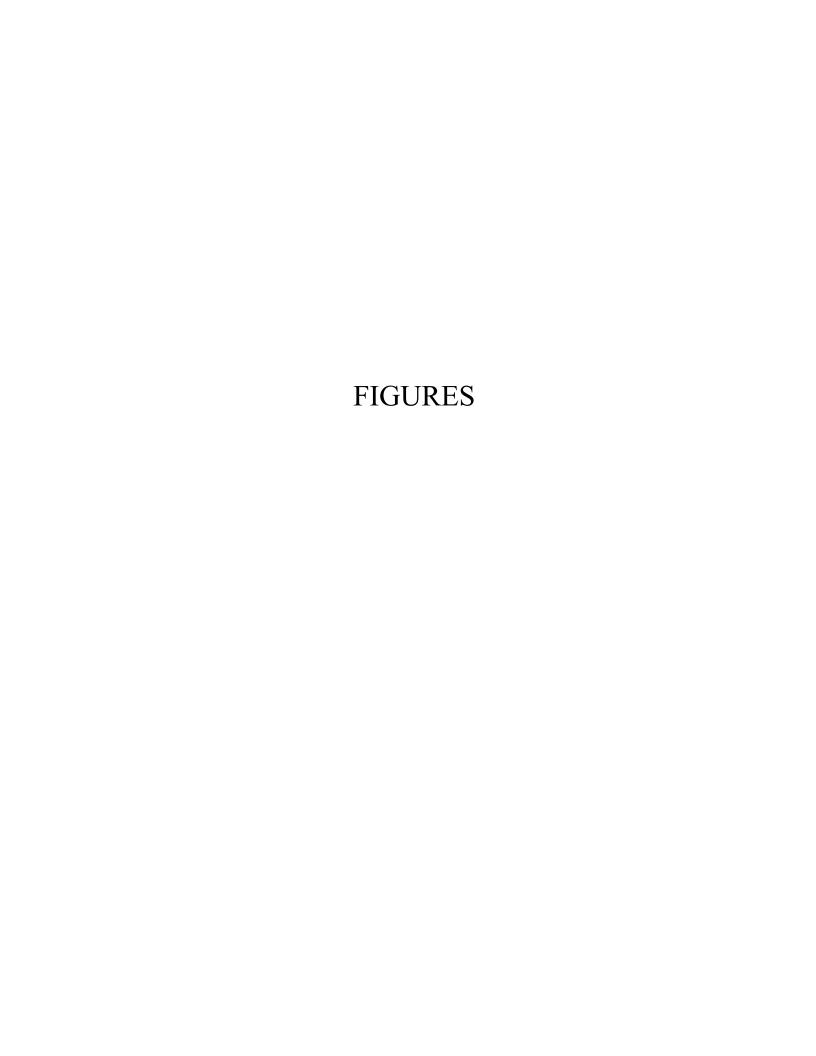
Table 3: X-Ray Diffraction Results West Bottom Ash Pond - H. W. Pirkey Plant

