

Emissions Representations for Produced Water

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. Below is a summary of calculation guidance followed by a detailed explanation of our current evaluation methods. This guidance has been established based on the characteristics of produced water which is included below.

Since the oil or condensate liquid floats on top of the water phase, it is the VOCs that are contributing to the partial pressure of the tank. Therefore, when estimating working and breathing losses, the tank should be assumed to have 100% VOC content. Additionally, it should be assumed that flash emissions will now contribute to that same partial pressure within the tank. Therefore, the calculated flash VOC emissions should then be combined with working and breathing results to represent an accurate VOC content within the tank. The agency does recognize that applicants may attain their own speciated sample from the tank which may reduce the VOC content entrained in the water. Therefore, at this time 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.

TCEQ Approved Methods for Calculation of Produced Water Emissions

Due to the large variation of crude and condensate properties throughout Texas, and from site to site, the commission is requiring that site-specific measurements are taken to estimate working, breathing, and flash (WBF) emissions for permitting purposes. To date, the Environmental Protection Agency's (EPA) published guidance on WBF gas emission determination is that the direct measurement technique provides the most accurate results, but the EPA has not standardized published reference test methods available at this time. The Air Permits Division of the Texas Commission on Environmental Quality (TCEQ) recognizes the following methods to estimate emissions and has listed them below in Table 1, Table 2, and Table 3. 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 relative accuracy of the methods shown below is a preliminary opinion only. As these methods improve, so too will our opinion of their relative accuracy.

Table 1: Produced Water Emissions Estimation Methods for WBF

No.	Method	Emissions Calculated	Comments
1	Direct measurement of tank emissions	Working, Breathing, Flash	Sampling and analysis are expensive, but the results are relatively accurate.
2	E&P Tanks Software, V 2.0, using an option that requires site-specific sampling. Geographical Data base option N/A.	Working, Breathing, Flash	A pressurized liquid and/or gas sample analysis from a separator will be needed. Applicants are encouraged to represent 100% VOC content but may represent 1% or greater VOC content as for produced water emissions.

Table 2: Produced Water Emissions Estimation Methods for Flash

No.	Method	Emissions Calculated	Comments
1	Process Simulator computer programs	Flash	There are several different process simulators (e.g. WinSim, Designer II, EPCON, HYSIM, HYSIS, VMG, and PROMAX, etc.). The software is accurate when based on a site-specific sample and analysis. Flash emissions should be combined with 100% of working and breathing (WB) emissions from Tanks 4.0 before submitted as representative of produced water emissions for simulators not capable of calculating emissions from WB. However, applicants may still represent 1% of greater VOC content within the produced water.
2	AQUALibrium	Flash	AQUALibrium was developed for calculating the fluid phase equilibria in systems composed of natural gas (sweet and sour, sour meaning they contain hydrogen sulfide) and acid gases (hydrogen sulfide and carbon dioxide) in the presence of water. Flash emissions should be combined with 100% of WB emissions from Tanks 4.0 before submitted as representative of produced water emissions. However, applicants may still represent 1% or greater VOC content within the produced water.

Table 2: Produced Water Emissions Estimation Methods for Flash (continued)

No.	Method	Emissions Calculated	Comments
3	Laboratory measurement of the Gas-Water-Ratio (GWR) from a Pressurized Liquid Sample	Flash	This is direct laboratory analysis of the flash gas emitted from a pressurized oil/condensate sample. Flash emissions should be combined with 100% of WB emissions from Tanks 4.0 before submitted as representative of produced water emissions. However, applicants may still represent 1% or greater VOC content within the produced water.
4	Vasquez-Beggs Equation (VBE)	Flash	A calculation method based on empirical data. The VBE variables must be supported with a lab sampling analysis that verifies the API gravity, separator gas gravity, stock tank gas molecular weight, and VOC fraction. If an operating variable used in the VBE calculations falls outside of the parameter limits, the applicant must use another method to calculate flash emissions. Flash emissions should be combined with 100% of WB emissions from Tanks 4.0 before submitted as representative of produced water emissions. However, applicants may still represent 1% or greater VOC content within the produced water.

Table 3: Produced Water Emissions Estimation Method for WB

No.	Method	Emissions Calculated	Comments
1	Tanks 4.0	Working and Breathing	Relatively accurate program used to determine working and breathing emissions within tanks. The program should be run assuming 100% of the inputs are VOCs then combined with a method capable of calculating flash emissions before submitted as representative of produced water emissions.

The TCEQ always prefers that the most accurate emission estimates be submitted, based on site-specific, representative, worst-case data when possible. Therefore, we would prefer that the Vasquez-Beggs method is not used. However, if the applicant can justify a method capable of representing a more accurate estimation of emissions this may be acceptable upon approval from the TCEQ. This is to account for and encourage the use of more current methodology that may become available. If the applicant should choose to use the Vasquez-Beggs Equation, they should be aware of the risk of potentially underestimating emissions at a site. Remember, no matter which method is used to calculate produced water emissions, verification of the inputs and calculation methods are required. State the calculation method used and any critical parameters in the project description so they are available to program personnel. If at an existing production site, the emission calculations should be determined from site-specific sampling or analysis. If a site is not yet in operation, a representative analysis may be used to determine the emissions following the representative analysis guidance in the Representative Analysis Protocol.

