# ALTERNATIVE SOURCE DEMONSTRATION REPORT TEXAS STATE CCR RULE

H.W. Pirkey Power Plant Flue Gas Desulfurization (FGD) Stackout Area Hallsville, Texas

Submitted to



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#### LIST OF ACRONYMS

AEP American Electric Power

ASD Alternative Source Demonstration

CCR Coal Combustion Residuals

EBAP East Bottom Ash Pond

EPRI Electric Power Research Institute

FGD Flue Gas Desulfurization

GSC Groundwater Stats Consulting, LLC

GWPS Groundwater Protection Standard

LCL Lower Confidence Limit

MCL Maximum Contaminant Level

QA Quality Assurance

QC Quality Control

SPLP Synthetic Precipitation Leaching Profile

SSL Statistically Significant Level

SU Standard Unit

TAC Texas Administrative Code

TCEQ Texas Commission on Environmental Quality

UTL Upper Tolerance Limit

USEPA United States Environmental Protection Agency

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 statistically significant levels (SSLs) for beryllium and cobalt in the groundwater monitoring network at the H.W. Pirkey Plant Flue Gas Desulfurization (FGD) Stackout Area, located in Hallsville, Texas, following the first semi-annual detection monitoring event of 2021. The FGD Stackout Area is registered as a waste pile 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 FGD Stackout Area (**Figure 1**). In May 2021, a semi-annual assessment monitoring event was conducted at the FGD Stackout Area 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 unit (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. Seasonal patterns were observed for beryllium, cadmium, cobalt, combined radium, fluoride, and lithium at AD-22 (Geosyntec, 2021a). To correctly account for seasonality, confidence intervals for these wells and constituents were constructed using deseasonalized values. 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). The following SSLs were identified at the Pirkey FGD Stackout Area (Geosyntec, 2021a):

- The deseasonalized LCL for beryllium exceeded the GWPS of 0.0040 mg/L at AD-22 (0.00577 mg/L); and
- The deseasonalized LCL for cobalt exceeded the GWPS of 0.0560 mg/L at AD-22 (0.0723 mg/L).

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 SSLs identified for beryllium and cobalt at AD-22 are from a source other than the FGD Stackout Area.

## 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 SSLs identified for beryllium and cobalt were based on a Type IV cause and not by a release from the Pirkey FGD Stackout Area.

#### **SECTION 2**

#### ALTERNATIVE SOURCE DEMONSTRATION

The TCEQ 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 SSLs identified for beryllium and 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 beryllium and 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 SSLs have been attributed to natural variation associated with seasonal effects, which is a Type IV (natural variation) issue.

## 2.1.1 Beryllium

An SSL was identified for beryllium at AD-22 using deseasonalized statistics (Geosyntec, 2021a). According to the Unified Guidance, "seasonal correction should be done both to minimize the chance of mistaking a seasonal effect for evidence of contaminated groundwater, and also to build more powerful background to compliance point tests. Problems can arise, for instance, from measurement variations associated with changing recharge rates during different seasons" (USEPA, 2009).

The seasonal effects observed in the statistical analysis occur in roughly annual cycles, with somewhat higher beryllium concentrations occurring in early spring and lower concentrations in early fall. For example, the beryllium concentration in 2021 at AD-22 was 0.00852 milligrams per liter (mg/L) in March 2021, in contrast to 0.00239 mg/L in November 2020. Previous ASDs for the FGD Stackout Area showed that beryllium concentrations at AD-22 appear to correlate with groundwater elevations at the well (Geosyntec, 2019; Geosyntec, 2020b; Geosyntec, 2020c; Geosyntec 2021b). This relationship still holds true (Figure 2). Beryllium concentrations at AD-22 are correlated with seasonal changes in other constituents, including calcium (Figure 3) and lithium (Figure 4). The correlation between beryllium and both monovalent (lithium) and divalent (calcium) cations suggests that the variability in observed beryllium concentrations is related to cation exchange behavior with clay minerals present in the native soil.

Soil boring SP-B4, which was advanced in March 2020 to re-log AD-22, found that clay materials were identified in the seasonally saturated zones above the permanent water table. The boring log for SP-B4 is provided in **Attachment A**, and the original boring log and well construction diagram

is provided in **Attachment B**. At AD-22, the depth to water fluctuated between approximately 3 and 12 ft below ground surface (bgs). Clay was identified from approximately 1.5 ft bgs to 13.3 ft bgs, where it transitioned to a clayey silt (**Figure 5**). Analysis by X-ray diffraction (XRD) confirmed the presence of clays within the seasonal water table and sand within the screened interval, as summarized in **Table 1**. The clay fraction of the uppermost sample collected from within the seasonal water table was further analyzed to identify the type of clays present. Smectite-type clays, which are 2:1-layer high-activity clays with characteristic cation exchange capacity, make up the majority of the clay minerals present at that interval.

