

CHEMICAL PROCESS ANALYSIS AND MODELING CASE STUDIES: LIQUID
DIFFUSION AND THERMODYNAMIC CONSIDERATIONS

by
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Abstract

Two case studies completed under the direction of Jacobs Engineering are presented and discussed. In the first case study, the economics of the installation of an oil cooler are examined. A vapor recovery unit (VRU) for an enhanced oil recovery (EOR) facility in Grieve, WY, will be installed to capture the vapors from an oil tank. With the installation of the VRU, a question arose: would an oil cooler proposed to be installed before the oil tank be necessary? A simulation and economic analysis of the process suggests that oil cooler installation is still economically favorable. When the low pressure (LP) separator is operated at the typical temperature of 140°F, nine additional barrels of oil per day (BOPD) are recovered through the use of an oil cooler. The net present worth (NPW) of oil cooler installation is calculated to be \$248,000. In the second case study, an overflow protection line was proposed to be installed for a gas flotation unit on an offshore oil rig. It was postulated that there might be a risk of hydrocarbon diffusion through the stagnant liquid in the line, presenting a hazard to equipment and personnel. Calculations were performed to approximate the rate of gas flux through the line. As the physical situation is difficult to model without precise information, alternative preventative methods are presented.

Table of Contents

Abstract.....	ii
Report on the Economics of Oil Cooler Installation.....	1
Introduction.....	1
Methods	4
Results.....	5
Conclusions and Recommendations	7
Analysis of Diffusion through a Proposed Overfill Protection Line on a Gas Flotation Unit	9
Introduction.....	9
Methods and Calculations.....	10
Results.....	13
Dispersion Considerations	13
Conclusions.....	15
Bibliography	17

Report on the Economics of Oil Cooler Installation

Introduction

As the price of oil grew through the years, the development of enhanced extraction techniques increased the yield from existing wells. These wells have already been subjected to primary and secondary recovery techniques: natural and artificial lift / waterflood and gas lift operations. The percentage of available oil recovered ranges from 5-15% for primary recovery and 25-35% for secondary recovery.

Tertiary oil recovery (also known as enhanced oil recovery, or EOR) is a term which encompasses a range of recovery techniques, and provides for an additional 5-15% recovery of original oil. The most common tertiary recovery technique is CO₂ injection. In this process, large amounts of CO₂ are injected into the well at high pressure. The CO₂ becomes supercritical at well conditions, and the oil becomes miscible in the supercritical CO₂ phase. This decreases the oil's viscosity and allows for additional recovery of "tight" oil.

Once the CO₂ and oil mix, the phase front is forced to the production well, where the supplied pressure forces it up the well pipe and to the surface. Pressure decreases significantly from the reservoir to the wellhead, due to potential energy change and frictional losses in the pipe. At surface conditions, pressures are typically in the range of 300-800 psi. At these conditions, three phases are present: a vapor phase consisting mainly of CO₂, an oil phase and a water phase. The oil and water phases contain significant amounts of CO₂ which must be separated before sale.

Denbury, Inc. is a company which specializes in tertiary oil recovery using CO₂ injection.

Denbury hired Jacobs Engineering to provide assistance with the design of a facility in Grieve,

Wyoming. I worked on several projects regarding the design of the facility. One of these projects related to the operating conditions of a stream in the separation train of a planned upstream oil facility.

At the proposed Grieve, WY, facility, separation occurs in three stages. The mixture from the wellhead first enters a high-pressure (HP) separator, which operates at wellhead pressures. The oil phase from that separator is then fed to a low pressure (LP) separator, which typically operates at or near 50 psi. The oil phase from the LP separator is then fed to an atmospheric tank. A process flow diagram for this process is shown in Figure 1.

