Review of Technical Basis for H2S in Boiler MACT Fuel Specification

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CH2M HILL performed a document search of the U.S. Environmental Protection Agency (EPA) docket for the "Boiler Maximum Achievable Control Technology (MACT)" rule promulgated March 21, 2011, for documents pertaining to the technical basis for the hydrogen sulfide (H_2S) fuel gas specification level established for allowing "other process gases" (Gas 2) to be treated as Gas 1. After reviewing relevant documents and documents referenced within them, CH2M HILL has concluded the following:

1. EPA has not established a valid rationale for the specific H_2S concentration of 4 parts per million by volume (ppmv) in the fuel specification. The specified concentration is based on natural gas sweetening for corrosion protection. However, boiler units generally do not require this level of protection. Fuel gases, including refinery gases, that have much higher H_2S levels, commonly are used in boilers without treatment to the fuel specification standard.
2. EPA has not established a valid rationale for using H_2S, at any concentration, as a fuel specification parameter to meet the MACT requirements. MACT regulates hazardous air pollutant (HAP) emissions. H_2S is not a HAP, nor has EPA established (or even suggested in its rationale of the fuel specification) any correlation of H_2S in fuel with any HAP or HAP surrogate emissions.

Rationale for the Fuel Specification

In the National Emission Standards for Hazardous Air Pollutants (NESHAPS) for Major Sources: Industrial, Commercial, and Institutional Boilers and Process Heaters, Final Rule, under 40 *Code of Federal Regulations* (CFR) Part 63 Subpart DDDDD, promulgated on March 21, 2011, commonly known as the Boiler MACT rule, EPA provided a mechanism for boilers using "other process gases" (Gas 2) to meet the same standards as boilers using certain traditional gaseous fuels (Gas 1). The Gas 1 standards require only that a "work practice standard" of good operation and maintenance practices be implemented, with no emissions limits or monitoring requirements. The mechanism is that owners of boilers using Gas 2 fuels must demonstrate that the Gas 2 fuels they are using meet a fuel specification standard for H_2S and mercury concentrations. The rationale given for this mechanism is stated in the preamble to the Boiler MACT rule (*Federal Register*, 2011):

> *EPA has determined that to the extent that process gases are comparable to natural gas and refinery gas, combustion of those gases in boilers and process heaters should be subject to the same standards as combustion of natural gas and refinery gas. Boilers that combust other gaseous fuels that have comparable emissions levels to Gas 1units are similar in class and type to Gas 1 units because they share common design, operation, and emissions characteristics. Therefore, we are providing a mechanism by which units that combust gaseous fuels other than natural gas and refinery gas can demonstrate that they are similar to Gas 1 units and will therefore be subject to the standards for Gas 1 units. EPA originally examined the possibility of basing such a demonstration on levels of mercury and chlorine content in the gases, but no information was available regarding the chlorine content of natural gas or refinery gas, and no proven test methods were identified to quantify chlorine content of natural gas. Therefore, EPA is requiring a demonstration that other gases have levels of H2S and Hg that are no higher than those found*

> *in Gas 1 units. Natural gas purity is commonly defined considering the sulfur content of the gas, in the form of H2S. Sweet natural gas, which is considered pipeline quality gas, contains no more than 4 ppmv H2S. Information on Hg levels typical of natural gas was available through literature, and domestic natural gas Hg concentrations range up to about 40 micrograms per cubic meter. Using H2S and Hg concentration as parameters for establishing equivalent contamination levels to natural gas, EPA is providing a fuel specification that can be used by facilities to qualify Gas 2 units for the Gas 1 standards. The fuel specification would also allow facilities to perform pre-combustion gas cleanup in order to qualify Gas 2 units for the Gas 1 standards. Boilers using process gases that do not meet the fuel specification and are not processed to meet the contaminant levels must meet the emissions limits for Gas 2 units.*

CH2M HILL reviewed the online docket for the Boiler MACT (Docket# OAR-2002-0058) in search of documents providing a technical basis for the selection of H_2S as a fuel specification parameter for this purpose, and for the specific concentration of H_2S cited in the rule preamble. Our review included a review of document titles and a detailed review of responses to comments contained in a two-volume summary of public comments on the rule and responses by EPA (2011). The only description of the fuel specification rationale was presented in a memorandum by Amanda Singleton and Bryan Lange of the Eastern Research Group (ERG) (ERG memo, 2011). That document contained several references pertaining to the H_2S specification standard, which were retrieved and reviewed, as described in the following text. No technical basis was presented in any of the responses to comments.

