TCEQ REGULATORY GUIDANCE
Air Permits Division
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Emissions Representations for Produced Water

Introduction

This guidance has been developed to establish the procedures for evaluation of emissions from produced water sources at oil and gas producing facilities and sites. This document contains a summary of calculation guidance followed by a detailed explanation of our current evaluation methods, which have been established based on the characteristics of produced water.

For produced water, the oil or condensate liquid floats on top of the water phase and forms a film between the water and the tank vapor space. Therefore, the water in the produced water tank is not expected to contribute to the partial pressure of the tank vapor space and, when estimating working and breathing losses, it should be assumed that the tank contents are 100% oil or condensate liquid. Calculated flashing emissions should be combined with working and breathing emissions to accurately represent produced water storage tank emissions.

The Texas Commission on Environmental Quality (TCEQ) does recognize that applicants may attain their own speciated sample from the tank, which may reduce the volatile organic compound (VOC) content entrained in the water. Therefore, applicants are encouraged to represent a VOC content of 1% or greater. These results should account for the three known types of emissions associated with produced water from storage tanks.

Section I: TCEQ Approved Methods for Calculation of Produced Water Emissions

Due to the large variation in crude and condensate properties from site to site throughout Texas, TCEQ requires that site-specific or representative samples be taken along with estimates of working, breathing, and flashing emissions for permitting purposes. The Air Permits Division recognizes the methods listed in Tables 1 through 3 below to estimate emissions. Each method for estimating emissions has specific constraints. Regardless of which method is used, all supporting data used to calculate the emissions—including identification of the calculation method, description of sampling methods, and copies of lab sampling analysis—must be provided with the emissions estimate. The accuracy of the methods shown below is dependent upon the quality of the inputs, calculations, and assumptions made in conjunction with the emissions estimate.

Table 1: Produced Water Emissions Estimation Methods for WBF

No.	Method	Emissions Calculated	Comments
1	Direct measurement of tank emissions	Working, Breathing, Flashing	Various methods for the direct measurement of tank emissions exist. Direct measurements of tank emissions are expensive, but the results are relatively accurate.
2	E&P Tanks software, V 3.0, using an option that requires site-specific sampling. Geographical Database, and AP-42, options may not be used.	Working, Breathing, Flashing	A pressurized liquid or gas sample analysis from a separator will be needed. Applicants are encouraged to represent 100% volatile organic compound (VOC) content, but may represent 1% or greater VOC content, for the produced water based on the expected VOC content of the produced water.
3	Process simulator computer programs	Working, Breathing, Flashing	There are several different process simulators (e.g., WinSim Design II, EPCON, HYSIM, HYSYS, VMG, ProMax, etc.). If accurate assumptions and methodologies are used, the software is accurate when based on a site-specific, or a representative, sample and analysis.

Table 2: Produced Water Emissions Estimation Methods for Flash

No.	Method	Emissions Calculated	Comments
1	Laboratory measurement of the gas-water-ratio (GWR) from a pressurized liquid sample	Flash	This is a direct laboratory analysis of the flash gas emitted from a pressurized produced water sample. The pressurized sample should be taken prior to separation in order to accurately measure the flash emissions. Flash emissions should be combined with 100% of the WB emissions in conjunction with estimating the total produced water emissions.

Table 3: Produced Water Emissions Estimation Method for WB

No.	Method	Emissions Calculated	Comments
1	AP-42 Chapter 7.1	Working and Breathing	EPA tank emission calculation method. It should be assumed that the tank contains 100% VOCs. This WB emissions calculation method should be combined with a method capable of calculating flash emissions as the total produced water emissions consist of the WBF emissions.

TCEQ always prefers that the most accurate emission estimates be submitted and based on site-specific, representative, worst-case data when possible. No matter which method is used to calculate produced water emissions, verification of the inputs and calculation methods are required. Please provide the calculation method used and any critical parameters in the project submission so they are available to program personnel. The emission calculations should be determined from site-specific sampling or analysis. Alternatively, a representative analysis may be used to determine the emissions following the representative analysis guidance in the representative analysis criteria.

Section II: Background

Produced water is any water trapped in underground formations that is brought to the surface along with oil and gas. However, a well which has been deemed absent of crude oil or condensate (also known as dry) does not necessarily imply that no hydrocarbons are entrained in the produced water. Produced water is by far the largest volume byproduct or waste stream associated with oil and gas production.

In subsurface formations, the void space of naturally occurring porous rocks contain fluids such as water, oil, or gas (or some combination of these fluids). The oil and gas migrate to trap locations in the formation, displacing some of the water and forming hydrocarbon reservoirs. Thus, reservoir rocks normally contain both petroleum hydrocarbons (liquid and gas) and water.