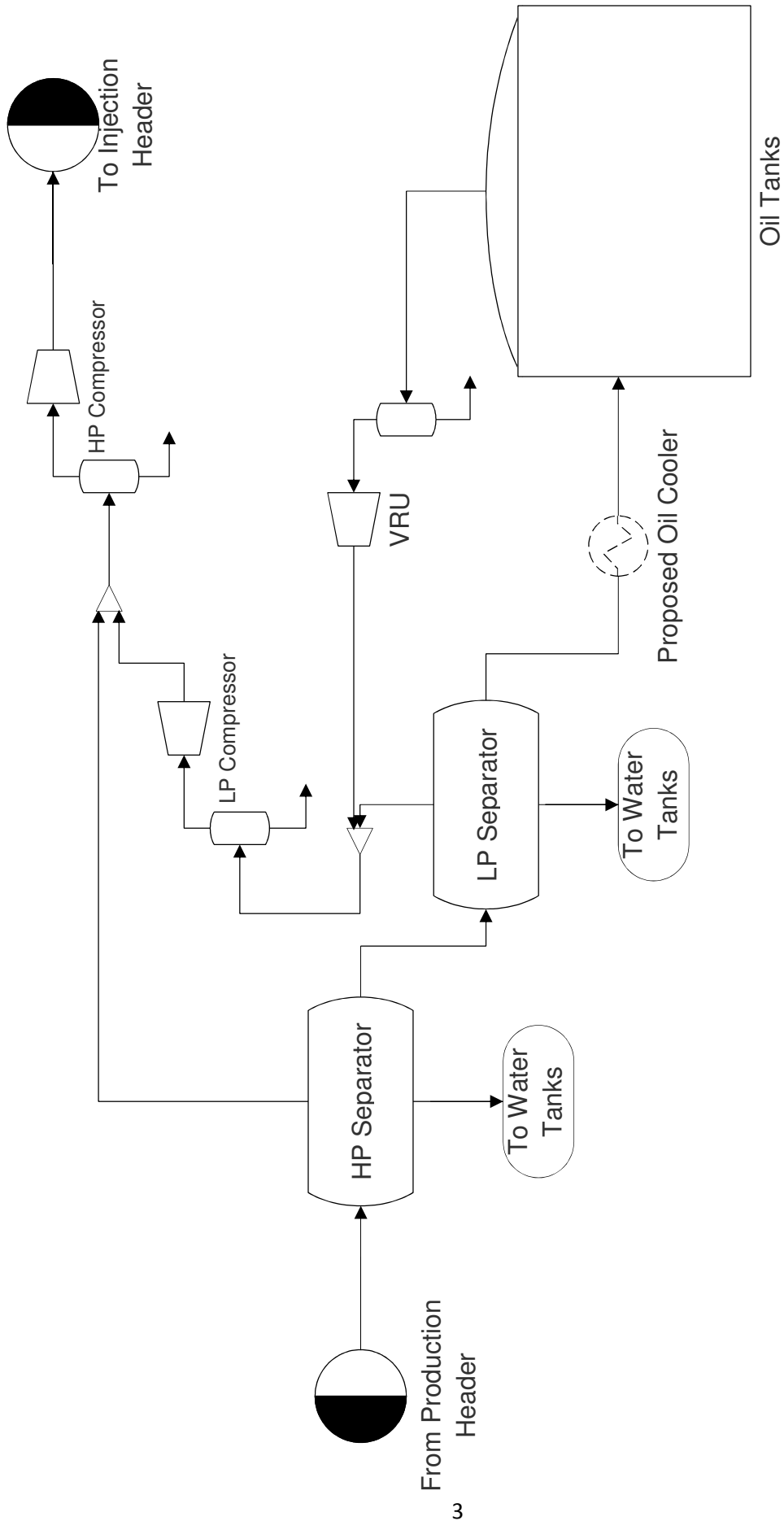


Figure 1 - Simplified Process Flow Diagram of the Facility

At each separation stage, the separated vapors are fed to a compression system, as the CO₂ from the well must be recovered for re-injection. The compression system consists of three compression stages. At the first stage, the atmospheric vapors from the oil tanks are compressed to 50 psi. This compressor is referred to as a vapor recovery unit (VRU). The compressed vapors then join with the vapor stream leaving the LP separator. The combined stream is then fed to the LP compressor which increases the pressure to 400 psi. Finally, the 400 psi stream mixes with the vapor stream from the HP separator. The combined stream is then fed to the HP compressors, which raises the pressure to roughly 2200 psi, allowing for the stream to be re-injected into the well.

The use of a VRU aids upstream facilities in meeting EPA emissions guidelines by reducing the amount of hydrocarbons flared. Depending on the rate of vapor production, its use is not always economical. An analysis was done on the proposed Grieve facility, and it was decided that a VRU was economically justifiable. After the decision was made to install a VRU to compress the vapors from the oil tank, it was suggested that a proposed oil cooler, intended to cool the liquid stream from the LP separator to the oil tank, would not be necessary. The rationale behind the suggestion was that as the vapors from the oil tank were being captured by the VRU, reducing the rate of vapor production was no longer necessary. I was tasked with evaluating this suggestion, and determining the consequences of operating the process with and without the proposed air cooler. I was asked to analyze the choice at 3 different LP separator temperatures. The LP separator temperatures analyzed were 140, 120, and 100°F.

