

June 9, 2011

Ms. Rachel Patton
Department of Environmental Quality
Tidewater Regional Office
5636 Southern Boulevard
Virginia Beach, VA 23462

RE: Addendum to the Nature and Extent Study and

**Assessment of Corrective Measures Report** 

Chesapeake Energy Center, Landfill Permit No. 440

Dear Ms. Patton:

Please find attached an addendum to the Nature and Extent Study and Assessment of Corrective Measures report addressing sulfide for inclusion in the Corrective Action Plan (CAP) for the Chesapeake Energy Center (CEC) Ash Landfill, Chesapeake, Virginia. The addendum is being submitted pursuant to conditions XIV.S.1 and XIV.S.2 of the amended Solid Waste Facility Permit for the CEC landfill. The purpose of the addendum is to demonstrate that the oxidation reactions that influence the movement of arsenic, beryllium and cobalt in groundwater at CEC are closely linked to the attenuation of sulfide, which has been included in the CAP.

Should you have any questions or comments, please feel free to contact me at (804) 273-2929, or Donald Hintz of Dominion Electric Environmental Services at (804) 273-3552.

Sincerely,

Cathy C. Taylor

Director

Electric Environmental Services

Attachment

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# CHESAPEAKE ENERGY CENTER INDUSTRIAL LANDFILL PERMIT #440 N&E/ASSESSMENT OF CORRECTIVE MEASURES (Originally submitted to DEQ June 19, 2003) ADDENDUM

### Summary

Recent studies completed for Dominion in support of the Corrective Action Plan (CAP) for the Chesapeake Energy Center Ash landfill conclude that sediment and pore water chemistry provides evidence that: 1) natural processes are oxidizing reduced iron to iron oxides and oxyhydroxides in groundwater as it nears the sediment-water interface in the surface water bodies surrounding the landfill, and 2) natural attenuation (adsorption) of arsenic, beryllium and cobalt by the subsurface formation of iron oxides and oxyhydroxides is occurring at the site.

The purpose of this addendum is to demonstrate that the oxidation reactions that influence the movement of arsenic, beryllium and cobalt in groundwater at CEC are closely linked to sulfide attenuation, which is now included in the CAP for the site. Information related to sulfide for this demonstration was obtained by a review of published literature and site specific data.

### Additions to the Corrective Action Plan

In addition to arsenic, beryllium and cobalt; sulfide has been added as a Constituent of Concern (COC) and part of the landfill's CAP. Sulfide was first detected in one background well (MW-4) and in two downgradient wells (CECW-4 and PO-8) above the groundwater protection standard (GPS) in September 2002. While the sulfide value may be related to background conditions, sulfide has been included as a Constituent of Concern (COC). Sulfide has been detected in eleven of fourteen compliance monitoring wells above the GPS since the 2002 sampling event. The GPS for the site has been established at 2.4 mg/l, which is the laboratory limit of quantification (LOQ) for sulfide.

# **Delineation of Sulfide in Groundwater**

The recent September 2010 groundwater sampling event reported four detections of sulfide above the GPS. The detections occurred in samples collected from downgradient wells CECW-2, CECW-5, PO-8 and PO-9. Historic sulfide concentrations for the CEC compliance monitoring well network are summarized on the attached Table 1. The attached figure (URS Figure 7-19) illustrates the location of the monitoring wells, including sulfide concentrations from the September 2002 sampling event (first detection of sulfide above the GPS). The number of existing monitoring wells is considered sufficient to assess sulfide in groundwater at the CEC landfill.

### Geochemical Behavior of Sulfide in the Subsurface

As reported by Battelle (March, 2006) the monitoring well water compositions indicate that nearly all the sulfur in these waters is in the oxidized sulfate form. The Eh values determined for these well water samples also indicate that all the sulfur in site groundwater should be in the form of sulfate. However, in several well samples the reduced form of sulfur (sulfide) was measured at concentrations above the LOQ. The sulfide concentrations measured are small compared to the sulfate concentrations (105 and 2,460 mg/L, respectively). The source of this sulfide cannot be determined with certainty. Fly ash is not a likely source because this material has been thoroughly oxidized during the combustion process and should contain no sulfide or reducing agents. It is possible that reducing conditions occur in organic-rich river sediments allowing sulfate reduction to occur.

