Produced Water Toxicity-An Overview

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"Section 101 of the Clean Water Act (CWA) states that '...it is the national policy that the discharge of toxic pollutants in toxic amounts be prohibited...' To insure that the CWA prohibitions on toxic discharges are met, EPA has issued a 'Policy for the Development of Water Quality-Based Permit Limitations for Toxic Pollutants (49 FR 9016-9019, 3/9/84'." This statement is taken directly from the USEPA post third round policy and strategy statements in the NPDES permit application and are part of the General Permit- GMG290000.

Since 1993 offshore produced water discharges have been tested for toxicity under a general permit restriction and limitation. There have been a number of changes in the testing procedures and minimum requirements for compliance. The procedures and requirements, and how they can affect your operations will be discussed in limited detail.

To understand produced water toxicity testing there are some fundamentals of the test that must be explained. Generally you expose a test organism to produced water over a specified time and record the dose response. Using a statistical program the NOEC (no observed effect concentration) is determined and reported. In this case it is 7-day chronic, static renewal toxicity test using two test species, a vertebrate and an invertebrate, recording the survival and growth values. The survival end point is reported on the annual Discharge Monitoring Report and will be the limiting value.

As originally proposed in GMG 290000 operators were to collect 3-24 hour composite samples and have a 7-day chronic toxicity test with EPA Method 1007.0 ***Mysidopsis bahia*** (mysid shrimp) and EPA Method 1004.0 ***Cyprinodon variegatus*** (minnow). Note: the species of minnow has been changed to the ***Menidia beryllina*** *EPA method 1006.0.* The composite sample was argued to be cost prohibitive and almost impossible to achieve due to the lack of adequate helicopter services and holding times restraints. This was modified in the final permit to a single grab sample.

The test methods that remained did not pose a problem for the operator but became a challenge for the laboratories. Quantity and quality of tests organism was the first and most difficult obstacle to overcome. The shrimp test requires 240, 7-day old organisms and the minnow test has 240, less than 24 hour old organisms. The volume of test organisms required on a weekly basis can be many thousands. It is extremely important that the quality of the test organism not vary from day to day, as any variation can have a dramatic effect on the toxicity of a given produced water sample.

To establish the critical dilution for each platform the following information must be provided by the operator: Diameter of discharge pipe; distance from end of pipe to seafloor; and flow rate last reported on the USEPA annual discharge monitoring report (DMR). The NOEC for either test species cannot fall below this critical dilution value.

The toxicity tests consist of a serial dilution of produced water with 5 concentrations, and a control each with 3-8 replicates. Those concentrations tested are the critical dilution and usually 2 concentrations above/2 below. With each group of tests a standard reference toxicant test is performed on each species. Tests organisms are selected and put into the test chambers. Each chamber is monitored and renewed daily noting the number of surviving organisms, salinity, temperature, and dissolved oxygen.

The most troublesome aspect of this pair of toxicity tests was the requirement for fecundity in the mysid shrimp. The minimum number of fecund females in the control had to be 50% or higher to use the fecundity data as an end point. Fecundity is a prime indicator of laboratory quality in terms of test organisms and technician experience. This parameter caused so many problems that in subsequent permit renewals it has been excluded.

Today toxicity testing is a routine part of each discharging platform. In general there are very few dischargers that fail this requirement. When a failure occurs the most common problem involves completion fluids, specifically, zinc bromide. This product causes toxicity even in very small quantities. Use of treatment chemicals can and will cause toxicity in some cases.

Production chemicals are the next area of toxicity concern. Over use of corrosion inhibitors, biocides, surfactants, oxygen scavengers, and algaecides, and under use of those chemical that help to remove the light end volatiles in the waste stream can all have a direct effect on toxicity.

Sounds like a catch 22 and it is. The problem starts with over use of these chemicals.

As oilfields age they typically produce additional amounts of oil/water mixtures that cannot be adequately separated by the mechanical equipment. Oil & grease and the "no sheen" limitations of the permit increase the reliance on chemicals. Where mechanical systems are extremely undersized permit constraints demand an ever-increasing dependence on chemicals. Unfortunately most of these chemicals can have toxic effects. This toxic effect has permit ramification that mandate action. If chemicals are used excessively, the results could be toxicity and sheen. Too little use of chemicals can cause oil & grease failures and large amounts of volatiles that can cause toxicity.

Excess chemical usage is both costly in terms of operating expenses and potentially toxic thus raising your operating cost with increased testing mandates. Should a platform fail a toxicity test it is required by permit to begin monthly toxicity testing until 3-consecutitive passing tests can be demonstrated. After which that facility must go back to the original requirement of quarterly (annual) testing for one year to demonstrate compliance. If successful a return to annual testing for permit compliance is in order.

But what if toxicity continues past 3-4 months? The cost of testing is in the range of $1400-1600 per test plus the added expense of sampling, freight to the shore base, and freight to the laboratory. In addition there is the cost of determining the cause of the failure and finding an effective solution. In most cases simply adding seawater, enlarging the flow line, adding a diffuser or vertical ports to the system can minimize toxicity. In the case of completion fluid it gets more complicated. The amount of completion fluid that will come out of the formation can vary. This can cause a toxicity failure one month and not the next, usually resulting in large volumes of seawater being added to the system to completely eliminate the problem. Over time completion fluid is flushed out of the formation and the need for seawater is diminished.

Will the EPA fine an operator for a toxicity failure? Most likely-yes. The dollar amount depends on how the problem was handled, and the overall environmental compliance of the offending operation. Do you have to report toxicity test failures? Yes-usually by an out of compliance report sent to the EPA within 24 hours of receipt of the report. Under the NPDES program toxicity is the most serious out of compliance situation prompting immediate action.

What are the potential fines for toxicity out of compliance? The range can vary from $11,000.00 per violation to $11,000.00 per day up to a maximum of $137,500.00. These are civil penalties. Criminal penalties can result in millions of dollars in fines and years in prison. Although this is rare it can and has happened in other industries. This problem cannot be ignored. That is a short overview of the requirements under the general permit. A detailed discussion of the toxicity test is not part of this paper.

Summary

Produced water toxicity is required for every OCS Western Gulf of Mexico produced water discharger. The testing frequency varies from quarterly to annually. Out of compliance increases the testing frequency to monthly until three consecutive months of compliant results are achieved.

Completion fluids are the single greatest source of toxicity followed by excess chemical use. These problems can be solved by the addition of seawater, increasing the size or length of the discharge pipe or by adding a diffuser or vertical ports to the discharge pipe. The charts that establish the critical dilution are used to assist in this process.

Finally a quality laboratory with a good library of standard reference toxicant data and in-house aquaculture is recommended. Inspect the laboratory and ask for reference toxicant data and DMR QA/QC study results. Do not base your opinion of a laboratory by price or the bias of the salesmen. Check out references, ask for qualifications, send spike or duplicate samples and **visit the laboratory**.