

**S A G E**

ENVIRONMENTAL CONSULTING

# **CARBON CANISTER DESIGN DOCUMENTATION UNDER BENZENE WASTE OPERATIONS NESHAP**

NPRA Environmental Conference, September 2009

Paper Number: ENV-09-16

Authors: Larry G. Darcey, P.E. – Sage Environmental Consulting, LP  
Ruth A. Cade, P.E. – Marathon Petroleum Company, LLC  
Emily L. Leidy – Marathon Petroleum Company, LLC



# WHY IS THIS IMPORTANT?

## *Introduction*

The lack of design documentation for carbon adsorption systems used to control air emissions from BWON-affected waste management units (WMUs) is a routine finding during refinery Benzene Waste Operations NESHAP (BWON) audits. Regulated facilities often rely on empirical data to determine carbon usage and monitoring frequencies. EPA has attempted to improve the performance of carbon adsorption systems by developing specific protocols for breakthrough monitoring and carbon replacement in refinery Consent Decrees. However, Consent Decree provisions do not necessarily fulfill the underlying regulatory requirements. In fact, the breakthrough concentrations defined by Consent Decrees are not always as stringent as the breakthrough concentration that would be determined based on carbon canister loading and the regulatory control requirements.



**FIGURE 1** | *Examples of typical dual carbon canister systems with manifolds to facilitate carbon changeout*



# WHAT ARE THE REQUIREMENTS?

*Regulatory Overview, page 1 of 2*

## Control Requirements [§61.349(a)(2)(ii)]

- + Control VOC at 95 percent efficiency or greater, or
- + Control benzene at 98 percent efficiency or greater

## Ongoing Compliance Demonstration [§61.354(d)]

Three options are provided for evaluating performance of carbon adsorptions systems:

- + Monitor for breakthrough daily
- + Monitor for breakthrough at intervals no greater than 20 percent of the design carbon replacement interval
- + Replace carbon at a regular predetermined interval that is less than the carbon replacement interval determined by the maximum design flow rate to the carbon and the VOC or benzene concentration in the gas stream vented to the carbon

## Design Documentation [§61.356(f)(2)(i)(G)]

The BWON requires that the design analysis consider and establish the following vent stream and design parameters:

- + Vent stream composition
- + Constituent concentration
- + Flow rate
- + Relative humidity
- + Temperature
- + Design exhaust vent stream organic compound or benzene concentration level (breakthrough concentration)
- + Capacity of the carbon bed
- + Type and working capacity of activated carbon used for carbon bed
- + Design carbon replacement interval based on total carbon working capacity and operating schedule

## Initial Compliance Demonstration [§61.349(c)]

- + Stack test the carbon adsorption system (generally not practical)
- + Prepare engineering calculations and design documentation to demonstrate that control requirements are met

## Breakthrough Definition

- + By definition, "breakthrough" is either two percent of the inlet concentration of benzene or five percent of the inlet concentration of VOC
- + Consent decrees often set breakthrough concentrations and require dual canister systems; breakthrough for these systems is evaluated between the primary and secondary canister
- + Design exhaust concentrations may be less than breakthrough defined by consent decrees