Sorption and desorption of beryllium from smectite-type clays is well documented (Boschi and Willenbring, 2016a; You, et al., 1989). Desorption was found to be affected by pH, with 75% of beryllium desorbed from a smectite-type clay as pH decreased from 6.0 standard units (SU) to 3.0 SU (Boschi and Willenbring, 2016b). The pH values recorded at AD-22 for groundwater samples collected under the Federal CCR Rule ranged from 3.6 to 5.1 SU, suggesting that conditions are favorable for beryllium desorption from smectite-type clays. The presence of these exchangeable clays provides further evidence that the exceedance of beryllium at AD-22 can be attributed to the effects of seasonal groundwater elevation changes, and the resulting cation exchange between groundwater and the exchangeable clay within the seasonal water table, on groundwater quality.

#### **2.1.2** Cobalt

An SSL was identified for cobalt at AD-22 using deseasonalized statistics (Geosyntec, 2021a). As shown in previous ASDs (Geosyntec, 2020b; Geosyntec, 2020c; Geosyntec, 2021b), the cobalt concentrations at AD-22 also appear to correlate with seasonal changes in groundwater elevation (**Figure 6**). In addition, the cobalt concentrations are well correlated with changes in other cations, including calcium and lithium (**Figure 7**), suggesting natural variability associated with interactions with the aquifer solids.

The concentration ratio between calcium and cobalt is consistently on the order of 1000:1 at both upgradient and downgradient locations (**Figure 8**). A sample was collected of the solid FGD sludge material accumulated on the FGD Stackout Area. The solid phase sample was leached using both USEPA's Synthetic Precipitation Leaching Profile (SPLP) testing procedure (SW-846 Test Method 1312 [USEPA, 1994]) and TCEQ's 7-Day Distilled Water Leachate Test Procedure (30 TAC 335.521 Appendix 4). While cobalt concentrations in both of the leached samples are consistent with those observed in the groundwater samples, the leached calcium concentrations are approximately two to three orders of magnitude higher. However, calcium concentrations in groundwater are generally consistent between AD-22 and upgradient well AD-13 (**Figure 9**). The different ratio between calcium and cobalt in the leached FGD sludge material (about 45,000:1) as compared to the ratio for groundwater indicate that dissolved calcium concentrations at AD-22 would be significantly higher if the groundwater at this location were affected by leachate. The similarity between upgradient and downgradient calcium concentrations provides an additional line of evidence that the exceedances observed at the FGD Stackout Area are not due to a release from the unit.

Siderite and pyrite, both reduced iron-bearing minerals, were identified below the seasonal water table (within the saturated zone) at AD-22. Cobalt is known to undergo isomorphic substitution for iron in both siderite and pyrite (Gross, 1965; Hitzman, et al., 2017; Krupka and Serne, 2002). This is due to the similarity of their ionic radii (approximately 1.56 angstrom (Å) for iron vs. 1.52 Å for cobalt [Clementi and Raimondi, 1963). The proposed substitution of cobalt for iron in the crystal lattice of pyrite has been documented in other ASDs prepared for the Pirkey Plant's East Bottom Ash Pond (EBAP; Geosyntec, 2021c) and West Bottom Ash Pond (WBAP; Geosyntec, 2021d).

Goethite (an iron oxide) was identified within the seasonally saturated zone and the screened interval at AD-22 (**Table 1**). The weathering of siderite and pyrite to goethite under oxidizing conditions is a well-understood phenomenon, including in formations in east Texas (Senkayi, et al., 1986; Dixon, et al., 1982) and may have occurred within the seasonally saturated zone. A review of geochemical conditions at AD-22 shows that the conditions observed at AD-22 are favorable for goethite formation (**Figure 10**). During weathering from reduced (pyrite or siderite) to oxidized (goethite) iron minerals, cobalt would be released from the mineral structure. The contribution of cobalt to groundwater via dissolution of siderite or pyrite within the saturated aquifer is not likely to change seasonally. However, the mobilization of cobalt which was released during weathering of siderite or pyrite to goethite in the seasonally saturated zone may explain the variability in aqueous cobalt concentrations and their correlation with the groundwater elevation.

#### 2.1.3 Conceptual Site Model

The seasonal fluctuations in beryllium and cobalt concentrations at AD-22 can be attributed to variations in the amount of the aquifer solids that are in contact with groundwater as the water table elevation changes. When the water table is higher, more clay material is in contact with groundwater, allowing greater desorption of cations (including beryllium) from the cation exchange sites on the clay. In the case of cobalt, more iron oxides are in contact with groundwater as the water table rises, allowing for the release of cobalt from mineral phases where it has isomorphically substituted for iron. Thus, the observed SSLs were attributed to natural variation associated with seasonal desorption of beryllium and cobalt as the amount of aquifer solids that are saturated increases.

