Calculating Produced Water Emissions Best Practices

Abstract

Measuring, calculating, and understanding emissions from water tanks is accomplished in various ways, but is increasingly consolidating into an industry standard. This work is meant to build from previous studies, share industry experience, and detail the procedure that most accurately represents emissions from water tanks and satisfies regulatory requirements. This includes addressing the "1% rule" and the various interpretations of its implementation. The Sample + Model approach detailed here leverages the strengths of laboratory analysis with the power of thermodynamic modeling to contribute a well-informed emission calculation to industry, regulators, and the community.

Submitted to GPA 2024 by:

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1.0 INTRODUCTION

As emissions reporting standards become increasingly stringent, best practices should be developed to provide reasonable calculations of produced water tank emissions. Current interpretations of the 1% rule, a rule of thumb used to account for entrainment of hydrocarbons in produced water, lead to wide ranging results [1]. While regulatory agencies generally accept many of these results, they are expected to soon require more rigorous, scientifically based calculations to satisfy their standards.

The previous work "Are Produced Water Emission Factors Accurate?" by K. Ross provided a detailed evaluation of how to calculate produced water tank emissions based on four definitions of the 1% rule that were discovered to be in use [1]. This effort builds on the work Ross completed and seeks to define best practices for calculating emissions from produced water tanks using the most accurate and reasonable interpretation of the 1% rule. This work uses ProMax® for all process simulation modeling [2].

2.0 SAMPLES AND PROCESS MODELING

The quality of information input to process simulation software directly correlates to the quality of information output by the software. To ensure the output data is reasonable from a process simulator, several guidelines should be followed. The goal of any sampling activity is to collect a representative aliquot of the product in the vessel for analysis. Sample collection imperfections, coupled with analytical error and process measurement and calculation anomalies can lead to compositional variability that contributes to high uncertainty in flash gas determinations. In particular, when sampling pressurized natural gas and liquid from a separator vessel it is extremely important that samples are collected in phase equilibrium with each other (Figure 2). Sub-saturated samples mean flashing emissions will be underestimated and 2-phase samples mean flashing emissions will be over-estimated. While the process of sample collection might seem simple and straightforward, when best practices are not followed errors in the process can cause a sample to appear out-of-phase with the vessel conditions, even if the vessel is at equilibrium. For natural gas, this means limiting atmospheric contamination in the sample and ensuring a sample probe is available to avoid heavy-end hydrocarbon contamination. For pressurized hydrocarbon liquid products this means being aware of sample collection initiation time, sample collection rates, sample cylinder type, sample collection location, equipment cycling frequencies, and the application of appropriate analytical methods.

Following industry best practices, GPA 2166 and GPA 2174 should be used for the collections of natural gas and pressurized hydrocarbon liquids respectively. Subsequently, the analysis of natural gas should be done according to GPA 2261 or GPA 2286 (depending on the level of speciation desired). For pressurized hydrocarbon liquids with a C6+ fraction greater than 20% GPA 2103 should be the compositional method used.

2.1 SAMPLE QUALITY VERIFICATION

The first and possibly most important guideline to follow is to perform a quality check of all samples. If the samples are inaccurate, it is not worth the effort to model the process.

The quality of the sample starts at the production facility. The location where the sample is taken should be well thought out, close to significant process equipment, where it can be assumed the process stream is well mixed, and where process conditions are well known or easy to measure. In all cases the sample collection location should also be easy to access and have a sample probe installed to ensure product is collected from the center 1/3 of the pipe. The sample should be taken carefully, and all necessary and recommended guidelines should be followed as outlined in section 2.0.

Once the sample is collected, it should be sealed, stored, and transported to a lab with care in order to preserve the integrity of the sample. After the sample is analyzed at the lab and the composition is known, it can be verified in a process simulator. A common test often used to evaluate whether the measured composition is representative of the product in the vessel at the time the sample was collected, is to determine the sample's bubble point. In this scenario, if the recreated process stream in the process simulator is at or close to its bubble point at the vessel operating temperature and pressure, it can be verified as a good sample.

It was long thought that the bubble point evaluation was a "silver bullet" approach to validating the analytical integrity of the measured compositions. However, over the years that line of thinking has changed. While bubble point might still be one of the better ways for evaluating compositional fidelity, it should only be used as a conservative indicator of sample integrity. As documented by Parker et al. error propagation by the factors described in section 2.0 (all factors unrelated to the chromatographic compositional data) on bubble point determination can compound to result in a calculated bubble point that is not representative of the sample. Therefore, the application of strict bubble point evaluation criteria (such as those often cited by CARB and the EPA) may increase the chance a "good" sample being rejected [3].

A practical example of this comes from older, low-flowing wells where the temperature of the product at the point of sample collection can be significantly different than the temperature of the product in the core of the vessel (often where the thermometer on the vessel is reading from). Where and how the temperature measurement is made during sample collection, and how closely that product was to equilibrium with those conditions, can result in a significant deviation from the bubble point determined from the measured composition. Alternatively, when sampling from newer, high-flowing wells vessel disequilibrium becomes a concern as the liquid in the vessel doesn't have enough time to equilibrate with the pressure and temperature conditions, resulting in a liquid that is over-saturated with respect to vessel conditions. In both examples, measured composition from chromatography is not the problem, and if bubble point is the sole metric being used to determine sample integrity, a producer can find themselves resampling the equipment repeatedly without achieving a different result. This is why the authors of Parker et al. 2021 advocated for a holistic approach to evaluate sample representativeness that takes into account the many other factors outlined above.