Organic-rich sediments often occur in river bottoms where silt and clay rich sediments are deposited. Sulfide is often produced in these sediments and could enter groundwater during inland flow induced by elevated river levels (tidal flux). The presence of high chloride and sodium concentrations and bromide/chloride ratios that are very similar to seawater indicate a significant seawater influence in groundwater wells located near the periphery of the CEC Ash Landfill.

The close link between iron and sulfur oxidation processes is very important in the context of the CEC Ash Landfill. It has been determined by AMEC (June, 2010) that natural processes are oxidizing reduced iron in groundwater as it nears the sediment-water interface in the surface water bodies surrounding the landfill. Using standard electrode potentials (a measure of the strength of the oxidation or reduction potential) it is observed that a much lower potential is required to oxidize sulfide than is required to oxidize ferrous iron.

In the context of groundwater in the Norfolk formation, this means that if oxidized iron is observed (rust) that reduced sulfur was oxidized before the ferrous iron. Wherever oxidized iron is observed, sulfide was previously oxidized (and attenuated) to sulfate. Because oxidized iron is the attenuator for arsenic, beryllium and cobalt at the landfill, wherever metals attenuation is occurring, it is known that sulfide also must have been attenuated.

Along any given flowpath that attenuates metals by adsorption to iron oxides, attenuation of sulfide by oxidation to sulfate has already taken place before metal adsorption. The speciationbased remedy for natural attenuation of sulfide (with long term monitoring) is an appropriate remedial alternative at the CEC ash landfill because thermodynamics requires that sulfide oxidation take place before metal attenuation by iron oxides. Because it is known that metal attenuation by iron oxides is taking place at the landfill, it can be surmised that sulfide attenuation must have preceded metal attenuation.

## **Health Effects of Sulfide**

Sulfur is an essential element in life processes and is found in all natural waters at some concentration level. Sulfur in the reduced form (sulfide) is associated with multiple industrial sources; however, is also naturally occurring. In analyzing for sulfides, the results reflect all sulfides present in the sample regardless of which type. There is no MCL for total sulfides in groundwater and a surface water criterion (water quality standard) has not been established.

The maximum concentration of sulfides found in background surface water located upstream of CEC within the Southern Branch of Deep Creek were not exceeded by any of the samples taken along the landfill's reaches of the surface water bodies. Therefore, it appears that the CEC groundwater contribution to total sulfide concentrations in adjacent surface water bodies is minimal and poses little risk to existing environmental conditions.

The potential impact of sulfides to human health and the environment differs depending upon its form. Health risks from sulfide are most commonly associated with the presence of hydrogen sulfide gas. Hydrogen sulfide gas is a waste product of sulfate-reducing bacteria; its rotten egg odor is often a marker for the presence of sulfate-reducing bacteria in nature. Hydrogen sulfide can react with metal ions in the water to produce insoluble metal sulfides.

Hydrogen sulfide is not regulated by the EPA and it is not part of the CAP for the CEC landfill. The Department of Health and Human Services (DHHS), the International Agency for Research on Cancer (IARC), and the EPA have not classified hydrogen sulfide for carcinogenicity (ATSDR, 2006).

There is no known use of the adjacent surface water as domestic water sources at CEC because adjacent surface water is saline. Groundwater is not used as a drinking water source in the vicinity of the site and it is unlikely that the shallow aquifer will be used in the foreseeable future because of salinity of the groundwater. CEC groundwater contribution of sulfide in adjacent surface water bodies is minimal and poses little risk to existing environmental conditions.

### Reasons to allow Sulfide in the CAP under Monitored Natural Attenuation

Literature review and site-specific data indicates that natural attenuation of sulfide along the landfill perimeter will follow the attenuation observed and documented for arsenic, beryllium and cobalt. A speciation-based, natural attenuation approach to remediation, with long term geochemical monitoring is supported for sulfide by geochemistry and site-specific data. Allowing sulfide to fall under the same site wide remedial option as arsenic, beryllium and cobalt will achieve the CAP objective of managing groundwater in the CEC area to protect human health and the environment. Also, this goal is consistent with expected future land-use, physical characteristics of the area, groundwater use, and with the remedial goals established within the CAP.