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 hydrocarbons are not still 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, naturally occurring rocks are generally permeated with fluids such as water, oil, or gas (or some combination of these fluids). These less dense hydrocarbons migrate to trap locations, displacing some of the water from the formation and become 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. The composition generally includes a mixture of either liquid or gaseous hydrocarbons, produced water, dissolved or suspended solids, produced solids such as sand or silt, and injected fluids and additives that may have been placed 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 process. The composition of this produced fluid 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 (BTEX), in addition to other volatile organic compounds. When the produced water flows from the separator into the storage tank, most of the hydrocarbons will either float to the top of the tank or partially dissolve in the water.

The physical and chemical properties of produced water vary considerably depending on the geographic location of the field, the geological formation with which the produced water has been in contact for thousands of years, and the type of hydrocarbon product being produced. Produced water properties and volume can even vary throughout the lifetime of a reservoir. If water flooding operations are conducted, these properties and volumes may vary even more dramatically as additional water is injected into the formation.

Components of Produced Water from Oil and Gas Production

Knowledge of the constituents of specific produced waters is needed for regulatory compliance. Oil and grease are the constituents of produced water that receive the most attention in both onshore and offshore operations, while salt content (expressed as salinity, conductivity, or TDS) is a primary constituent of concern in onshore operations. In addition, 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 production may also contain groundwater or seawater (generally called “source” water) injected 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/water separation process. In produced water, these chemicals can affect the oil/water partition coefficient, toxicity, bioavailability, and biodegradability (Brendehaug et al. 1992).

In addition to formation water, produced water from gas operations also includes condensed water. Studies indicate that the produced waters discharged from gas/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 “White Paper,” prepared by Argonne National Laboratory, which describes produced water from the production of crude oil, natural gas, and coal bed methane.

Tibbetts, P.J.C., I.T. Buchanan, L.J. Gawel, and R. Large, 1992, “A Comprehensive Determination of Produced Water Composition,” in Produced Water, J.P. Ray and F.R. Englehart (eds.), Plenum Press, New York.

Cline, J.T., 1998, “Treatment and Discharge of Produced Water for Deep Offshore Disposal,” presented at the API Produced Water Management Technical Forum and Exhibition, Lafayette, LA, Nov. 17-18.

Brendehaug, J., S. Johnsen, K.H. Bryne, A.L. Gjose, and T.H. Eide, 1992, “Toxicity Testing and Chemical Characterization of Produced Water – A Preliminary Study,” in Produced Water, J.P. Ray and F.R. Englehart (eds.), Plenum Press, New York.

Jacobs, R.P.W.M., R.O.H. Grant, J. Kwant, J.M. Marqueine, and E. Mentzer, 1992, “The Composition of Produced Water from Shell Operated Oil and Gas Production in the North Sea,” Produced Water, J.P. Ray and F.R. Englehart (eds.), Plenum Press, New York.

Stephenson, M.T., 1992, “A Survey of Produced Water Studies,” in Produced Water, J.P. Ray and F.R. Englehart (eds.), Plenum Press, New York.

Utvik, T.I., 2003 “Composition and Characteristics of Produced Water in the North Sea,” Produced Water Workshop, Aberdeen, Scotland, March 26-27.

Evaluating Sources of Produced Water

In order 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 phases exist. The first, as the produced water enters the tank it starts out as a flowing mixture. The second, as this mixture begins to settle it separates out with the crude oil or condensate rising to the top layer. This relationship can be visualized below. During these two-phase shifts, emissions are being produced. The emissions are accounted for as emissions from working, breathing, and flash (WBF). With the frequent unloading operations of these tanks at oil and gas sites, there is a short time for settling to occur. Therefore, working emissions are typically much higher than breathing emissions. Until very recently emissions estimates for most oil and gas site tanks were represented as only working and breathing losses. However, flash emissions are now a widely accepted source of emissions.

Representation:

All tanks receiving processed liquids (crude oil, condensate, and water) will have flash emissions if the pressure to the tank drops. These emissions will consist of both hydrocarbons and H₂S. During this decrease in pressure upon the liquid, the lighter hydrocarbon compounds dissolved in the liquid are released or “flashed” off from the liquid. Additionally, some of the compounds that are liquids at the initial pressure and temperature of the tanks will transform from a liquid into a gas/vapor, and contribute to the vapor pressure within the tank as emissions from working and breathing. 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 as the magnitude of the temperature and pressure drop increases, and as the amount of lighter hydrocarbons found in the liquid increases. Furthermore, the temperature of the liquid and the storage tank will influence the amount of WBF losses since the ability of a solution to dissolve or hold a gas is related to temperature. If the final temperature is lowered, the final solution can hold more gas, which will result in slightly lower WBF gas emissions. Consequently, the estimation of WBF gas losses becomes a complex process when considering all measured and theoretical properties of the fluids.

Now that we know what is going on inside the tank the relationship between oil and water and how this affects sampling of produced water must be addressed. According to Dalton's Law the total pressure of a mixture of ideal gases is the sum of the partial pressures of each gas component. Ideal gas behavior can be assumed for real gases at moderate pressures. For example, when obtaining a sample of produced water in order to determine flash emissions, the pressure inside the sample container should be equal to the separator pressure. Because of Dalton's Law of partial pressure, we know that the pressure in the sample contains the sum of all hydrocarbons. You can now determine the hydrocarbon component within the sample container accurately once the vapor pressure of the water you collected is separated out. Vapor pressure of water is published in most chemistry books. What remains when the vapor pressure of water is subtracted are the total hydrocarbons which are anticipated to be emitted or “flashed” to atmosphere. The result should be a true representation of emissions from produced water tanks.