2.2 NECESSARY DATA FOR PROCESS SIMULATION

Modeling an entire production facility in a process simulator requires more information than sample compositions and the operating conditions near the sample locations. There are many ways a production facility could be configured. **Figure 1** illustrates the configuration discussed in this paper. There are several possibilities for sample locations in this configuration. For all configurations, the operating conditions at each piece of equipment modeled should be well known.
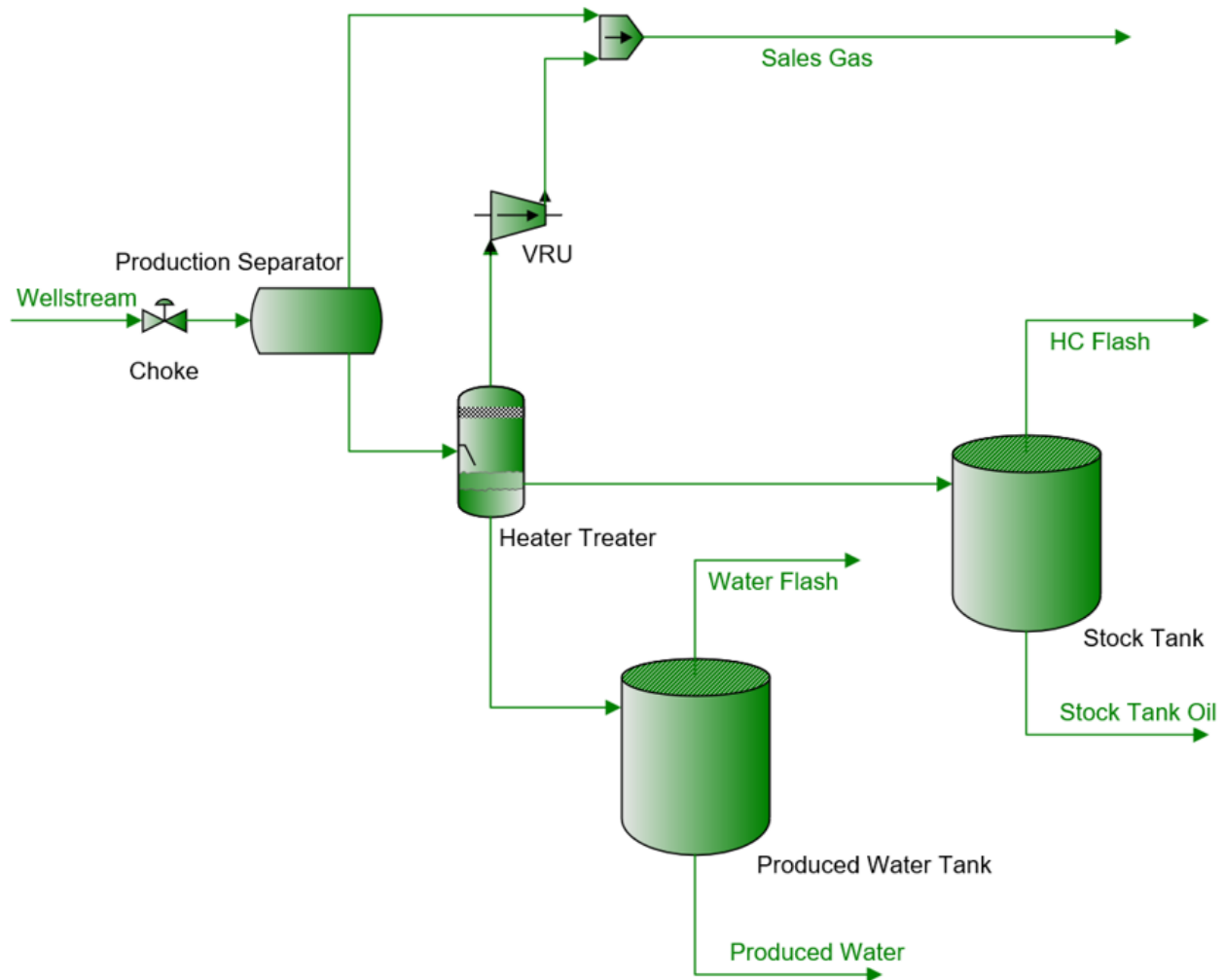
Figure 1: Typical Production Facility Configuration

EXAMPLE 1

Figure 2 shows the typical production facility with a possible combination of sample locations. In this case, the sales gas and oil from the stock tank could be sampled. For the most accurate results in this case, the stock tank oil would need to be saturated or mostly saturated, not significantly weathered. The flash emission flowrates will be calculated by the process simulator and thus do