### References:

Agency for Toxic Substances and Disease Registry (ASTDR), 2006. Toxicological Profile for Hydrogen Sulfide. Atlanta, Georgia. U.S. Department of Health and Human Services, Public Health Services, Agency for Toxic Substances and Disease Registry. CAS# 7783-06-4

AMEC, 2010, Natural Attenuation of Arsenic Demonstration, Chesapeake Energy Center Ash Landfill, Chesapeake, Virginia, June 7, 2010.

Battelle, 2006, "Geochemical Testing and Analysis of Arsenic Occurrence and Mobility at the CEC Ash Landfill". Report to Dominion.

Bekins BA, BE Rittman, JA MacDonald. 2001. "Natural Attenuation strategy for Groundwater Cleanup Focuses on Demonstrating Cause and Effect." USGS, Toxic Substances Hydrology Program.

Brown, Theodore L. and LeMay, H. Eugene, Jr. 1981. Chemistry: The central science. 2<sup>nd</sup> Edition. Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

MACTEC, 2003, "Risk Assessment for the Chesapeake Energy Center". Report to Dominion U.S. Environmental Protection Agency (USEPA), 2004b. Issue Paper on the environmental chemistry of metals. August. USEPA Risk Assessment Forum.

# Sulfide Concentrations Chesapeake Energy Center TABLE 1

PO-11	1	<2.4	1.0.1	<2.4	<2.4	2.0 J	<2.4	<2.4	0.60 J	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	400	200
_		<u> </u>	1	V	<u> </u>	2	V	V	0	V	V	<u> </u>	<u> </u>	V	V	4	_
PO-10	<0.2	<2.4	<2.4	1.6 J	0.60 J	1.8 J	3.0	3.0	0.80	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<200	<200
PO-9	<0.2	0.60 J	9.9	0.60 J	3.81	3.0	9.9	9.9	7.4	4.0	3.0	2.0	1.4 J	<2.4	1.6 J	1,600	009
PO-8	0.4	<2.4	2.6	2.6	5.2	3.8	7.0	7.0	9.6	7.6	7.0	4.8	1.6 J	18.4	1.6 J	1,000	400
MW-5	<0.2	<2.4	0.80	<2.4	<2.4	1.8 J	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<200	200
MW-4R	-	1	ı	Ī	1	1		1	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<200	200
MW-4	0.4	<2.4	2.4	1.0 J	1.0 J	2.6	<2.4	<2.4	1	1	E	1	1	ı	ı	ł	1
CECW-61	-	1	-	-	-	ŀ	ı	1		ı	-	<2.4	<2.4	<2.4	<2.4	400	200
CECW-6	-	<2.4	2.0 J	<2.4	<2.4	1.6 J	1	1	1	1	1	1	1	ı	1	1	1
CECW-5	<0.2	<2.4	1.4 J	1	2.0 J	1.4 J	1.8 J	1.6 J	2.8	1.4 J	<2.4	<2.4	<2.4	19.4	<2.4	400	800
CECW-4	0.4	1.4 J	7.0.1	13.4	2.2 J	4.6	2.8	3.0	9.5	4.6	6.2	0.60 J	<2.4	<2.4	2.0 J	<200	200
CECW-3	<0.2	<2.4	1.8 J	0.80	0.80	1.6 J	1.6 J	1.4 )	<2.4	<2.4	<2.4	<2.4	2.6	<2.4	<2.4	200	<200
CECW-1 CECW-2 CECW-3	<0.2	2.6	3.6	0.80	0.80	3.4	5.8	5.8	4.8	<2.4	<2.4	3.6	1.2 J	19.2	1.41	800	009
	<0.2	<2.4	<2.4	<2.4	<2.4	1.6 J	0.60 J	09:0	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	800	<200
Units	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	ng/L	ng/L
Date	September-02	March-03	October-03	March-04	September-04	March-05	September-05	March-06	September-06	March-07	September-07	March-08	September-08	March-09	September-09	March-10	September-10 ug/L

Notes: < = Less than LOQ Bold = Detected above LOD

= Greater than GPS (which is the LOQ)