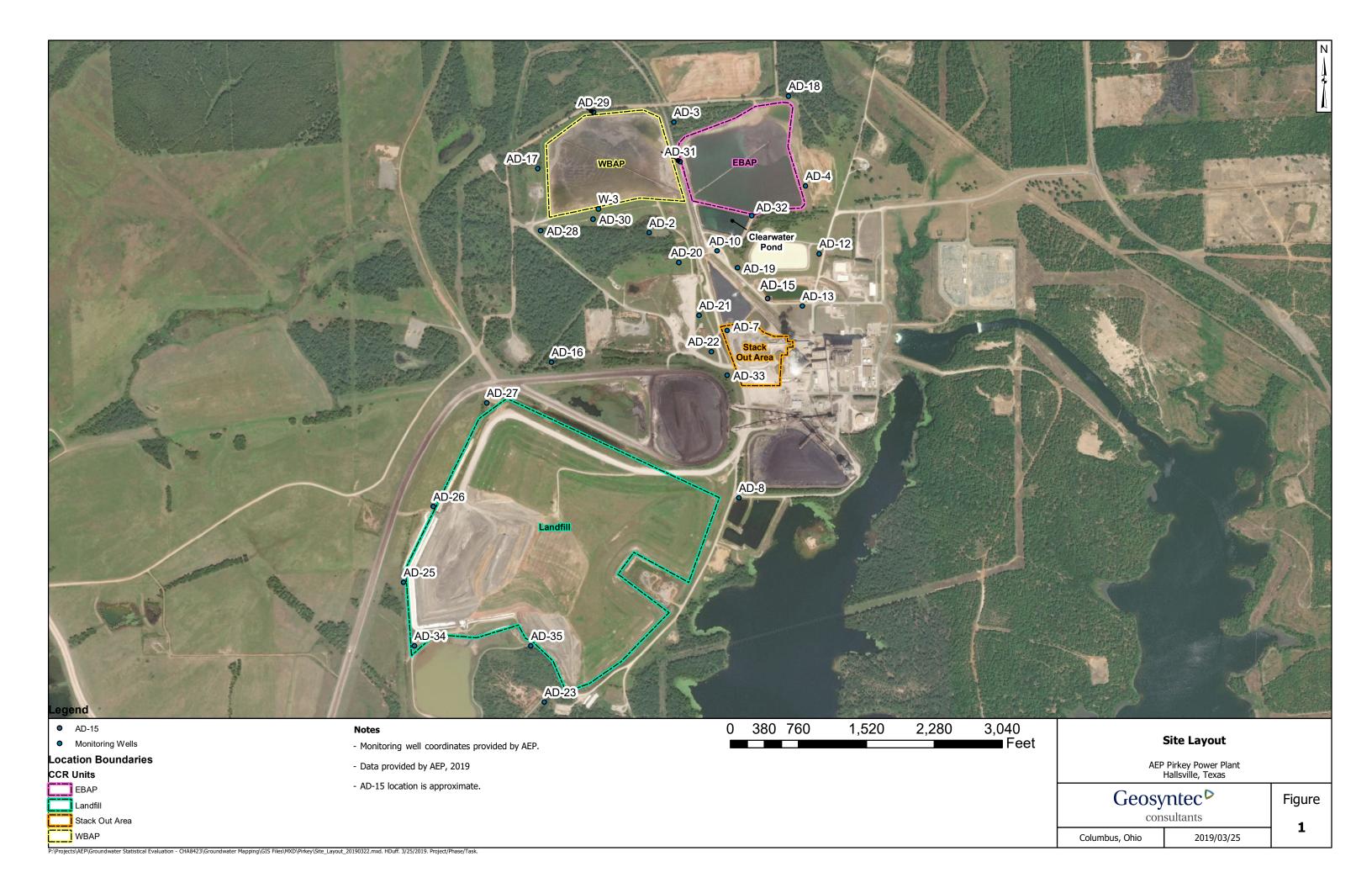
Constituent	VAP-B3-(40-45)
Quartz	15
Plagioclase Feldspar	0.5
Orthoclase	ND
Calcite	ND
Dolomite	ND
Siderite	0.5
Goethite	ND
Hematite	2
Pyrite	3
Kaolinte	42
Chlorite	4
Illite/Mica	6
Smectite	12
Amorphous	15