not need to be sampled or have a measured flowrate. The advantage to this configuration is that the oil sample is easier to handle, with less possibility of light ends escaping. However, it is not as likely that the stock tank oil will be at its bubble point. The more time the oil spends in the stock tank and weathers, the more light hydrocarbons will vaporize, and the further the oil will get from its bubble point.
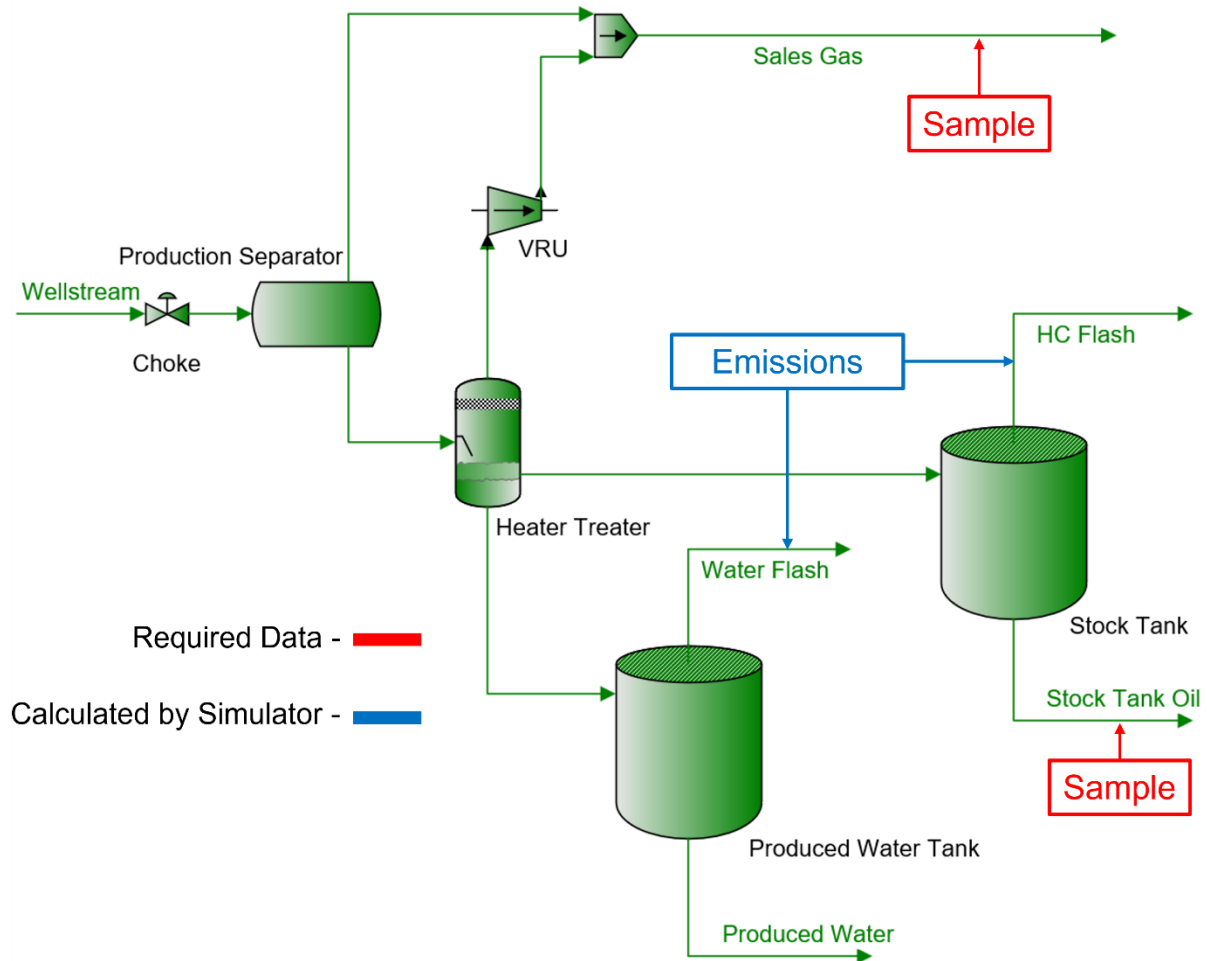

Figure 2: Example 1 of a Typical Production Facility Configuration with Sample Locations

<u>EXAMPLE 2</u>

Figure 3 shows another configuration of sample locations. It is like **Figure 2**, but the oil sample is taken downstream of the heater treater. This is usually a preferable location since the sample includes the light hydrocarbons that flash at the stock tank. This can improve the accuracy of the production facility since it should always be at the bubble point and easy to verify. The main disadvantage to this sample location is the sensitivity of the bubble point. If even a small fraction of the light ends escape, the sample results may lead to significant changes in emission results. However, if done correctly this can lead to good, reliable results.
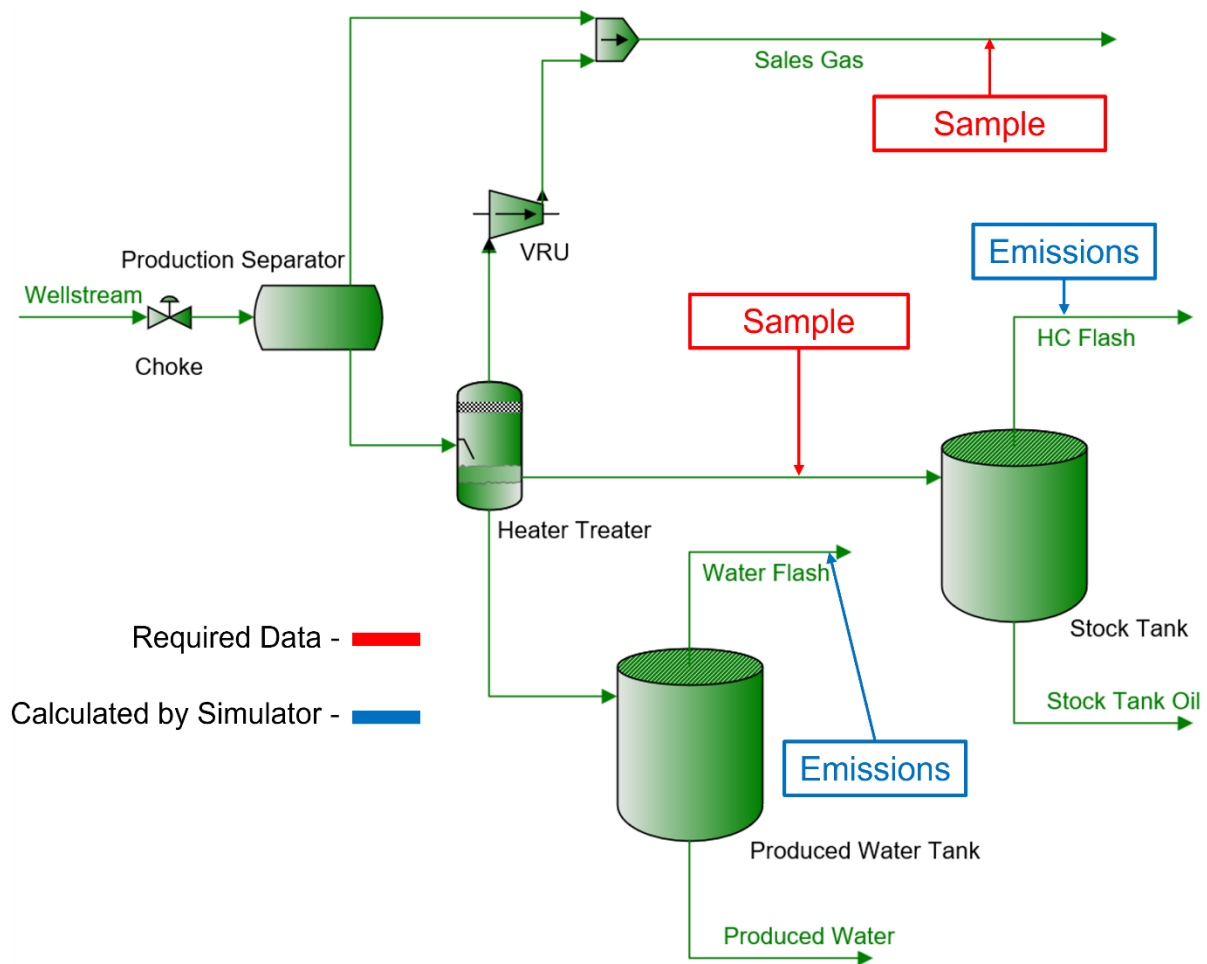
Figure 3: *Example 2 of Sample Locations*