Methods

To perform the analysis, a simulation of the plant was used. The simulation was created using HYSYS, and includes all process units relevant to the scope of the analysis. The process was

compared with and without an oil cooler on the line leading to the oil tank. The cooler was operated with an outlet at 100°F. Though lower temperatures provide better recovery of hydrocarbons, this temperature was chosen to reduce the possibility of paraffin deposition.

The plant was simulated and analyzed at three different LP separator temperatures: 140, 120, and 100°F. At an LP separator temperature of 100°F, the process with and without a cooler are identical. At 140 and 120°F, the plant was compared with and without an oil cooler.

To perform the economic evaluation, a minimum attractive rate of return (MARR) of 10% was used, along with a stream factor of 0.9. A project length of 5 years was assumed. A price per barrel of oil of \$40 was used. The cost of electricity was assumed to be \$0.07/kWh. The well production flow rates for the early life case were used, and are expected to hold constant for the project duration chosen.

Results

When comparing the effect of having an oil cooler at higher LP separator temperatures, the biggest change is the flow rate of hydrocarbons C3-C12 (propane through dodecane) in the oil product. Without the cooler, more hydrocarbons flash across the 50 psi pressure drop. Figure 2 shows the change in flow rate of C1-C9 in the final product as a result of cooler installation.

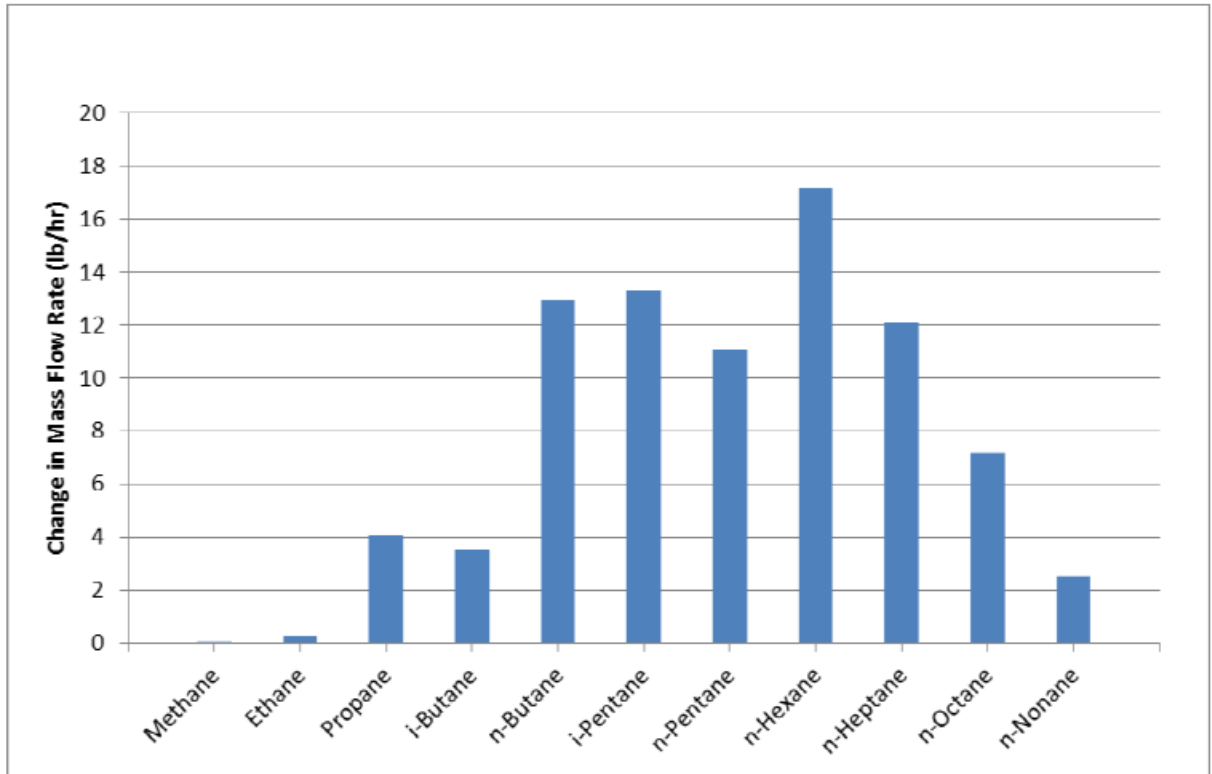


Figure 2- Additional Recovery of Hydrocarbons due to Cooler Installation

Without the installation of a cooler, these hydrocarbons are sent through the compression train. They do not drop out before the VRU, and do not drop out appreciably before the LP or HP compressors. As the LP separator temperature is lowered, the additional recovery of hydrocarbons provided by oil cooler installation decreases. At 140°F, the facility produces nine more barrels of oil per day with the installation of an oil cooler. At 120°F, the facility produces four more barrels of oil per day.

An increase in oil recovery correlates to a decrease in the flow rate to the VRU. At an LP separator temperature of 140 °F, the installation of an oil cooler reduces the load to the VRU by 10%. At an LP separator temperature of 120 °F, a 4.3% reduction occurs. Although a decrease in the flow rate to the VRU results in a decrease in CO₂ re-introduced into the well, the decrease

is not large enough to require the purchase of additional CO₂. The decrease in gas to be re-injected is calculated to be approximately 0.04% by mole at an LP separator temperature of 140°F.