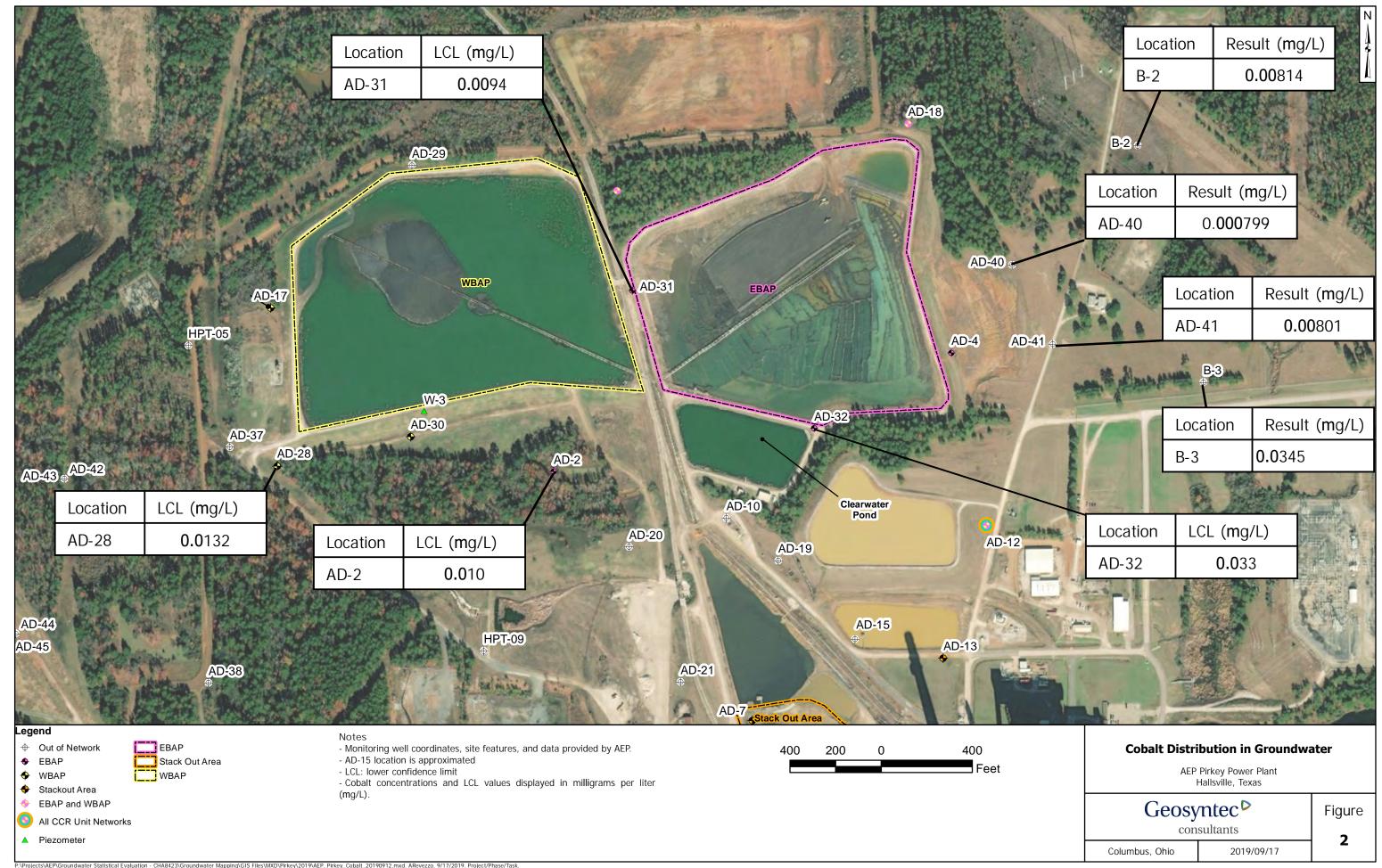
Notes:

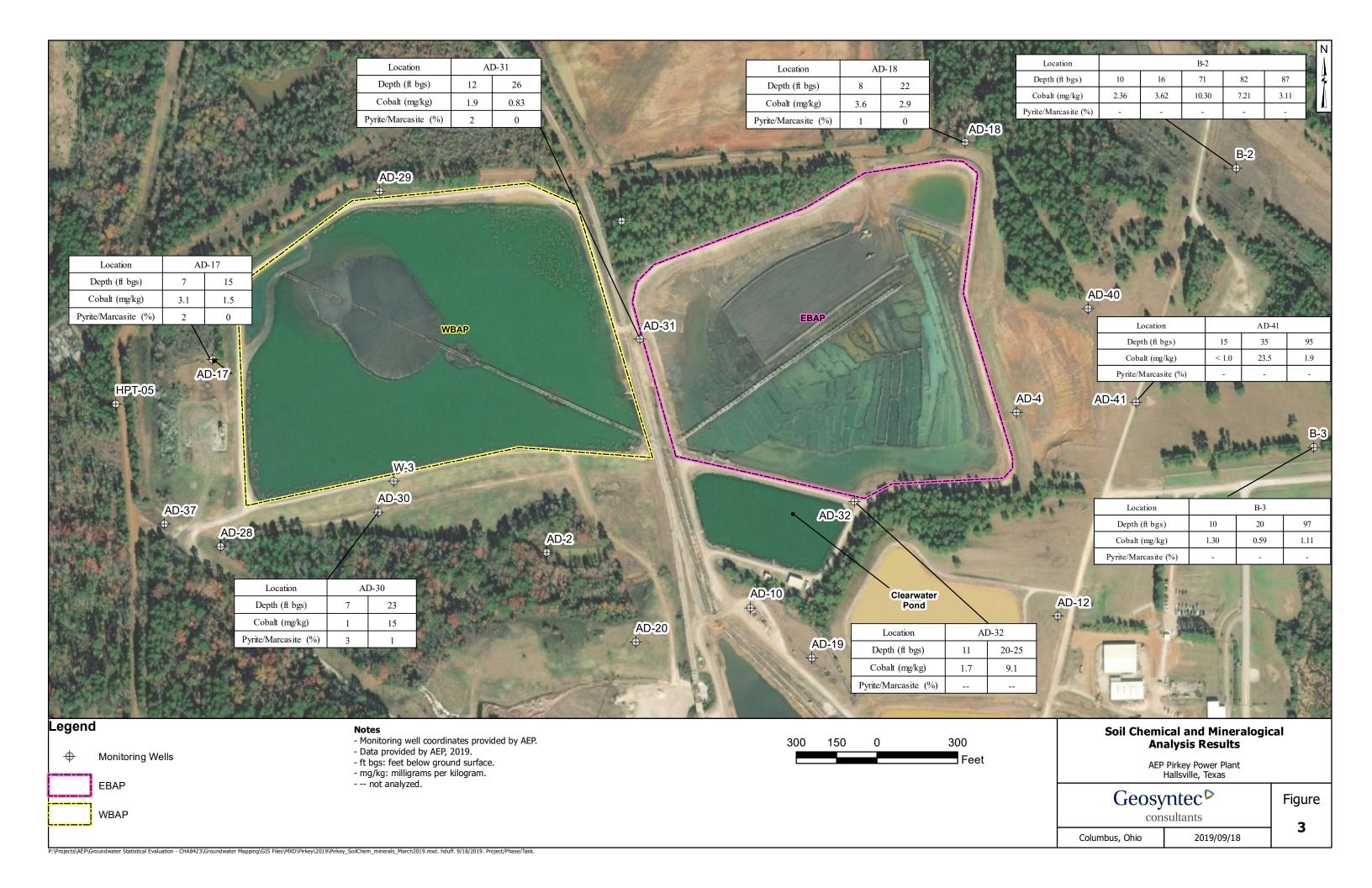
ND: Not detected

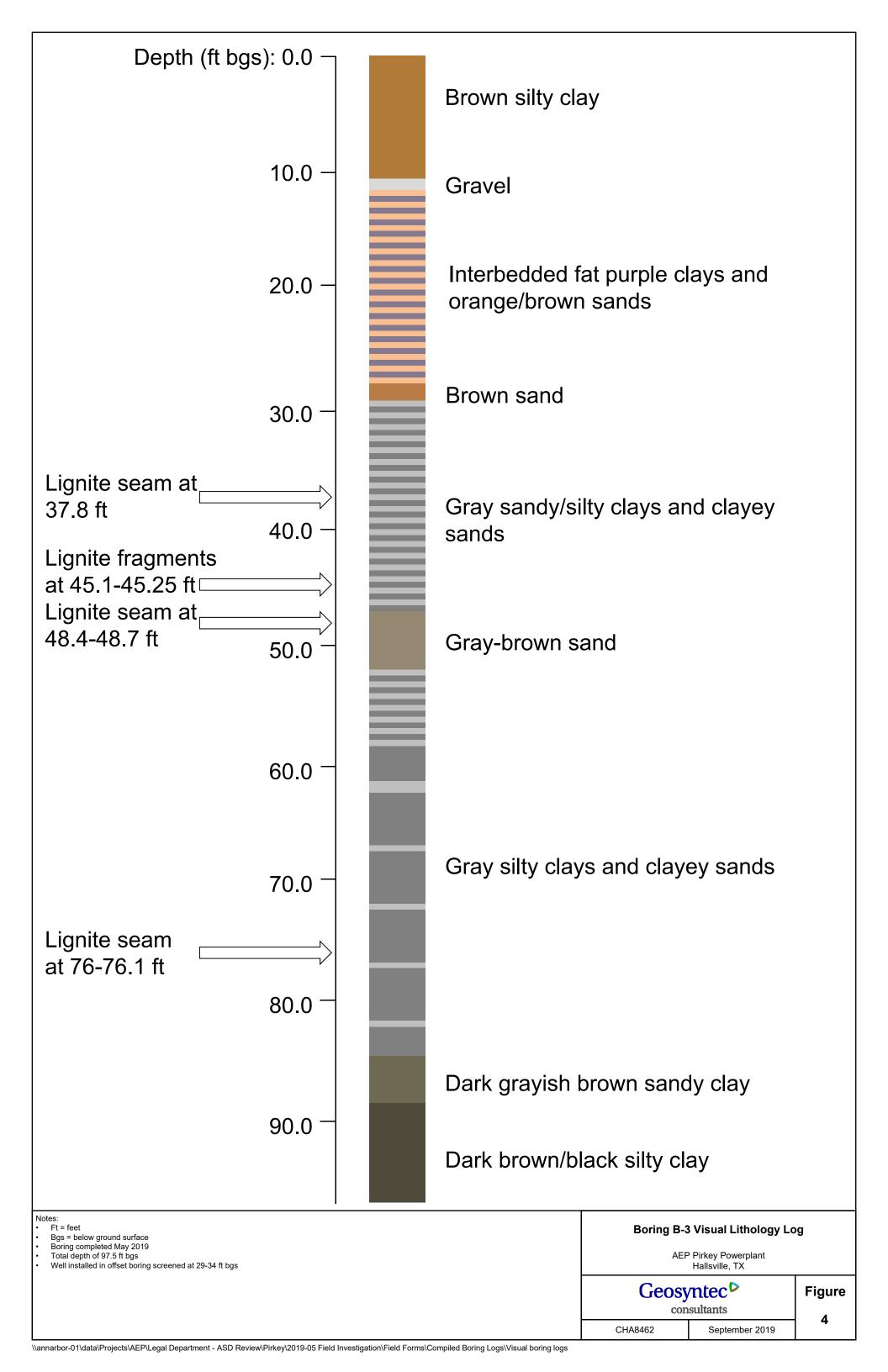
VAP-B3-(40-45) is the centrifuged solid material from the groundwater sample collected at that interval.