<u>**EXAMPLE 3**</u>

Figure 4 is a third configuration of possible locations for sampling and necessary flow rates. It is important to note that the liquid sample downstream of the production separator should only be taken of the oil phase. How this is done will depend on the separator. In most cases, it will likely be best to take a sample from an oil phase sample point directly at the separator. Many production separators are three phase, making the process liquid easier to sample. The advantage for this configuration is the liquid sample captures all the hydrocarbons moving through the heater treater and the tanks. This sample is also more forgiving of sample errors due to an additional stage of separation between the sample and the emission points. The main disadvantage to sampling at the inlet separator is that the pressure is highest here. Procedures must be strictly followed to ensure safety and a good sample.
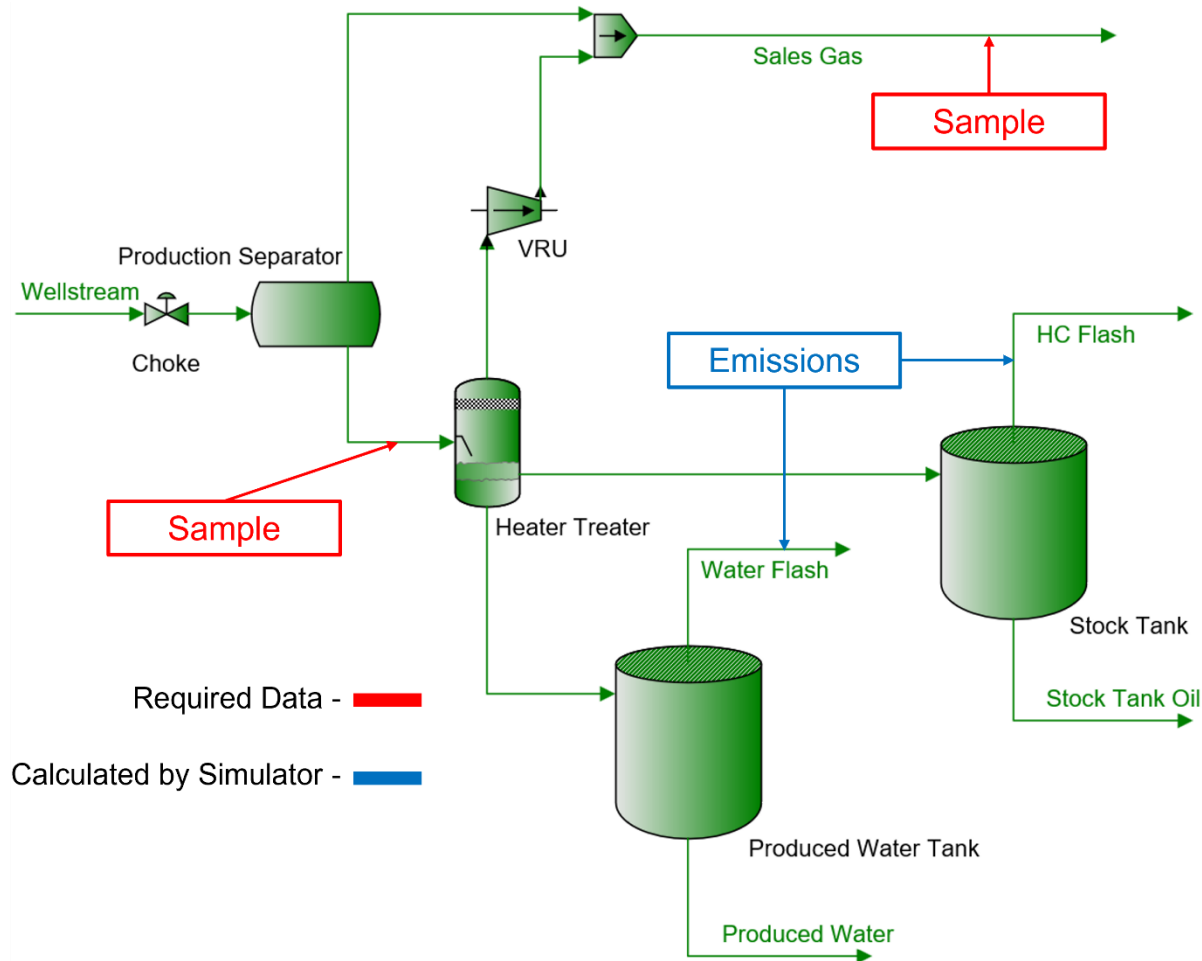
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Figure 4: *Example 3 of Sample Locations*

2.3 PROCESS SIMULATION

If good samples and plant data are step one, modeling is step two. The process simulator marries hundreds of years of research into thermodynamics and modern scientific developments. Until recently, emission factors were the best approximation for estimating emissions. However, an operator recently explained colorfully, "Emission factors are like placing your feet in the oven and your head in the freezer and only reporting the average temperature." With simulators like ProMax becoming widely adopted throughout industry, emission calculations are now deeply physics-based. While emission factors can break the laws of thermodynamics, process simulators do not. Leveraging these powerful tools correctly provides much more accuracy.