An economic analysis of the process was conducted using the typical LP separator temperature of 140°F. As the only costs associated with an increase in production are the purchase, installation, and operation of the cooler, the project is economically favorable. At an MARR of 10%, the NPW of oil cooler use is \$248,000. The project has a discounted payback period of 21 months, and the discounted cash flow rate of return (DCFROR) of the project is 60%. The analysis was performed assuming early life projections for production rates. At predicted mid-life rates, the NPW is \$139,000.

Conclusions and Recommendations

While it was initially thought that the installation of a VRU would make oil cooler installation superfluous, an economic analysis suggests otherwise. It was believed that additional hydrocarbons sent to the VRU would be recovered before the compressors, but this is not the case. An abundance of CO₂ in the separated vapor streams prevents the hydrocarbons from becoming saturated. The additional hydrocarbons sent to the VRU remain in the vapor phase until re-injection.

The installation of an oil cooler is predicted to provide significant additional recovery of oil, as well as a decrease in load to the VRU. Based on the results of this study, oil cooler installation is economically favorable at the typical LP separator temperature of 140 °F. Although there was some concern about a decrease in well re-injection gas, this decrease is projected to be minimal. If the LP separator is to be operated at 140 °F, the installation of an oil cooler is recommended.

It was also observed that operating the LP separator at lower temperatures is economically beneficial. Based on the results of the simulation, an additional ten barrels of oil are recovered using an LP separator temperature of 100 °F, compared to operating the LP separator at 140 °F and subsequently cooling the stream to 100 °F. It is typical Denbury practice to operate the LP separator at 140 °F at any given facility, due to concerns about emulsion persistence. However, the temperature required to prevent emulsion persistence varies from site to site. It is recommended that the temperature required for each site be investigated, and the LP separator be operated at the lowest temperature possible to achieve optimal oil recovery.

Analysis of Diffusion through a Proposed Overfill Protection Line on a Gas Flotation Unit

Introduction

On an offshore oil rig, an induced gas flotation unit removes hydrocarbon particles from a water stream. In the unit, hydrocarbon gas is mixed with the process water in a series of stages. The hydrocarbon gas forms bubbles which are attracted to oil droplets. The bubbles and oil droplets rise to the surface, where they are removed. The units are highly effective, removing up to 98% of entrained hydrocarbon particles, and are one of the last treatment steps for process water before it can be discharged overboard. A diagram of the gas flotation unit is found in Figure 3.