# NO 2

## WHAT ARE THE REQUIREMENTS?

Regulatory Overview, page 2 of 2

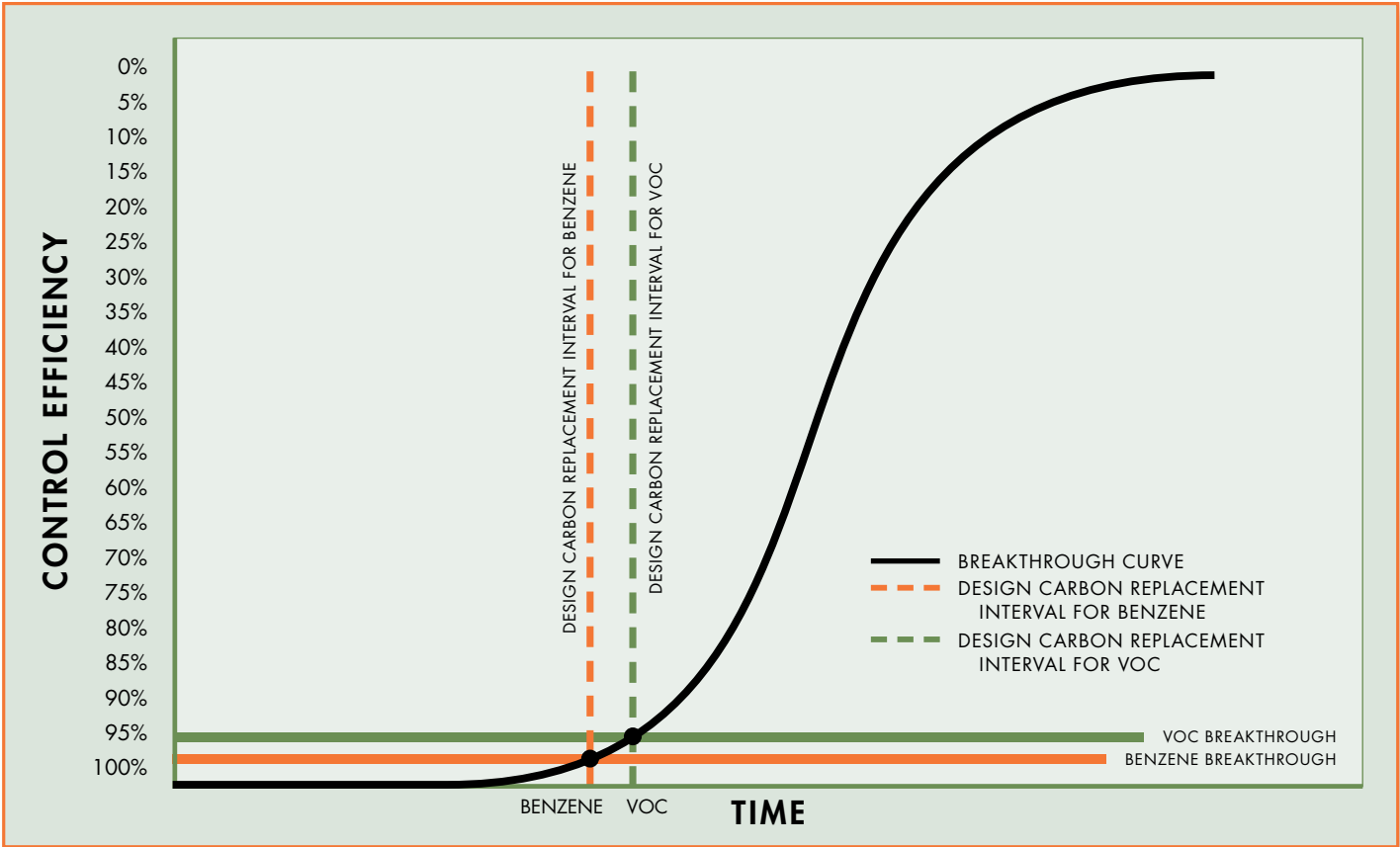


FIGURE 2

Representation of Breakthrough Curves for VOC and Benzene

# NO 3

## WHAT DID WE STUDY?

### *Design Documentation Methodology*

The carbon canister systems at a refinery were evaluated and robust design documentation were developed to meet BWON requirements. A combination of design bases were evaluated including empirical carbon breakthrough data, engineering basis for flow rates and vapor concentrations, and sampling of waste gas streams. This data was compared to determine and document appropriate carbon adsorption system design. As part of this analysis, break-through was evaluated for volatile organic compounds (VOCs) and benzene to determine the limiting pollutant. Further, competitive absorption for various VOCs and non-VOCs in the waste gas was considered in this analysis to ensure carbon usage was appropriately characterized for the spectrum of compounds present.

