Water Soluble Organics: Definitions & Removal Methods

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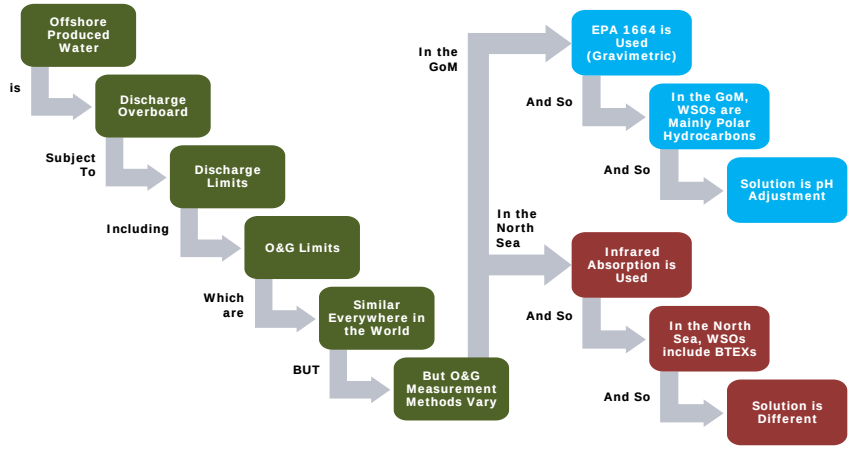
info@gateinc.com

Produced water overboard discharge is permitted in much of the world, but is subject to discharge limits. In the Gulf of Mexico (GoM), oil and grease (O&G) in produced water is limited to 29 mg/l average and 42 mg/l for excursions. Similar limits are in place in much of the rest of the world.

O&G consists mainly of dispersed organics, but some organics dissolve in water in measurable concentrations. Produced water separation systems focus on removing dispersed oil via gravity-based separation methods. These work effectively on dispersed, O&G; however, these systems do not effectively remove water soluble organics (WSOs). Where WSOs exist in concentrations greater than 29 mg/l, conventional produced water treating systems cannot achieve GoM overboard discharge limits.



Dissolved Oil & Water Soluble Organics

US regulations legally define O&G as those compounds which extract into n-hexane solvent from water at a pH less than 2, and which remain after the solvent has been boiled away (EPA 1664 gravimetric method). Hence, O&G includes only relatively non-volatile compounds; the volatile compounds are vaporized in the boiling step. BTEX is not measured in this technique.

Adjustment of the pH to 2 prior to extraction is a very important feature of this test. All hydrocarbons will partition to some extent to the water phase. Some species, notably aromatics such as benzene, toluene, ethylbenzene, and xylenes (BTEX), partition to the water in measurable quantities, but the solubility of most substances is not very sensitive to pH. An exception to this are some polar hydrocarbons, in particular carboxylic acids (fatty acids), which are soluble in water at higher pH's, but partition mainly to the oil phase at low pH.

In basic environments, the carboxylic acids tend to exist in an ionic state (negatively charged salt R^-COO^- plus H^+ ion). These ions are soluble in water. In the presence of stronger acids (acid environment; lower pH), the carboxylic acids exist as molecules (acids). The carboxylic acid molecule is much less soluble in water and partitions mainly to the oil phase. This is shown in Figure 1.

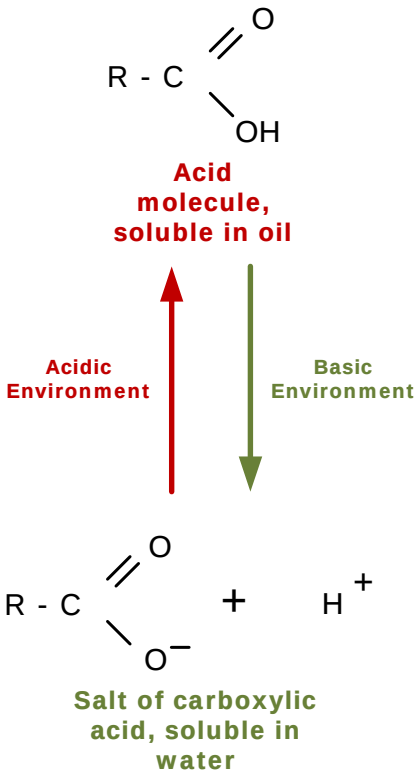


Figure 1: Carboxylic Acid Chemistry Behavior

At typical operating pH values, a significant fraction of the fatty acids are dissociated and dissolved in the water. The fatty acids dissolved in the water are not removed by dispersed oil removal processes, which principally depend on gravity (or enhanced gravity) separation.