#### 2.2 **Sampling Requirements**

As the ASD presented above supports the position that the identified SSLs are not due to a release from the Pirkey FGD Stackout Area, 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

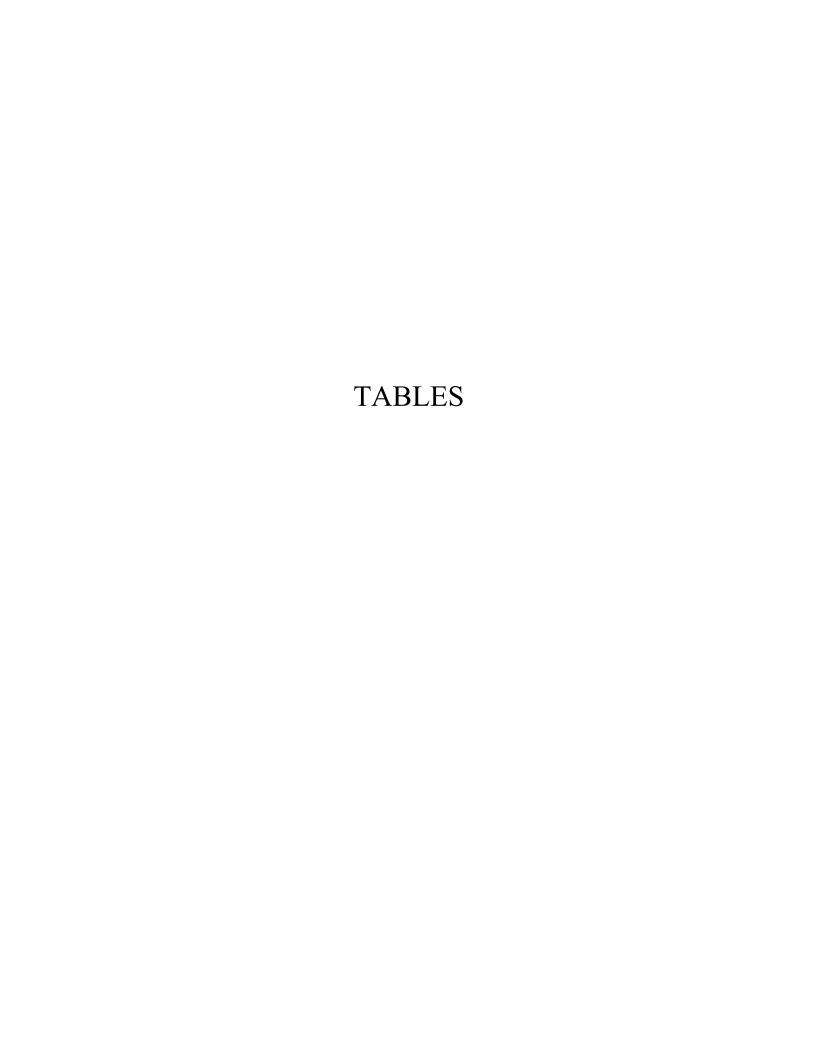
The preceding information serves as the ASD prepared in accordance with 30 TAC §352.951(e) and supports the position that the SSLs of beryllium and cobalt at AD-22 identified during the first semiannual assessment monitoring event of 2021 were not due to a release from the FGD Stackout Area. The identified SSLs were, instead, attributed to natural variation related to seasonal desorption or dissolution of beryllium and cobalt from the aquifer solids. Therefore, no further action is warranted, and the Pirkey FGD Stackout Area will remain in the assessment monitoring program. Certification of this ASD by a qualified professional engineer is provided in **Attachment C.** 

#### **SECTION 4**

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# Table 1: X-Ray Diffraction Results FGD Stackout Pad - H. W. Pirkey Plant

Boring Location	SP-B4					
Associated Well	AD-22					
Depth (ft bgs)	6-8	18-20	28-30			
Sample Location	Within Seasonal Water Table	Below Seasonal Water Table	Within Screened Interval			
Quartz	28	47.5	95			
Plagioclase Feldspar	< 0.5	< 0.5	1			
K-Feldspar	1 0.5		-			
Goethite	1	-	2			
Hematite	-	-	-			
Chlorite	1	-	-			
Siderite	-	10	-			
Pyrite	-	2	-			
Clays	*	40	2			
Kaolinite	13					
Illite/Mica	2					
Smectite	43					
Mixed-Layered Illite/Smectite	11					

