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
- 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
- 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 second semiannual detection monitoring event of 2020. 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 November 2020, 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 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 the background concentration and the maximum contaminant level (MCL) or, for constituents without an MCL, the 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 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 0.0134 milligrams per liter (mg/L) exceeded the calculated GWPS of 0.0090 mg/L (Geosyntec, 2021). No other SSLs were identified.

1.1 <u>CCR Rule Requirements</u>

USEPA regulations regarding assessment monitoring programs for 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 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 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 <u>Proposed Alternative Source</u>

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 the Federal CCR Rule and draft TCEQ guidance for groundwater monitoring (TCEQ, 2020). 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). 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**).

A surface water sample was collected directly from the WBAP on November 4, 2020. Cobalt was detected at a concentration of 0.000501 mg/L in the WBAP sample (**Table 1**). This concentration is 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) 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 transformation to iron oxide minerals.

As described in an ASD previously generated for the Pirkey Plant's East Bottom Ash Pond (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 pyrite 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 <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.

SECTION 3

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 for cobalt identified at AD-28 during assessment monitoring in November 2020 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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TABLES

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

Sample	Sample Date	Unit	Cobalt Concentration
Bottom Ash	2/11/2019	mg/kg	5.8
SPLP Leachate	2/11/2019	mg/L	< 0.01
WBAP Pond Water	11/4/2020	mg/L	0.000501
AD-28 - Average	May 2016 - November 2020	mg/L	0.0145

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 DataWest Bottom Ash Pond - H.W. Pirkey Plant

Location ID	Location	Sample Depth (ft bgs)	Cobalt (mg/kg)						
Bulk Soil Samples									
		6-6.5	< 2.38						
AD 28	WDAD Notwork	15.5-16	4.53						
AD-28	WDAF NELWOIK	25-30	< 2.50						
		40-41	8.70						
AD 20	WDAD Notwork	7	1.00						
AD-30	WDAP 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						
Solid Material Retained After Filtration									
AD-30	WBAP Network	15-25	9.3 J						
B-2	Upgradient	38-48	4.3 J						
P 3	Ungradient	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 ResultsWest 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	Within 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.

West Bottom Ash Pond - H. W. Pirkey Plant						
Constituent	VAP-B3-(40-45)					
Quartz	15					
Plagioclase Feldspar	0.5					

 Table 4: B-3 X-Ray Diffraction Results

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.

FIGURES





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EBAP

WBAP

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- -- not analyzed.

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ATTACHMENT A SB-28 Boring Log

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Cof AS-28/MW-28

ATTACHMENT B SB-28 Boring Photographic Log

Client: American Electri	c Power	Project Number: CHA8495/1	2A/02		
Site Name: H.W. Pirkey	Plant WBAP	Site Location: Hallsville, Texas			
Photograph 1					
Date: 4/21/2020					
Direction: N/A		WAR READER			
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



September 16, 2019

Dr. Bruce Sass

941 Chatham Lane, Suite 103, Columbus, OH 43221

via Email: <u>BSass@geosyntec.com</u> Imbus, OH 43221





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.

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

<u>Beth Ann Gross</u> Printed Name of Licensed Professional Engineer

Beth an Geors

Signature



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Texas Registered Engineering Firm No. F-1182

79864 License Number Texas ______ Licensing State

5/28/202) Date