A variety of WSO treatment options have been identified, researched, and tried including:

- Adsorption onto Non Re-Generable Media such as Organoclays and Activated Carbon
- Adsorption onto Re-generable Porous Media
- Reverse Osmosis
- Biological Degradation
- Distillation
- Addition of Condensate to the Water Stream After Removal of Insoluble Organics – Results in Partitioning of Some Dissolved Hydrocarbons into the Condensate
- Acid Treatment with a Variety of Acids
- Chemical Reactions such as Oxidation via Ozone
- Demulsifiers to Remove Fatty Acids Existing as Emulsions Rather than in Solution

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Removal of Water Soluble Organics: Acid Treatments

It is not surprising that the leading technology in the GoM for removal of WSOs is acid treatment. Reducing the water pH by adding an acid forces the carboxylic acids into the molecular form and into the oil phase. It is important to note that this will be effective only if there is an oil phase for the acid to partition to.

Acid treatments must be added at a stage where both oil and water phases exist. Phosphorous acid is commonly used and chemical vendors provide proprietary acid blends that contain buffering agents. The objective of these proprietary acids is to achieve the required WSO removal at the highest possible pH to minimize corrosion. The downside is that these buffered products sometimes increase emulsion tendencies and water clarification issues.

Effective mixing of the WSO acid into the total stream is important to achieve effective removal. The acid must mix effectively with the water phase to achieve the target pH and the water and oil phases must mix effectively to achieve mass transfer of the acid molecules from the water phase to the oil phase. Separators are very poor mixers. If the acid is injected immediately upstream of the separator, it is likely that the resulting dispersion of WSO will only reach about 20% of the equilibrium value.

An important feature of fatty acids is that they are surfactants (one water soluble end and one oil soluble end) and tend to stabilize oil-in-water emulsions. These emulsions resist removal by conventional separation technology and fatty acid molecules, bound up in these emulsions, will show up in analyses as WSOs, even though the acid is not truly dissolved in the water**.** Another problem with WSO removal is that they come out of solution as very small droplets.

Materials of Construction Considerations

Lowering the pH of the produced water stream for WSO control may make the stream significantly more corrosive. Where WSOs are expected or possible, materials of construction should accommodate acid injection. Injection through a quill is a must, both to promote efficient mixing of the acid and to keep the concentrated solution away from the pipe wall. Where flow rates may not be sufficient to prevent filming of acid, then carbon steel piping and equipment may need additional corrosion inhibitor treatment or replacement with corrosion resistant alloy (CRA) materials that resist acid corrosion. Increased non-destructive testing and corrosion monitoring is typically undertaken on carbon steel components downstream of the acid injection point to ensure that corrosion rates are being effectively controlled.

Other Treatment Options

Other treatment options exist. Carboxylic acids are readily biodegradable, hence an activated sludge process would likely be effective for land applications, though activated sludge is very intolerant of oil. Biological treatment would be far too heavy for offshore applications. Activated carbon is very effective—and very expensive. Absorption onto other media including clays may be feasible, but requires testing on the individual stream. Research has been conducted to find a chemical reaction solution, including oxidizing the acid with ozone, but until now without commercial success.

WSOs Removal in Other Parts of the World

As mentioned before, WSOs in the GoM are largely polar organic compounds. This is due to the way O&G is measured in the GoM. O&G is defined differently in other parts of the world, and hence the species that count as WSOs are different. In the North Sea, for instance, infrared absorption is the commonly accepted measurement technique. This technique measures light hydrocarbons including BTEX, that EPA 1664 does not measure. Hence, WSO control methods in the North Sea are often focused on the elimination or reduction of discharged produced water volumes in order to control the annual release of BTEX components.