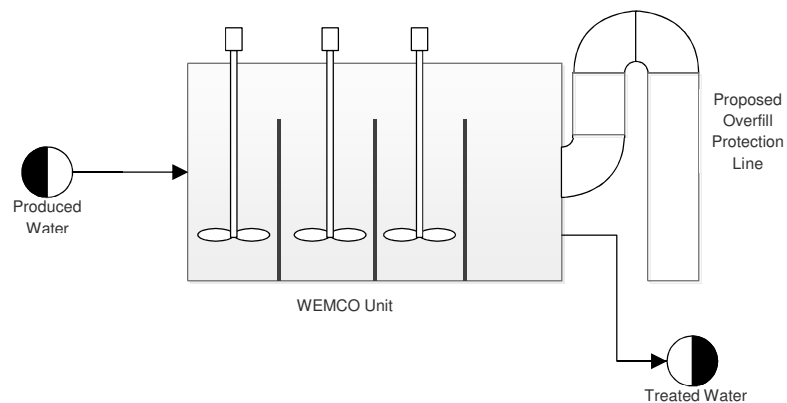


Figure 3: Simplified Diagram of WEMCO unit

In order to provide adequate relieving capability in the event of a process upset, it was proposed that an overfill prevention line could be added to the existing gas flotation unit on the platform. Concern has been raised over the possibility of hydrocarbon

gasses diffusing through the open overfill prevention line and presenting an explosion hazard/exposure risk on the platform. The overfill line would connect to the existing unit at the last cell, and would be open to the atmosphere. Calculations were performed to approximate the rate of diffusion through the overfill prevention line.

Methods and Calculations

At steady state, there are two rates of diffusion in the system: the rate of diffusion of dissolved gas through the liquid, and the rate of diffusion through the gas above the liquid in the overfill prevention line. Per Fundamentals of Momentum, Heat, and Mass Transfer, diffusivity coefficients of solutes through liquids are on the order of 10^4 times smaller than their diffusivity through gas [1]. As a first approximation, a stagnant liquid layer and a comparable distance for diffusion through liquid and gas were assumed. Under these conditions, the rate of diffusion through the gas layer will be significantly higher than the rate of diffusion through the liquid layer. Thus, only the rate of diffusion through the liquid was considered.

To perform initial calculations, it was assumed that there are no entrained bubbles in the liquid at the inlet to the overfill protection line. It was also assumed that routine operation does not cause liquid to be circulated through the entire pipe segment. It was assumed that the liquid in the line, through eddies and small currents, would be saturated with hydrocarbons at a 2 ft depth; i.e. that only the top two feet of the liquid in the overfill protection line would be stagnant. Thus, the diffusion rates were calculated through the top two feet of the pipe.

The concentration of hydrocarbons in the saturated liquid was calculated using Henry's Law, with a fuel gas composition of 90% CH₄, 5% CO₂, and 5% H₂S. The equation used to calculate saturation concentrations is found below.

$$y_A P = x_A H(T)$$

Symbol	Description	Units
y_A	Mole fraction of A in gas phase	$\frac{mol_A}{mol_{total}}$
P	Pressure	<i>atm</i>
x_A	Mole fraction of A in liquid phase	$\frac{mol_A}{mol_{solution}}$
$H(T)$	Henry's law constant	<i>atm</i>

The calculated concentrations are provided in Table 1. Henry's law constants for CH₄ and H₂S were obtained from *Perry's Chemical Engineer's Handbook, 7th Edition* [2]. The Henry's law constant for CO₂ was obtained from Lide and Frederikse [3].

Table 1: Predicted Liquid Concentrations in WEMCO unit

Component	Henry's Law Constant (atm)	Concentration (mol/L)
CH ₄	4.13×10^{-5}	0.00128
CO ₂	6.24×10^{-4}	0.00183
H ₂ S	5.45×10^{-2}	0.00538

The diffusion of the gases through the water in the overflow protection line was modeled using Fick's law of diffusion, with a steady-state assumption. Diffusivity constants were obtained from the *CRC Handbook of Chemistry and Physics* [4].

Though these constants are based on diffusion through fresh water, an increase in salinity causes a reduction in diffusivity. Therefore, the use of fresh water diffusivity constants results in a conservative estimate. The equation used to calculate molar flux is as follows:

$$N_{A,z} = \frac{cD_{AB}}{(z_2 - z_1)} \ln \left(\frac{1-x_2}{1-x_1} \right)$$

Symbol	Description	Units
$N_{A,z}$	Molar flux of A in the z direction	$\frac{mol}{m^2 s}$
c	Concentration of mixture	$\frac{mol}{m^3}$
D_{AB}	Diffusivity of A through B	$\frac{m}{s^2}$
z_1	Position at $z = z_1$	m
z_2	Position at $z = z_2$	m
x_1	Mole fraction at $z = z_1$	$\frac{mol_A}{mol_{solution}}$
x_2	Mole fraction at $z = z_2$	$\frac{mol_A}{mol_{solution}}$

After the molar flux was calculated, the area at the interface was used to calculate a flow rate for the components.