- + Estimate design flow rates to the carbon adsorption systems (measured flows and engineering calculations)
- + Gather representative vent stream composition data (vent stream sampling or Raoult's Law and liquid phase concentrations)
- + Determine design carbon consumption rates (carbon vendor software that considered competitive adsorption)
- + Calculate the design carbon replacement interval (DCRI) based on carbon consumption rates and flow rates to carbon adsorption systems
- + Compare design basis to historical breakthrough monitoring data



**FIGURE 3**

*Carbon canister monitoring using photo-ionizing device for VOC breakthrough*



**FIGURE 4**

*Summa canister sampling of vent stream to carbon*



## SUMMARY OF CARBON ADSORPTION SYSTEM DESIGN

*Documentation & Historical Breakthrough, page 1 of 2*

1. Data reflected represents breakthrough data gathered over a four and one-half year period.
2. The design carbon consumption was provided by the carbon vendor and was determined using a proprietary model. The model takes into consideration the total vent stream composition when determining carbon consumption. Speciated VOC concentration data for each vent gas stream was provided to carbon vendor. As a conservative basis, the design relative humidity was set at >70% and the design temperature was assumed to be 100°F in the model. The VOC with the highest carbon consumption is considered the “critical” VOC since the rate of consumption represented for that compound includes adsorption of the VOC listed with lower carbon consumption rates. See Figure 5 for an example of the model output.
3. Two canisters in series are operated at each carbon canister location and VOC breakthrough is monitored between the primary and secondary canister. However, as a design basis, only one carbon canister is considered for the design carbon replacement interval.
4. Design flow rate based on engineering calculations or actual measured flow at each location from stack testing or flow meters. As a conservative basis either a max flow rate was used or a safety factor was added to the flow as the design basis.
5. The operating schedule for all carbon installations was conservatively assumed to be year round or 8,760 hours per year.
6. The VOC inlet concentration is based on the sum of the concentrations for the VOC species identified in both the EPA TO-15 and ASTM-1946 test methods or Raoult’s Law calculations.
7. The design exhaust vent concentration is based on the control requirements for VOC and benzene reflected under the BWON, §61.349(a)(2)(ii). The rule specifies at 98% or 95% mass emission control for benzene or VOC, respectively.
8. The design carbon replacement interval is calculated as the carbon canister working capacity divided by the product of the design carbon consumption and the design flow rate to the carbon.