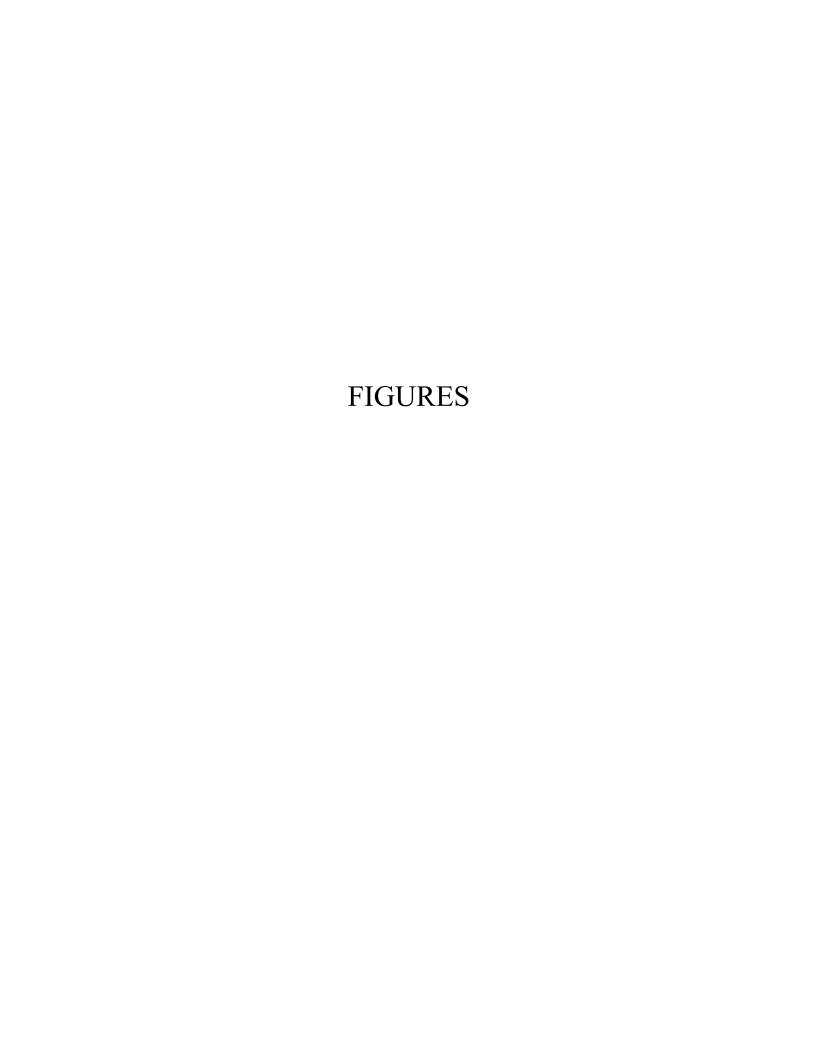
Notes:

Mineral constituents are reported in percentage.

Values shown as less than indicate the mineral constituent is present but below the quantification limit.

<sup>-:</sup> not detected

<sup>\*</sup>The clay fraction at SP-B4-6-8 was further analyzed to characterize the types of clays present, as listed below.





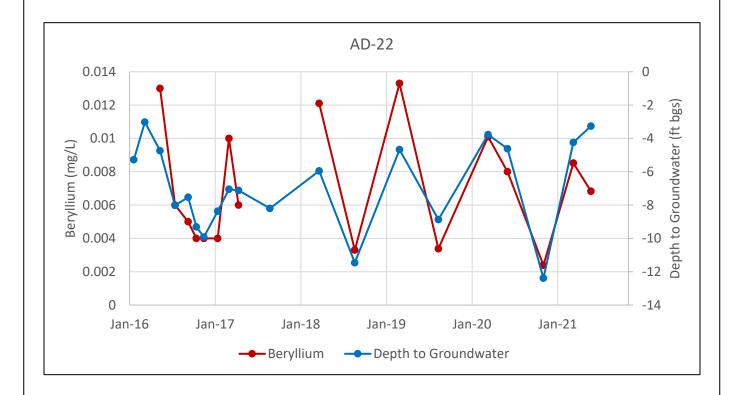
2020 Soil Borings

Stackout Pad

Upgradient Monitoring Well

AEP Pirkey Power Plant Hallsville, Texas

Geosyntec consultants AMERICAN ELECTRIC POWER Figure 1 Columbus, Ohio 2020/03/27



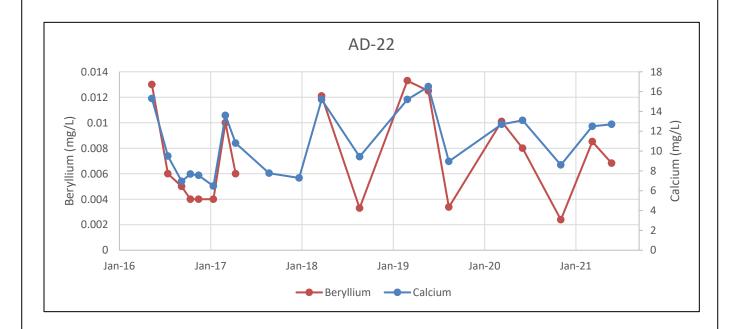
Notes: Beryllium concentrations are shown in milligrams per liter (mg/L). Depth to water is shown as feet below ground surface (ft bgs). The gap in beryllium data represents the time period in which detection monitoring took place and samples were not analyzed for beryllium.