Results

The calculated flux for each gas is presented in table 2.

Table 2: Preliminary Calculation of Flux Rate

Component	Diffusivity (cm ² /s)	Flux (SCMD)
CH ₄	1.84 x 10 ⁻⁵	1.41 x 10 ⁻⁵
CO ₂	1.91 x 10 ⁻⁵	2.1 x 10 ⁻⁵
H ₂ S	1.36 x 10 ⁻⁵	4.4 x 10 ⁻⁵

Dispersion Considerations

Although the assumptions of a stagnant liquid layer and comparable diffusion lengths allow for a first approximation at flow rate of gas exiting the overflow protection line, a more realistic estimate can be obtained with more precise knowledge of the system.

In the system, it is unlikely that the water in the overflow protection line is truly stagnant. A temperature gradient, caused by process water warmer than the ambient air, would cause convection of the fluid inside the overflow line. This would increase the transfer of hydrocarbons to the surface, and would thus result in a greater flux. If information about the heat transfer was known, a mass transfer analogy could be used to approximate the molar flux of hydrocarbons in the system.

In addition to the possibility of a temperature gradient, there are other issues with a stagnant molecular diffusion model. If the scale of the system is considered, turbulent diffusivity is a more accurate model than molecular diffusion. Over “large”

distances in real systems, transport occurs via advection. As discussed by Schwarzenbach, et al, there exists a distance, L_{crit} , where advection and molecular diffusion play an equal role in transport [5]. At distances greater than this length, transport by advection is faster than transport by molecular diffusion.

Schwarzenbach, et al, provide 2×10^3 cm of liquid as a large value for L_{crit} [5]. At the distances considered in this analysis, advective transport is the governing mechanism. Advective transport in large systems can be modeled using turbulent diffusion coefficients (also called eddy diffusion coefficients). The flux is then calculated via the following equation, where F is the flux, and E is the turbulent diffusion coefficient:

$$F = E \frac{dC}{dx}$$

In the case at hand, water column stability is an applicable model. The Brunt-Vaisala frequency is a measure of the stability of a stratified water column. The Brunt-Vaisala frequency is defined as:

$$N = \left(\frac{g}{\rho} \frac{d\rho}{dz} \right)^{0.5} [T^{-1}]$$

where $d\rho/dz$ is the vertical gradient of water density, and g is the acceleration due to gravity. It can be inferred from this equation that larger density gradients provide more stable stratification. Welander proposed a relationship to calculate the turbulent diffusivity coefficient in a stratified liquid system [6]. The relationship is:

$$E_z = a(N^2)^{-q}$$

where a depends on the kinetic energy input into the system, and q relates to the mechanism by which this energy is transformed into turbulent motion. For shear-generated turbulence, $q = 0.5$, and for turbulence caused by energy cascading from large-scale fluid motion (such as the motion of the fluid in the gas flotation unit), $q = 1$. Though not enough information is available to calculate turbulent diffusivity coefficients in the system at hand, Schwarzenbach, et al suggest a range of 10^{-3} to 10^{-1} cm^2/s for vertical turbulent diffusivity coefficients in deep water [5]. Here, deep water is defined as water not exposed to the mixing forces near the surface, such as wind and waves. Using a diffusivity coefficient of 10^{-1} cm^2/s , the following fluxes were calculated:

Table 3: Calculated Flux

Component	Flux (SCFD)
CH ₄	0.0077
CO ₂	0.11
H ₂ S	0.324

Conclusions

A number of assumptions are made in this analysis. First, it is assumed that there are no entrained bubbles present in the fluid in the last stage of the gas flotation unit. If bubbles remain from the previous stages, the transport of hydrocarbons through the line could be much greater than estimates provided by the methods suggested in this

report. It was also initially assumed that the liquid in the overflow protection line is stagnant. Although this assumption could establish a minimum flux of gases through the liquid layer, this is not a realistic assumption. Using a heat-mass transfer analogy or turbulent diffusion coefficients might provide a more realistic estimate for the flux of gases through the line.

As calculations for this system are unreliable without more process information, a better approach to the problem might be to simply isolate the system from the surrounding environment. A rupture disk installed at the exit of the overflow protection line would allow for appropriate relief protection, while preventing any gasses inside the line from escaping into the surrounding environment. Rupture discs are relatively inexpensive, and such a solution would not require significant modifications to the proposed design.

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