Once verified sample data is available and necessary flow rates are known, a model of the production facility can be built in a process simulator. To fully model the production facility, the operating conditions at each significant piece of equipment must be known. For the example production facility shown in **Figures 2-4**, the following conditions should be known:

1. Temperature and pressure of the production separator
2. Temperature and pressure of the heater treater

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3. Location, temperature, and pressure of the tanks
4. Produced oil, gas, and water flowrates

To model the production facility shown in **Figure 5,** a method called back blending was used. Back blending is done by creating individual inlet streams for the gas, liquid, and water and mixing them together. These streams are populated with the sample data of the gas and oil and the flowrates of the gas, oil, and water. The water inlet stream is considered to be pure water. The flowrates are adjusted to match reported rates from the field.
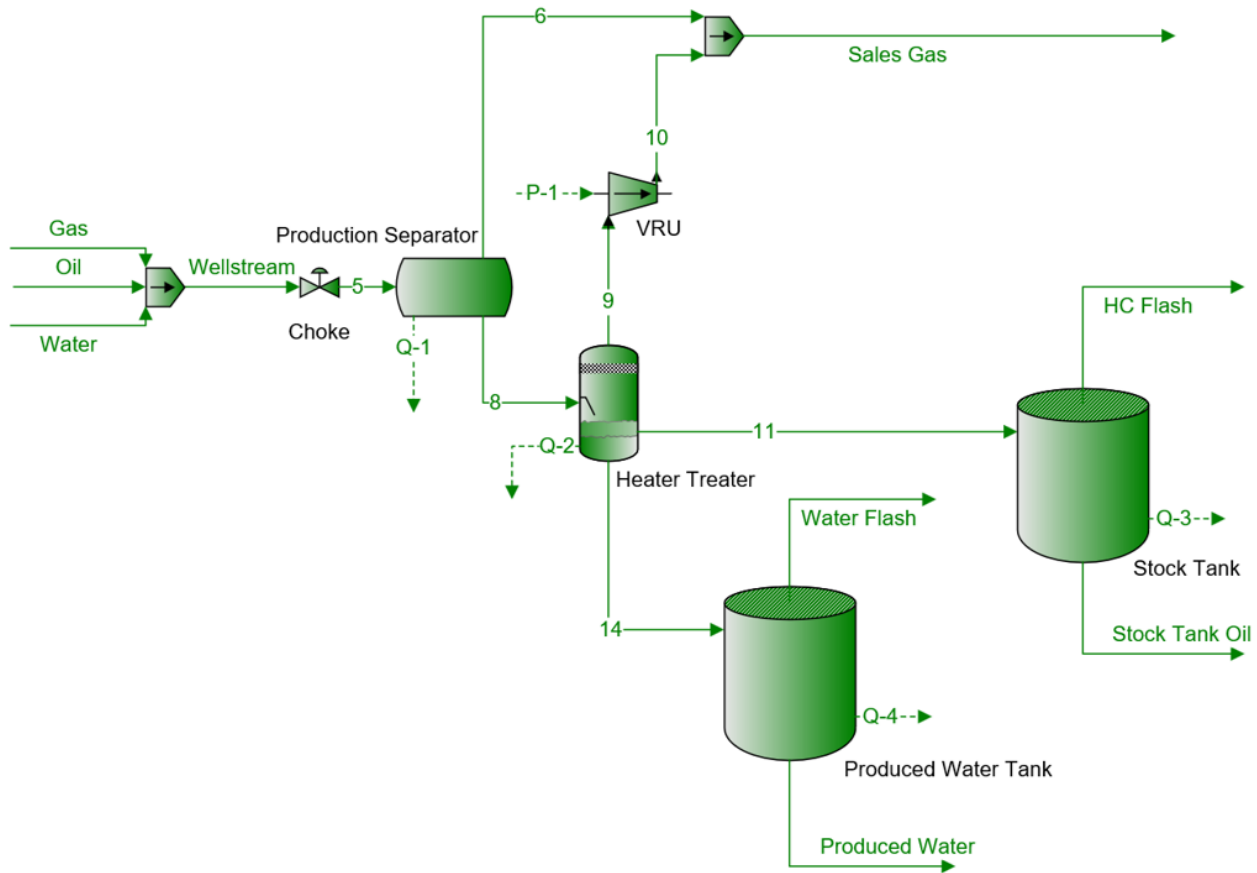
Figure 5: Flowsheet Set Up for Process Modeling of a Typical Production Facility

3.0 PRODUCED WATER EMISSIONS

Due to equipment inefficiencies, production separators often provide imperfect separation. The problem is every separator is different and has a different efficiency. Beyond equilibrium, how much hydrocarbon goes with the water? How much water goes with the hydrocarbon? A good simulator should already predict the equilibrium solubility of one within the other, but what about the inefficiency? While work is being done to improve predictions for inefficiency, it is still difficult to do with accuracy. This is the problem the 1% rule is attempting to solve; however, there are several interpretations of the 1% rule.