# Beryllium v. Depth to Groundwater Pirkey FGD Stackout Pad

Figure

2



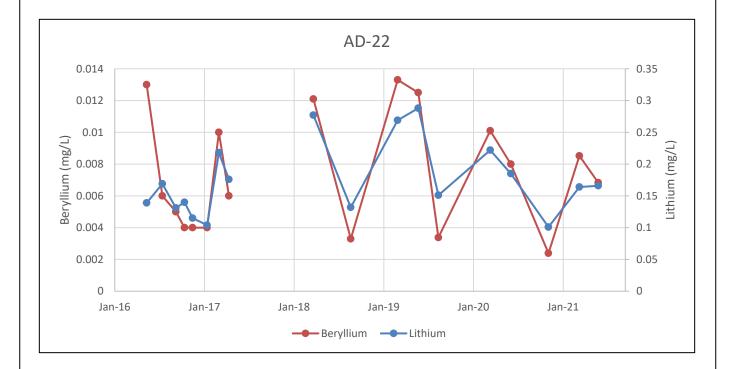


Notes: Beryllium and calcium concentrations are shown in milligrams per liter (mg/L). The gaps in beryllium data represent the time period in which detection monitoring took place and samples were not analyzed for beryllium.

# Beryllium v. Calcium Concentrations Pirkey FGD Stackout Pad



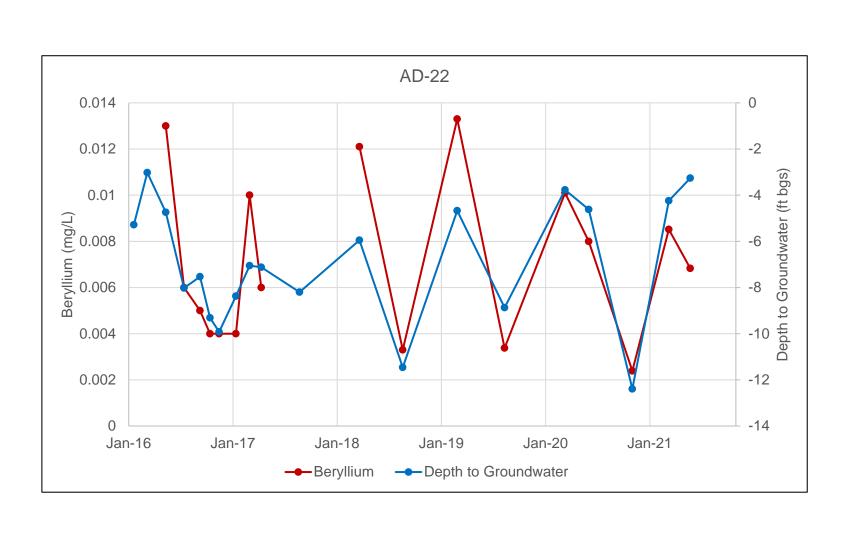
3



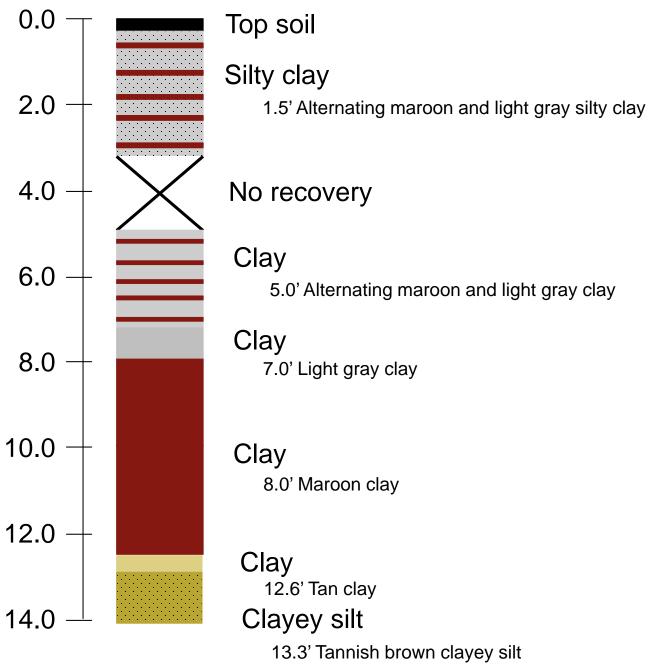
Notes: Beryllium and lithium concentrations are shown in milligrams per liter (mg/L). The gaps in data represents the time period in which detection monitoring took place and samples were not analyzed for beryllium or lithium.