Sources of this water may include flow from above or below the hydrocarbon zone, flow from within the hydrocarbon zone, or flow from injected fluids and additives resulting from production activities. This water is frequently referred to as "connate water" or "formation water" and becomes produced water when the reservoir is tapped, and these fluids are brought to the surface. Materials produced by a well generally include a mixture of liquid or gaseous hydrocarbons, produced water, dissolved or suspended solids, solids such as sand or silt, and injected fluids and additives that may be present in the formation as a result of exploration and production activities such as hydraulic fracturing.

As produced water is brought to the surface, it is separated from the crude oil and natural gas during the production and separation processes. The composition of the produced water is dependent on whether crude oil or natural gas is being produced and generally contains a mixture of aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene, in addition to other VOCs. When the produced water flows from the separator into the storage tank, most of the hydrocarbons will either float to the surface of the liquid in the tank, be released or "flashed" off from the liquid, or remain partially dissolved in the water.

The physical and chemical properties of produced water vary considerably depending on the geographic location of the field, the geological formation from which the produced water was produced, and the type of hydrocarbon product being produced. The produced water properties and production rate can vary throughout the life of a well. If waterflooding operations are conducted, the produced water properties and production rate may vary even more dramatically as additional water is injected into the formation.

Knowledge of the constituents of specific produced waters is needed for regulatory compliance. Oil and grease are the primary constituents of interest for produced water. Additionally, salt content (expressed as salinity, conductivity, or TDS) is a primary concern for onshore operations. Produced water contains many organic and inorganic compounds, which can be in a variety of physical states including solution, suspension, emulsion, adsorbed particles, and particulates (Tibbetts et al. 1992).

In addition to its natural components, produced waters from oil and gas production may also contain groundwater or seawater which was injected into the well to maintain reservoir pressure, as well as miscellaneous solids and bacteria. Most produced waters are more saline than seawater (Cline 1998). They may also include chemical additives used in drilling and producing operations and in the oil and water separation process. In produced water, these chemicals can affect the oil and water partition coefficient, toxicity, bioavailability, and biodegradability (Brendehaug et al. 1992).

In addition to the water in the formation and injected water, produced water from gas operations also includes condensed water. Studies indicate that the produced waters discharged from gas or condensate platforms are about 10 times more toxic than the produced waters discharged from oil platforms (Jacobs et al. 1992). The chemicals used for gas processing typically include dehydration chemicals, hydrogen sulfide-removal chemicals, and chemicals to inhibit hydrates. Well-stimulation chemicals that may be found in produced water from gas operations can include mineral acids, dense brines, and additives (Stephenson 1992). Volatile hydrocarbons can occur naturally in produced water. Concentrations of these compounds are usually higher in produced water from gas-condensate-producing platforms than in produced water from oil-producing platforms (Utvik 2003).

For more information concerning the components of produced water, please reference the Argonne National Laboratory paper "Produced Water Volumes and Management Practices in the United States" (Clark & Veil, 2009), which describes produced water from the production of crude oil, natural gas, and coal bed methane.

Section III: Emissions Discussion

To account for emissions from produced water, an overview of the insoluble relationship between oil-condensate and water taking place within the tank must be addressed. Within the tank, two liquid phases exist. As the produced water enters the tank it settles, and the crude oil or condensate separates from the water and rises to the surface. Additionally, if a pressure drop in the tank occurs, lighter compounds dissolved in the liquid are released or "flashed" off from the liquid. The total emissions are accounted for as emissions from working, breathing and flashing. With the frequent unloading operations of produced water storage tanks at oil and gas sites, there is a short time in which settling occurs. Therefore, working emissions are typically much higher than breathing emissions.

All tanks receiving processed liquids (crude oil, condensate, and produced water) will have flash emissions if a pressure drop in the tank occurs. These emissions will consist primarily of hydrocarbons and, potentially, inorganic compounds such as hydrogen sulfide (H_2S). As these gases are released, some of the heavier hydrocarbon compounds in the liquid may become entrained in these gases and emitted. The magnitude of the flash gases will increase with respect to the magnitude of the pressure drop, and the mole fraction of lighter hydrocarbons in the liquid.

Finally, the temperature change of the liquid will affect the amount of flashing losses since the solubility of a gas in a solution is related to temperature. If the final temperature is lowered, the final solution can hold more gas, which will result in slightly lower flashing losses. Consequently, the estimation of flashing losses becomes a complex process when considering all properties of the solution.

Citations

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