3.1 DEFINING THE 1% RULE

The "1% Rule" is better understood as a rule of thumb. Rules of thumb exist to apply industry experience, knowledge, or scientifically based, repeatable calculations to real world operations. Estimating emissions from produced water tanks is difficult because of oil entrainment into the aqueous phase. It is equally important to recognize that it is hard to know the degree of hydrocarbon entrainment in produced water. It varies from facility to facility and is currently unpredictable using any known formulas. Therefore, the 1% rule is used to assign an entrainment value to the facility. Parsing through the various interpretations of the 1% rule floating around, one definition rises to the top. Simply put, the 1% rule is:

For oil or condensate production facilities, to account for entrainment, it is assumed 1% of the hydrocarbon liquid will leave with the water at the first point of liquid/liquid separation.

This definition has three main advantages. First, it defines the 1% rule in terms of entrainment, the phenomenon it is attempting to account for. Second, it is a scientific approach, that is repeatable, but more importantly testable. Third, it is unambiguous, simple, and keeps the fundamental principles based in physical and chemical sciences instead of the various interpretations Ross documented as having significant scientific flaws. Another benefit to following this definition is the ease of which it may be adjusted in the future as more experimental data becomes available. This rule of thumb could easily become the 0.5% rule or the 2% rule in the future based on future studies. Since this definition is directly related to entrainment of oil into the water phase, a topic of equal interest for engineers and emission regulators, there is a higher probability research experiments may take place to predict entrainment more accurately.

3.2 APPLYING THE 1% RULE

In November 2023, samples were taken at five production facilities in the Bakken formation and tested by SPL. The five production facilities were modeled, and one is shown in **Figure 6**. This Sample + Model approach provides several benefits. First, as shown in **Figure 6**, the emissions from both the oil and water tanks at the facility are calculated in the same model from the same samples. The oil and water tanks are also set up as tanks that calculate AP-42 emissions. Flashing, Working, Standing, and Loading emissions are calculated based on the sample data from the lab and the properties of the facility. The gas lab analysis is shown in **Figure 7**; however, due to confidentiality, production rates, temperatures, and pressures have been changed.
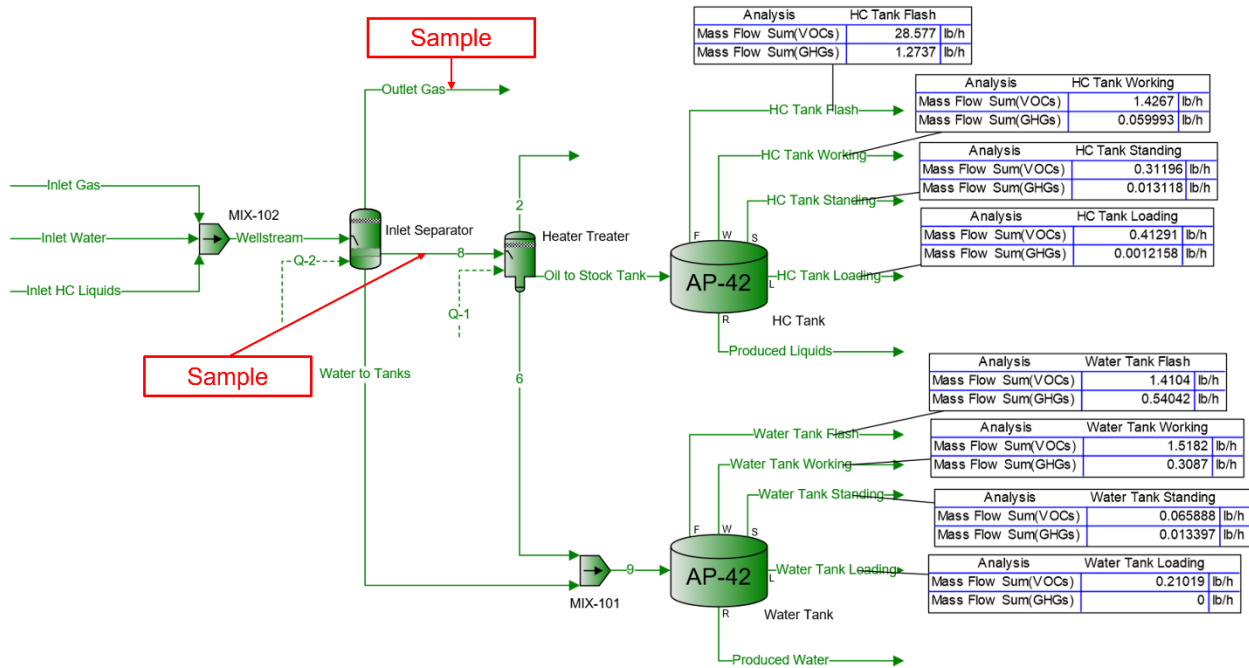
Figure 6: *Completed Model of Production Facility 1 with VOC and GHG Emissions Displayed*

Figure 7: *Gas Lab Analysis used in the Model of Production Facility 1*

Second, when the model is created, the 1% Rule using entrainment can be built in easily. In 3-phase separator blocks, there is an option to create entrainment. The "Light Liquid" (AKA the hydrocarbon phase) is entrained in the "Heavy liquid" (AKA the water phase). The basis of the entrainment is a volume fraction titled "Fraction From Phase" with 1% of the volume of the