# Beryllium v. Lithium Concentrations Pirkey FGD Stackout Pad





## Depth (ft bgs)



-A sample was collected for analysis of mineralogy from 6-8

-The full boring log is available in Attachment A.

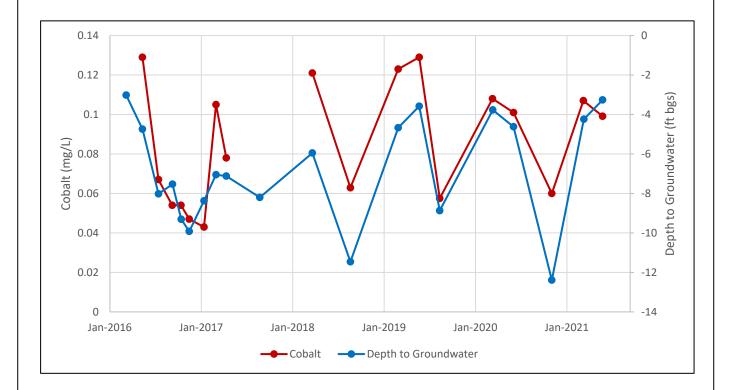
**AD-22 Seasonal Water Table Geology** H. W. Pirkey Plant – FGD Stackout Pad



Figure

Columbus, OH

02-Nov-2020



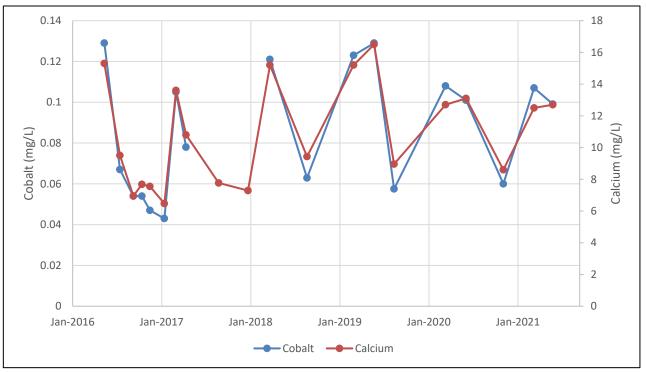
Notes: Cobalt concentrations are shown in milligrams per liter (mg/L). Depth to water is shown as feet below ground surface (ft bgs). The gap in cobalt data represents the time period in which detection monitoring took place and samples were not analyzed for cobalt.

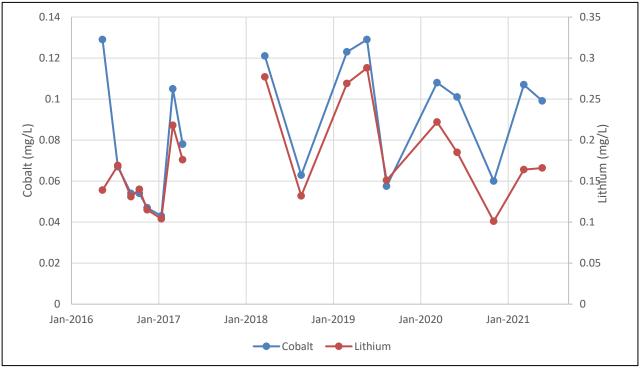
# AD-22 Cobalt v. Depth to Groundwater Pirkey FGD Stackout Pad



Figure

6





Notes: Cobalt, calcium, and lithium concentrations are shown in milligrams per liter (mg/L). The gaps in cobalt and lithium data represent the time period during which detection monitoring took place and samples were not analyzed for cobalt and lithium.

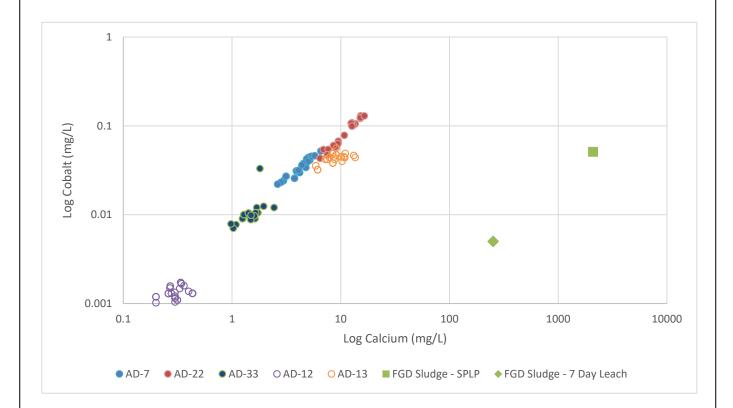
#### AD-22 Cobalt v. Calcium and Lithium

Pirkey FGD Stackout Pad



Figure

7



Notes: Cobalt and calcium concentrations are shown in milligrams per liter (mg/L). Upgradient wells are shown with hollow circles. 'FGD Sludge-SPLP' and 'FGD Sludge 7 Day Leach' present the leached concentrations of cobalt and calcium using the Synthetic Precipitation Leaching Procedure (SW-846 Test Method 1312) and the 7-Day Distilled Water Leachate Test Procedure (30 TAC 335.521 Appendix 4), respectively.