# SUMMARY OF CARBON ADSORPTION SYSTEM DESIGN

Documentation & Historical Breakthrough, page 2 of 2

**TABLE 1 — Summary of Carbon Adsorption System Design**

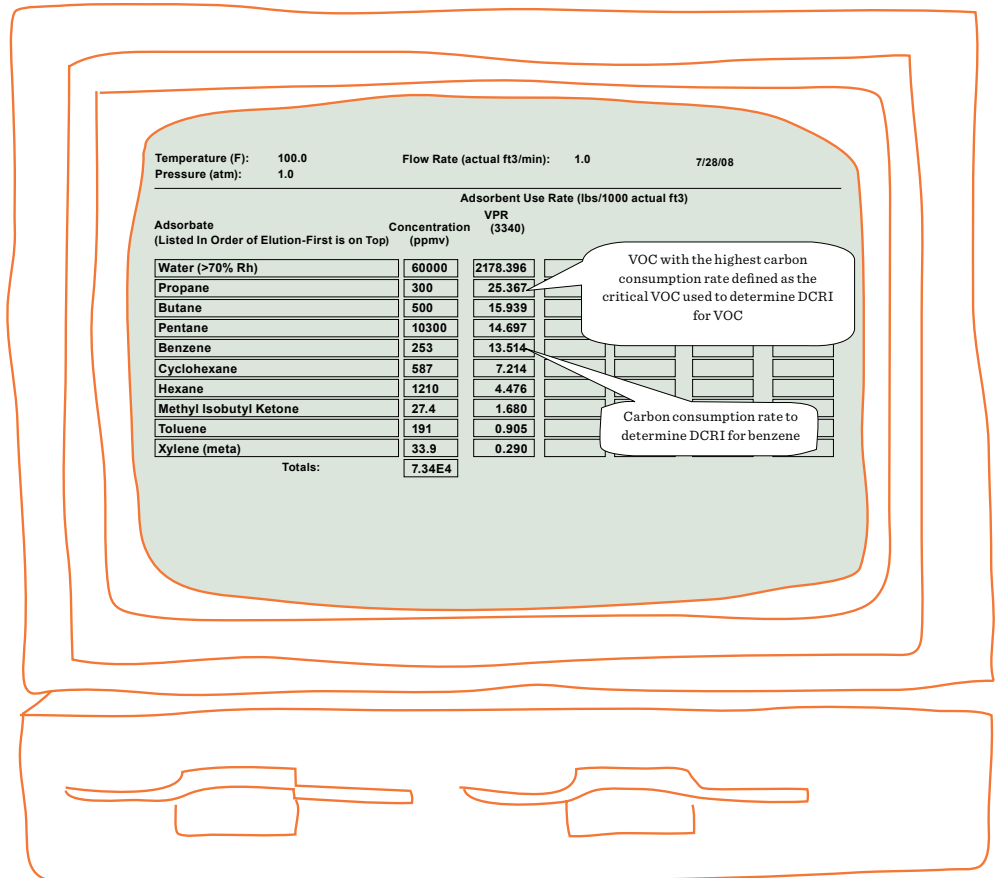
CARBON CANISTER SYSTEM NUMBER	No. OF BREAK-THROUGH EVENTS [1]	AVERAGE DAYS BETWEEN BREAK-THROUGH EVENTS (days) [1]	DESIGN CARBON CONSUMPTION (lb/1000ft <sup>2</sup> ) [2]	CARBON CANISTER WORKING CAPACITY (lbs)	DESIGN FLOW (cfm) [4]	OPERATING SCHEDULE (hrs/yr) [5]	BENZENE INLET CONC. (ppmv) [6]	VOC INLET CONC. (ppmv) [6]	DESIGN EXHAUST VENT STREAM CONCENTRATION (ppmv) [7]		DESIGN CARBON REPLACEMENT INTERVAL (days) [8]	
									BENZENE	VOC	BENZENE	VOC
1	15	21.0	2.05	1,000	15.22	8,760	0.19	4.17	0.004	0.209	22	3
2	19	17.7	107.31	1,000	1.67	8,760	1,840	150,980	36.8	7,549	3	2
3	111	10.3	13.51	180	0.68	8,760	253	13,402	5.06	670	13	7
4	422	2.9	8.65	1,000	1.93	8,760	63	51,196	1.26	2,560	41	5
5	133	8.8	15.90	180	0.80	8,760	723	24,793	14.5	1,240	9	4
6	126	8.9	3.43	180	0.80	8,760	227	5,051	4.54	253	45	8
7	4	118.0	1.85	180	0.19	8,760	5.11	248	0.102	12.4	352	78
8	6	131.7	2.18	180	0.23	8,760	31	4,912	0.626	246	245	50
9	109	6.3	40.46	180	0.30	8,760	24,500	57,380	490	2,869	10	4
10	5	155.6	8.17	1,000	0.002	8,760	744	6,778	14.9	339	36,180	29,632
11	17	21.5	4.93	1,000	2.05	8,760	60	8,832	1.20	442	68	7
12	8	146.3	6.52	180	0.001	8,760	831	19,742	16.6	987	19,130	3,792
13	4	150.5	25.91	180	0.001	8,760	636	30,682	12.7	1,534	4,817	3,511
14	36	15.9	2.96	1,000	21.49	8,760	130	1,181	2.60	59.0	10	10
15	41	17.0	2.12	180	5.01	8,760	9.2	52	0.184	2.60	11	6
16	95	9.6	9.62	1,000	6.25	8,760	170	12,385	3.40	619	11	4

# NO 5

## WHAT ARE THE LESSONS LEARNED?

### Conclusions

- + VOC was generally determined to be the limiting pollutant for carbon breakthrough, which may indicate that monitoring for benzene breakthrough concentration could reduce carbon change-out frequency. Carbon adsorption is weaker for lighter VOC compounds such as propane.
- + Design analysis is only representative of the configuration and operating conditions at the time of the design analysis and carbon performance can be greatly affected by variations in the characteristics of the inlet waste gas.
- + It is critical that there be a routine review of each carbon system’s design basis relative to historical performance to ensure that monitoring frequency is effectively identifying breakthrough in a timely manner.
- + Management of change should also consider impacts on carbon performance.
- + See Table 1 for details on the results of the design analysis.



**FIGURE 5** | Example model output used to predict carbon usage



# REFERENCES

Adsorption Design Guide (DG 1110-1-2), Department of Defense, United States Army Corps of Engineers, Page 1-1, October 2001.

T. Reynolds and P. Richards, Unit Operation and Processes in Environmental Engineering, pg 350-364, PWS, 1996.