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hydrocarbon phase being entrained. **Figure 8** shows the entrainment settings in the inlet separator for this facility.
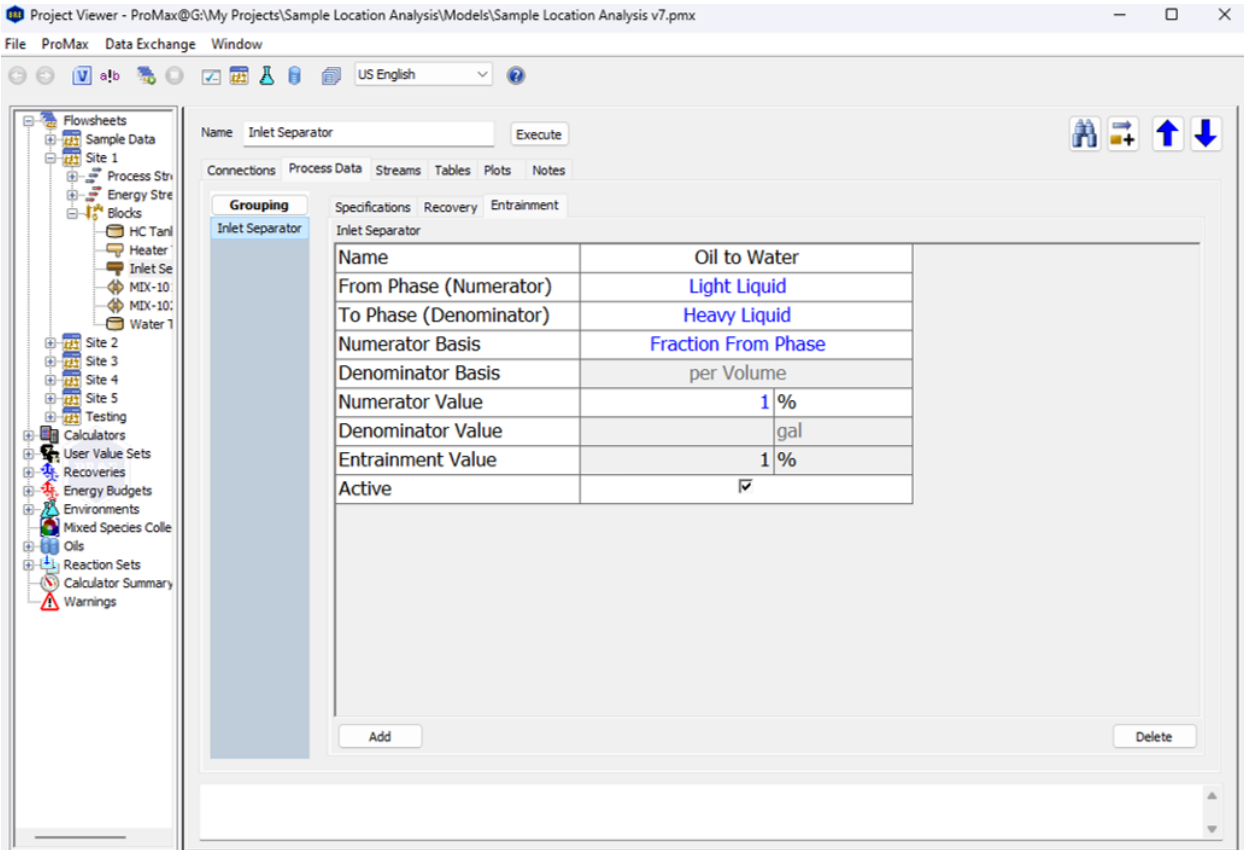

Figure 8: Entrainment settings for the Inlet Separator of Production Facility 1

Third, a report of the emissions can be made for the tank emissions from the entire site. The report may be submitted directly to the regulatory agencies. The report summary page of the emissions from the water tank is shown in **Figure 9.** Additional detailed pages of the report are also created when the report is generated.
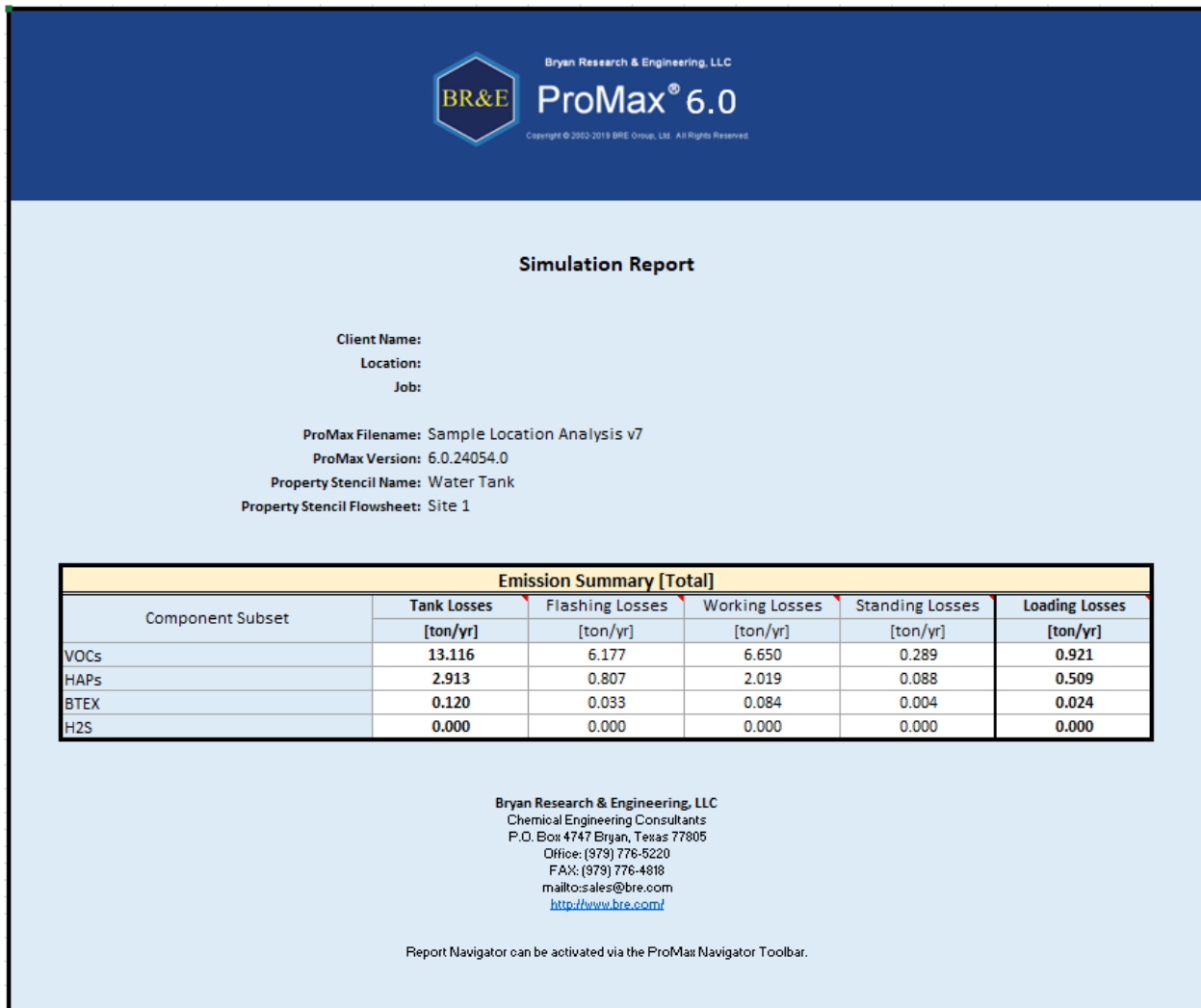
Figure 9: Report Summary Page of Water Tank Emissions from Production Facility 1