Review of the Rationale for the Specific Hydrogen Sulfide Concentration

The ERG memo (2011) examined levels of mercury, chlorine compounds, and H_2S found in Gas 1 fuels and established proposed Gas 2 fuel specification levels for mercury and H_2S that would demonstrate equivalency to Gas 1. It concluded that a fuel specification standard for chlorine was not appropriate. The mercury fuel specification "was established to the level equivalent to the *maximum concentration* of mercury identified in natural gas…" as representing "the typical Hg concentrations that would be expected to have been present in the natural gas *and refinery gas* fuels that were combusted during the emission tests that showed levels below the level that can be accurately measured" (emphasis added). Thus, for mercury, the fuel specification was correlated to the emissions of Hg, which is a HAP, establishing a maximum below which it had been demonstrated that no measurable emissions would result from combustion. Note that, for the mercury specification, specific reference is made to refinery gas, which is a Gas 1 fuel, natural gas being the only other Gas 1 fuel.

For H_2S, the ERG memo (2011) established 4 ppmv as the fuel specification. The rationale for this level is contained in the following two sentences: "H2S is both highly toxic and acidic enough to precipitate corrosion. Gas is required to be sweetened to contain no more than a quarter grain H2S per 100 standard cubic feet (4 parts per million)." The only support for the 4-ppm level is a reference to a Dow Chemical brochure (1998) referenced in the ERG memo. The Dow Chemical brochure introduction states that, "Because of the corrosiveness of H2S and C02 in the presence of water and because of the toxicity of H2S and the lack of heating value of C02, sales gas is required to be sweetened to contain no more than a quarter grain H2S per 100 standard cubic feet (4 parts per million) and to have a heating value of no less than 920 to 980 Btu/SCF, depending on the contract."

The remainder of the brochure (Dow, 1998) describes various treatment processes and operational technicalities. There is no further documentation of the basis for the specific concentration of 4-ppm H_2S. The Dow brochure only addresses natural gas sweetening. The rationale for the H_2S concentration ignores the presence and higher concentrations of H_2S in the other Gas 1, refinery gas.

The only other supporting documents cited for the H_2S standard in the ERG memo (2011) were two descriptions of commonly used and emerging technologies for sulfide removal, but these did not address the rationale for achieving the specific concentration of H_2S in the fuel specification.

The corrosion protection requirement referenced in the Dow brochure is not specific to use in boilers, and in fact it is known that many industrial boilers use refinery gas with much higher concentrations of H_2S. A Delucchi (2003) study established a range of 100 to 200 ppmv as the likely range of H_2S found in refinery gas burned as fuel. Under 40 CFR 60 Subpart Ja, refinery gases containing up to 162 ppmv may be burned as fuel. A study of treatment requirements for using landfill gas mixed with refinery gas (Edgar, 2008) concluded that treatment for sulfur removal

at typical landfill gas concentrations of 25 ppm would not be necessary. Thus, the argument in the Boiler MACT preamble that, "Boilers that combust other gaseous fuels that have comparable emissions levels to Gas 1units are similar in class and type to Gas 1 units because they share common design, operation, and emissions characteristics," supports a higher H_2S concentration because boilers fueled by refinery gas, which is a Gas 1, are designed to operate with higher levels of H_2S than the 4-ppmv fuel specification.

Review of the Rationale for Hydrogen Sulfide as a Fuel Specification Parameter

The MACT standards are promulgated to control emissions of specific chemical substances and other parameters established as HAPs. HAPs regulated by the MACT standards consist of a specific list of chemical compounds and other parameters, listed at http://www.epa.gov/ttnatw01/187polls.html. The Boiler MACT is intended to regulate a list of only six parameters:

- Mercury
- Dioxins/furans
- Particulate matter (PM) (as a surrogate for non-mercury metals)
- Hydrochloric acid (HCl) (as a surrogate for acid gases)
- Carbon monoxide (CO) (as a surrogate for non-dioxin organic air toxics)

The acid gases referenced in this list, for which HCl is established as the surrogate, are the specific acid gases that are HAPs, such as chlorine, hydrogen fluoride, and hydrogen cyanide. They do not include sulfuric acid that might form if sulfur dioxide (SO_2) reacts with water in boiler flues, which can be controlled by maintaining a high enough temperature to inhibit this reaction before SO_2 is discharged to the air.

In contrast to the rationale for the mercury concentration in the fuel specification, the rationale for the H_2S concentration does not address any connection between H_2S concentrations and any of the Boiler MACT parameters, or indeed, any HAP concentrations. Thus, there is no basis for a fuel gas H2S concentration to be specified in the Boiler MACT.

References

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Eastern Research Group (ERG). 2011. "Gas Specification for Industrial, Commercial, Institutional Boilers and Process Heaters National Emission Standards for Hazardous Air Pollutants – Major Source." Memorandum to Brian Schrager/EPA from Amanda Singleton and Bryan Lange/ERG. January.

Edgar, Thomas F. 2008. *Evaluation of Environmental Emissions for Combustion of Landfill Gas in a Texas Petrochemical Plant*. University of Texas–Austin.

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U.S. Environmental Protection Agency (EPA). 2011. Accessed September 30. http://www.epa.gov/ttnatw01/187polls.html.