Methanol in Produced Water Discharge

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Methanol (MeOH) is widely used in multiple applications in the offshore oil and gas industry. MeOH has three primary applications offshore:

- Hydrate inhibition during well start-up.
- Displacement of trees, well jumpers and well tubing (bullheading) for hydrate inhibition during shutdown operations.
- To equalize differential pressure across subsea valves.

The target MeOH concentration required to inhibit hydrates is commonly 25 to 50% by volume in produced water (0.5 to 1 barrel MeOH per barrel water).

It is typical practice for offshore oil production facilities to treat and dispose of produced water via overboard discharge, making MeOH one of the highest volume discharges of production-treating chemicals. Considering the significant volumes and concentrations described above, it becomes necessary for every asset to consider the environmental effects of MeOH overboard discharge and to assess appropriate mitigation strategies, as required.

Methanol Degradation

MeOH is a single carbon alcohol, organic liquid that is miscible in seawater at all proportions. MeOH biodegrades quickly and this begins immediately upon discharge to the marine environment. The instantaneous degradation rate of 11% per day results in a half-life of approximately 6 days.

At high concentrations MeOH is toxic to bacteria. At low concentrations, MeOH is readily biodegradable in the presence of oxygen and with sufficient residence time. MeOH disassociates into carbon dioxide (CO_2) and water as seen in Equation 1.

$$2CH_3OH + 3\ O_2 \longrightarrow 2\ CO_2 + 4\ H_2O$$

Equation 1: Methanol Degradation

It is not advantageous to promote bacteria growth in facilities. Bacteria can induce corrosion and generate byproducts such as hydrogen sulfide that are hazardous to personnel. Biodegradability test reports vary widely, but based on published reports, acclimation times for MeOH degradation range from instantaneous to 1 day. An example degradation is given in the Table 1. Degradation should be considered when the MeOH enters the seawater environment, not for storage purposes.

Duration, Days	MeOH Degradation, %
5	69
10	84
15	85
20	97

Table 1: Methanol Degradation Percentages

Methanol Toxicity

MeOH produces measurable aquatic toxicity levels only at high concentrations. Published results of LC_{50} (the concentration lethal to 50% of organisms that would not have died naturally) toxicity tests on marine species show reported acute toxicity ranges of MeOH (LC_{50}, ppm), as shown in Table 2.

LC_{50} Toxicity Tests on Marine Species	
Brine Shrimp (Artemia Salina)	43,600 mg/l (48 hr test)
Water Flea (Daphia Magna)	13,250 mg/l (48 hr test)

Table 2: Methanol Toxicity

In the deepwater GOM, bioassay tests are performed (as required by NPDES) at approximately 1.5% effluent concentration (67/1 dilution) to account for the level of immediate dilution following discharge of produced water to the environment. For a MeOH in water concentration of 1:1 by volume, a 67/1 dilution yields a MeOH concentration of about 6,000 mg/l, well below the measured LC_{50}. These findings emphasize the fact that MeOH discharges are likely to have a minimal environmental impact at typical overboard discharge levels.

Table 3 contains worldwide oil and grease (O&G) regulations presented by Fredrick Jones, Arthur Leuterman, and Ian Still, *Discharge Practices and Standards for Offshore Operations around the World*, at the 7th International Petroleum Environmental Conference in Albuquerque, New Mexico in November, 2000.

Methanol Partitioning to the Water Phase

The majority of the injected methanol partitions to the water phase. The partitioning factors vary with oil properties. Typically the concentration of MeOH in the water phase will be about 100 times the concentration of methanol in the oil phase.

$$\frac{\textbf{Concentration of Methanol in Water Phase}}{\textbf{Concentration of Methanol in Oil Phase}} = \mathbf{100}$$

MeOH contamination of the water is not significant in itself, but MeOH can impact water clarification efforts and increase the oil and grease (O&G) levels/readings in the overboard water. In addition, MeOH increases the solubility of hydrocarbons in water, and dissolved hydrocarbons are not removed in the separation technology typically used offshore.

MeOH also alters the relative density between oil and water, making traditional separation techniques less effective. This can diminish the effectiveness of topsides equipment and chemical treatments. It is typically difficult to meet overboard specs in systems treated with high volumes of MeOH.

MeOH can also impact oil-in-water readings making them inaccurate, depending on what measurement method is used.

MeOH also interferes with the activity of water clarifiers by reversing the polarity of the chemical. This results in reduced coagulation of hydrocarbons. To counter this reduction, the coagulant component of water clarifier dosage must be increased. However, adding coagulant necessitates increasing the flocculant injection rate to keep the ratio constant.

Methods for Detecting Methanol in Produced Water

Use of gas chromatography (GC) in MeOH testing is widely used in the oil and gas industry. Mass spectrometry can also be used to accomplish MeOH detection. GC utilizes small volumes of fluid to identify various hydrocarbon components in the mixture and is similar to fractional distillation, since both processes separate the components of a mixture primarily based on boiling point (or vapor pressure) differences.

There are some wet chemistry tests that can be performed offshore in a laboratory. These are typically oxidation tests that employ the use of chemicals such as potassium permanganate or potassium dichromate.

Additionally, CHEMETS® test kits for the detection of MeOH are available.

Currently there are no known online monitors proven in the oilfield environment that are able to detect MeOH in water. Typical O&G monitors work on the basis of fluorescence technology. In order for the instrument to detect the oils, the oils must be fluorescent to UV light. MeOH is not fluorescent in oil and therefore the monitors are unable to detect it.

Treatment Methods for Methanol in Produced Water

Treatment for overdose of MeOH in produced water for overboard discharge is not required. Some agencies employ restrictions on overboard discharge of MeOH such as offshore chemical notification scheme (OCNS) applied in the North Sea. OCNS classifies MeOH is a Class E chemical and so discharge of MeOH is limited to approximately 8,000 bbl/yr.

Conclusion

Produced water is the highest volume waste product associated with oil and gas production. Depending on treatment rates, MeOH discharge in produced water into the open ocean typically poses little to no threat to the environment, rendering it environmentally benign. The primary reasons why MeOH is not harmful to the environment is that MeOH is miscible in water, biodegrades quickly, and is only aquatically toxic at very high concentrations. As a result, very few MeOH discharge regulations exist around the world for offshore oil and gas producing facilities.

Legal Basis	O&G Limit
Barcelona Convention	40 mg/l 100 mg/l max
KUWAIT Convention	40 mg/l 100 mg/l max
OSPAR Convention	30 mg/l (set in 2006)
Act RSC 1987	40 mg/l 80 mg/l max
HELCOM Convention	15 mg/l max 40 mg/l (Alternative)
40 CFR 435	29 mg/l avg 42 mg/l max

Legal Basis	Country
Barcelona Convention	Albania; Algeria; France (Mediterranean); Greece; Lebanon; Libya; Monaco; Morocco; Spain (Mediterranean); Syria; Turkey (Mediterranean); Yugoslavia
KUWAIT Convention	Bahrain; Iran; Iraq; Kuwait; Qatar; Oman; Saudi Arabia; United Arab Emirates
OSPAR Convention	Belgium; Denmark (North Sea); Finland (North Sea); France (North Sea); Germany (North Sea); Netherlands; Norway; Portugal; Spain (North Sea); Sweden (North Sea); United Kingdom
Act RSC 1987	Canada
HELCOM Convention	Denmark (Baltic Sea); Estonia; Finland (Baltic Sea); Germany (Baltic Sea); Lithuania; Poland; Russia (Baltic Sea); Sweden (Baltic Sea)
40 CFR 435	United States

Table 3: O&G Regulations