4.0 STEP-BY-STEP PRODUCTION FACILITY EMISSIONS GUIDE

While there are many production facility configurations, there are best practices to follow in order to accurately calculate emissions. These are the recommended steps to follow for calculating facility emissions:

1. Take and validate samples
2. Collect production facility data
3. Model production facility
4. Generate Report

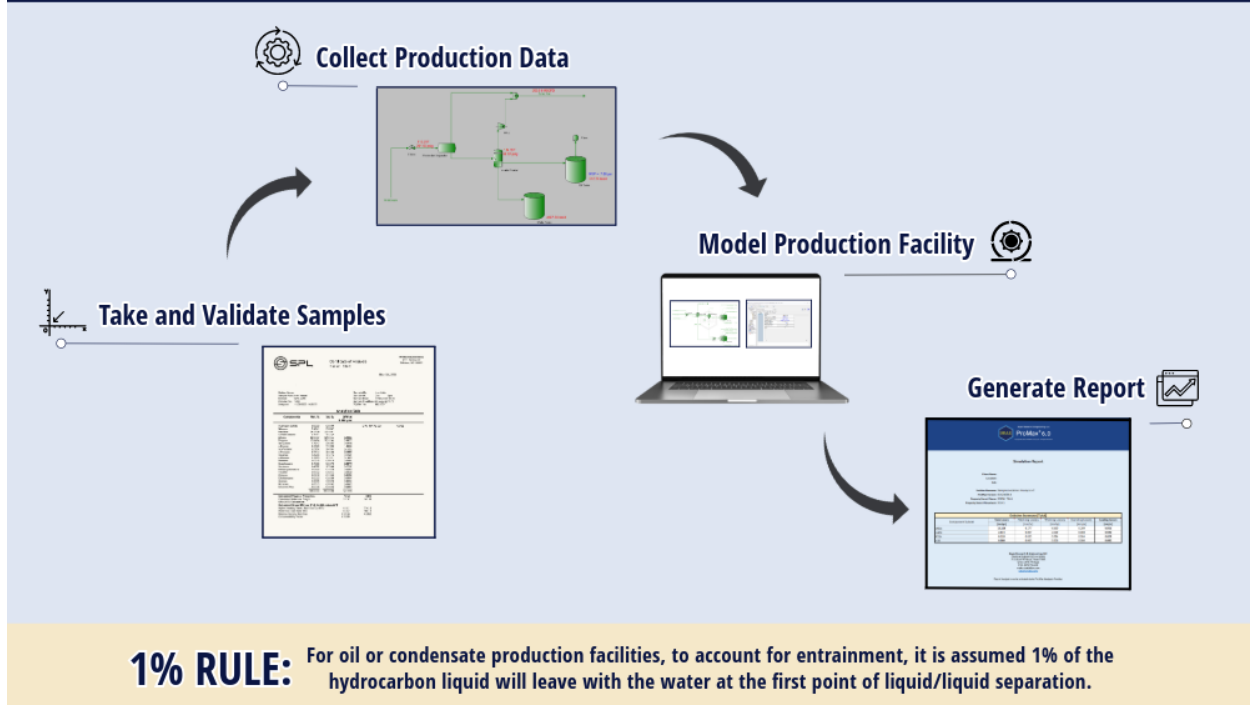**Figure 10** shows a roadmap of this guide.

Figure 10: Sample + Model Roadmap for a Production Facility

5.0 CONCLUSION

With increased scrutiny from regulatory agencies and more stringent rules, it is now essential to use a process simulator to calculate produced water tank emissions at production facilities. A good sample plus a good model will equal the most accurate emissions calculation. When appropriate, the 1% rule should be applied as follows:

For oil or condensate production facilities, to account for entrainment, it is assumed 1% of the hydrocarbon liquid will leave with the water at the first point of liquid/liquid separation.

Using the Sample + Model approach, the 1% Rule can easily be applied as an entrainment specification in the inlet separator of a modeled facility. This approach allows for the consolidation of calculations into a single model file, easy calculations of AP-42 tank losses, and streamlined emissions report generation.

Works Cited

[1] K. Ross, "Are Produced Water Emission Factors Accurate," in *GPA Conference*, San Antonio, 2016.

[2] Bryan Research & Engineering, LLC, "ProMax 6.0," Bryan, 2022.

[3] P. B. C. S. J. L. Andrew Parker, *Sample Integrity Checks for Pressurized Liquid Hydrocarbon Compositions Applied to Air Emissions Applications,* 2021.