## **Cobalt and Calcium Concentration** Distribution

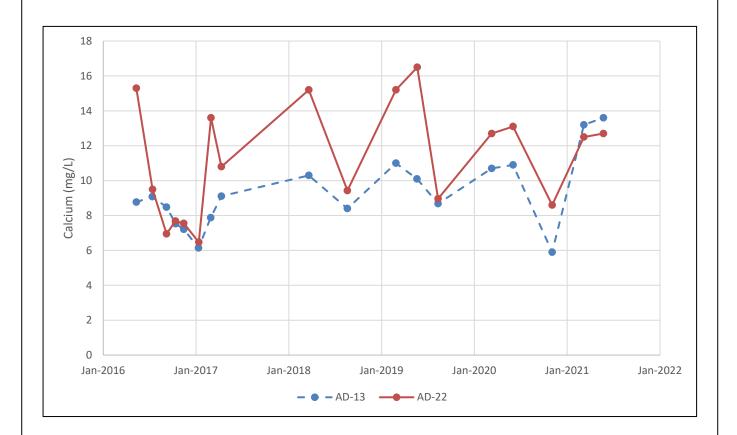
Pirkey FGD Stackout Pad



**Figure** 

8

26-October-2021



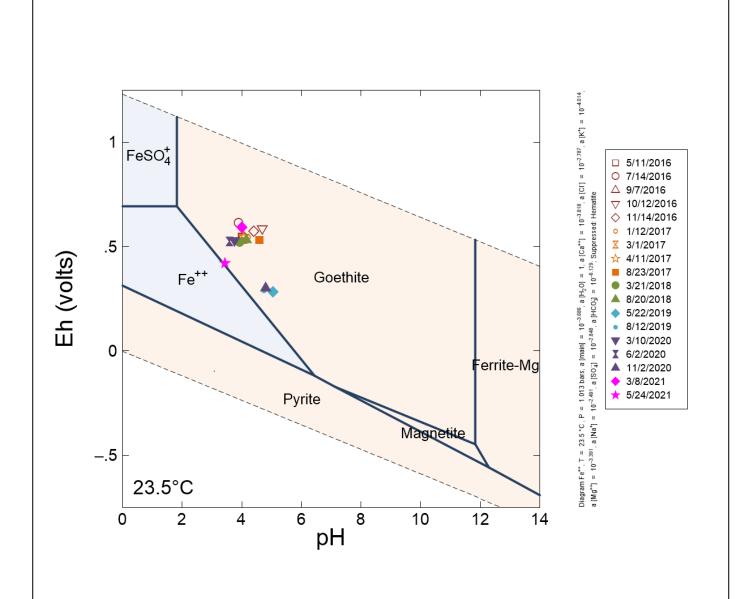
Notes: Calcium concentrations are shown in milligrams per liter (mg/L). AD-13 is shown with a dashed line because it is an upgradient location.

# Calcium Time Series Graph Pirkey FGD Stackout Pad



**Figure** 

9



Notes: Average groundwater concentrations of major cations and anions at AD-22 were used to establish baseline conditions for the diagram. Eh and pH values for sampling dates at AD-22 are shown on the diagram.