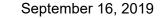








# ATTACHMENT A SEM/EDS Analysis



via Email: <a href="mailto:BSass@geosyntec.com">BSass@geosyntec.com</a>

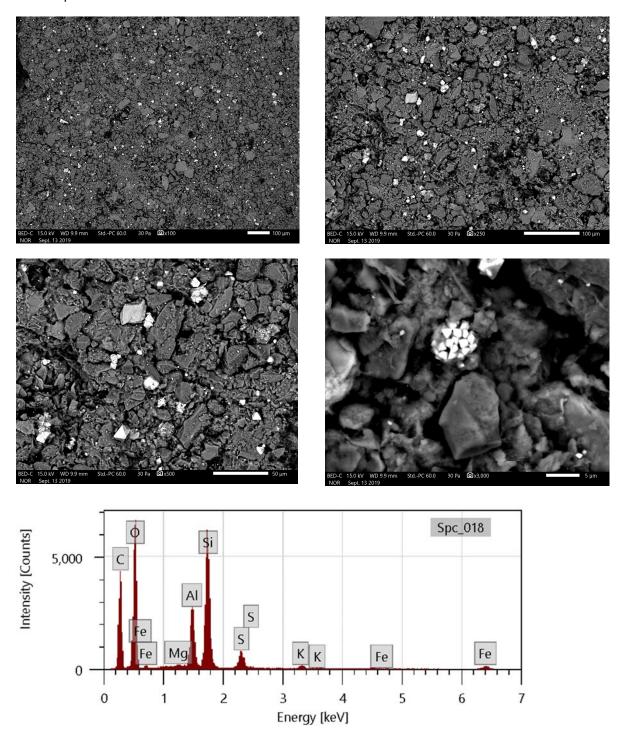


Dr. Bruce Sass 941 Chatham Lane, Suite 103, Columbus, OH 43221

Spc\_004 Intensity [Counts] 1,500 Αl 1,000 500 Fe

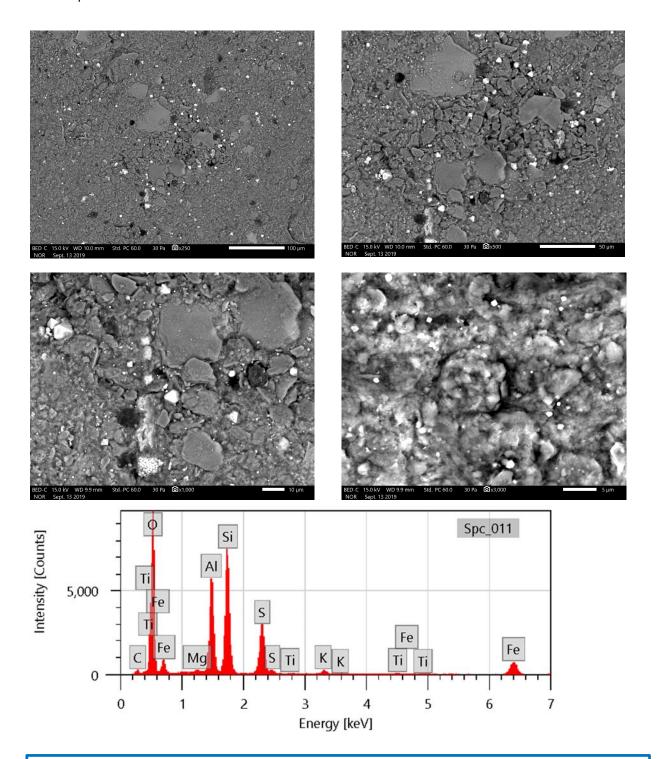
Lignite. Backscattered electron micrographs show the sample at 100X, 1,100X, and 1,500X. EDS spectrum at bottom is an area scan of the region shown in top right micrograph. Bright particles are mostly quartz and feldspar. Major peaks for carbon, oxygen, silicon, and aluminum suggest coal and clay.

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 B 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 40 CFR 257.95(g)(3)(ii) have been met.

Beth Ann Gross Printed Name of Licer	nsed Professional Engineer	BETH ANN GROSS	
Beth ar Signature	m Bross	79864 & CENSE SIONAL EN	
Signature		Geosyntec Consultants 8217 Shoal Creek Blvd., Suite 200 Austin, TX 78757	
		Texas Registered Engineering Firm No. F-1182	
70964	Toyog	10/3/2019	

Date

Licensing State

License Number