## AD-22 Eh-pH Diagram

Pirkey FGD Stackout Pad



AMERICAN ELECTRIC POWER

Figure

10

Columbus, Ohio

28-October-2021

# ATTACHMENT A SP-B4 Boring Logs

		Soil Bo	oring Log	
Projec	t: AEP Pirkey		Boring/Well Name:SP-B4	
Projec	ct Location:	Hallsville, TX	Boring Date: 3/3/2020	
	Soil Profile			
Feet Water Table		Des	cription	PID*
_	pp= pocket per	netrometer		
0	0.0'-0.4':	Top soil, black silt, vegetation		
	0.4'-0.7':	Brown clayey silt, good cohesion		
	0.7'-1.5':	Red and light gray silty clay, moderate stiffnes	s (pp. 2.5), high plasticity	
	1.5'-3.7':	Maroon and light gray clay, high stiffness (pp.	4.5-5.0), low plasticity; iron ore present 3.1'-3.7'	
	3.7'-5.0':	NO RECOVERY		
;	5.0'-7.0':	Maroon and light gray clay, high stiffness (pp.	4.5-5.0), low plasticity; iron ore present throughout	
	7.0'-8.0':	Light gray clay with iron ore, moderate stiffnes		
	8.0'-10.0':	Maroon clay, moderate stiffness (pp. 3.5), mod	derate plasticity; iron ore present; moist at 9'	
,	10.0'-12.6':	Maroon clay, moderate stiffness (pp. 3.5), mod	derate plasticity; iron ore present; wet at 12'	
	7			
	12.6'-13.3':	Tan clay, low stiffness (pp.1.5), high plasticity;		
	13.3'-18.5':	Tan and brown clayey silt, moderate cohesion	; iron ore present; wet	
	18.5'-20.3':	Maroon silty clay, low stiffness (pp. 1.0), mode	erate plasticity; iron ore; wet	
0	00.01.04.41	Deduces the second	A.C.) biologicalistic conditions of	
	20.3'-21.1':	Dark gray/black clay, trace silt, low stiffness (p	pp. 1.5), high plasticity; wet	
	21.1'-21.3':	Dark gray silt, good cohesion; wet		
	21.3'-21.9':	Dark gray silty clay, low stiffness (pp. 1.5), hig	n piasticity; wet	
	21.9'-22.3':	Dark gray silt, moderate cohesion; wet		
	22.3'-22.7':	light brown silt; low cohesion; wet	/high stiffness (pp.3.5), moderate plasticity; wet,	
	22.7'-24.4':	glauconite present	Trigit stiffless (pp.5.5), moderate plasticity, wet,	
,	24.4'-27.8':	Dark green/gray fine grained sand, well sorted		
	27.8'-30.0':	Red and orange fine grained sand, well sorted	I, with iron ore; wet	
30				
		Samples collected at 6-8'; 18-20'; 28-30'		
		TD at 30' bgs; refusal		
		*PID readings not collected		
15				
	ig Geoprobe 3230 D		Coownton Consultanta	
	g Contractor: :_DJ Diduch		Geosyntec Consultants	

# ATTACHMENT B AD-22 Boring Log and Well Installation Diagram

APEX I	PROJE	CT NO.: _	110-089			□ BORING	BORING NUMBER:		FOR WELL ELL NUMBER:	AD-22	
FACILITY NAME: AEP- Pirkey Power Plant			FACILITY ID NO	).: <u>N/A</u>		.					
FACIL	ITY AD	DRESS: 1	Hallsville, Texa	ıs							.
DRILL	ING CO	OMPANY/	METHOD/RI	G: _	Apex Ge	oscience I	nc. / Hollow-ste	m Augers/ CME-55 Track Ri	<u> </u>		.
DRILL	ER:	Ed Wilson	, Apex Geoscie	nce In	c		COM	MPLETION DATE: 12/16/2	2010		.
PREPA	RED B	Y: David E	Bedford					LOGGED BY: David	Bedford		
LATTI	TUDE:	N 32°27'0	3.3"		Datum: \	WGS-84	V	VELL LOCATION: Triangl	e- South side Quansit Hu	t	
		W94°29'4					•				
DEPTH (FEET)	PID (PPM)	SAMPLE	WELL LO			USCS CODE		SOIL DESCRIPTION AND C	COMMENTS	Odor	Moisture
			F	7							
1				<b></b>	0-0.5	SC	Clayey sand, li	ght brown, very fine grained		None	Moist
2 3 4 5 6 7 8					0.5-12	CL		t brown mottled with light gra		None	Slightly Moist
9 10 11 12 13 14 15 16			V		12-20	SC	very fine grain Slightly wet @	grayish brown with orangish by led 12.5' from seepage of iron ore 15-17'	rown streaks,	None	Slightly Wet
17 18 19 20							Very firm 18-	18.5'			
21 22 23 24 25					20-25	SC		line rock 21-21.1'), light brow s, mica, black clay streaks, ver		None	Wet
26 27 28 29 30					25-30	SM	Sand, greenisl very fine grain	n brown (1') grading to orangi ned	sh brown, silty,	None	Wet
31 32 33 34 35 36 37 38 39 40							Boring Termi	nated at 30'			
		******	Cement			<i>VIIII</i>	_	Filter S			,
Total Depth:    Apex   Filter Sand (Size/Interval):   geoscience inc.   Grout (Type/Interval):   Surface Completio			8-30' Grout from 0	0-2'; Bentonite from 2-8'	Riser Interval: Screen Interval: Water level: Above Ground	+3 (ags)-10 10-30' 12.5' 3'					

# ATTACHMENT C Certification by a 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 FGD Stackout Area CCR management area and that the requirements of 30 TAC §352.951(e) have been met.

Beth	Ann	Gross
Dom		OT 022

Printed Name of Licensed Professional Engineer

Buh am Buss Signature BETH ANN GROSS
79864
CENSE

Geosyntec Consultants 2039 Centre Pointe Blvd, Suite 103 Tallahassee, Florida 32308

Texas Registered Engineering Firm No. F-1182

79864

**Texas** 

License Number Licensing State

12/22/2021

Date