

## Comparing Neutral Anolyte Biocide to Other Chlorination Products

Chlorination has been used since 1908 to disinfect water. Because chlorine gas is highly toxic, it has been replaced by hypochlorites. Both calcium hypochlorite and sodium hypochlorite are effective against a wide range of microbes, plus they are non-poisonous to man at recommended dosages. An added benefit is their low cost. Due to their acceptance as disinfectants, hypochlorites serve as standards for testing the effectiveness of other biocides.

Chemically produced sodium hypochlorite is often made by combining  $Cl_2$  with caustic soda (lye) to stabilize the chlorine. Most electrolysis units eliminate the use of lye by instead using membrane technology to remove sodium. Elimination of the lye makes disinfection possible without the high pH associated with sodium hypochlorite. This means that Neutral Anolyte Biocide, being produced at a neutral pH, does not pose a safety issue to oil field workers.

When hypochlorites are added to water, they create a pH-dependent mixture of chlorine, hypochlorous acid, and hydrochloric acid. Depending upon the pH, hypochlorous acid will partly dissociate to hydrogen ions and hypochlorite ions. Hypochlorous acid is a stronger disinfectant than the hypochlorite ion. At a neutral pH of 7, the free chlorine exists as roughly 75% hypochlorous acid and 25% hypochlorite ions. At higher pH levels, the amount of hypochlorous acid decreases while hypochlorite ions increase.

In frac flowback water some of the free available chlorine (FAC) in chlorine-based biocides combines with debris, soluble iron, manganese, ammonia, and other organics to form chloramines. Chloramines are very poor disinfectants. This fact points to the benefit of subjecting the water in a frac pit to aeration using a FracCure aerator. If the frac pit is aerated before FAC is added, the oxygen ramps up aerobic bacteria populations. These aerobes reduce debris levels and form higher mineral oxides which drop to the bottom as sediment. As the aerobes remove food sources, the anaerobes die. Shortly thereafter, the aerobes themselves begin to die for lack of food. The benefit of aeration is that it lets FAC act as a disinfectant as intended, and not be lost as it forms chloramines with the

contaminants in the frac water. Aeration reduces the required volume, and thus the cost, of chlorine disinfectants including Neutral Anolyte. The cost of aeration is more than offset by the savings in the cost of most chlorine disinfectants.

The sum of chloramines and FAC gives the measurement of total chlorine. However, only FAC is of concern because it alone measures the level of killing power. Chlorine demand is the difference between the amount of chlorine added to the water and the total chlorine detectable in the water.

Chlorine does not disinfect the frac water immediately. The time needed to kill various types of microbes varies greatly. Since pH affects the killing power of chlorination, contact time is related to pH.

FAC dissipates quickly in frac water, but it leaves a residual that minimizes recontamination. It is important to maintain residual levels of FAC at all times in frac water to keep bacteria under control. Thus, knowledge of residual levels is important in determining the amount of FAC used initially.

In earlier days calcium hypochlorite was used as the chlorine specie of choice to disinfect frac water. However, calcium interfered with friction reducers. Sodium hypochlorite, though more difficult to apply, was tested and did not interfere with the friction reducers.

Some frac operators have used hypochlorites due to their ease of application, low cost, and effective killing power. However, hypochlorites can dissipate too quickly, requiring retreatment. Also, the reaction of hypochlorites with the naturally occurring elements in frac water such as organic compounds can create disinfection byproducts (DBPs) such as trihalomethanes, a known carcinogen.

Another concern is the corrosion potential of hypochlorite solutions with a free chlorine content of 10 ppm or greater. It is at this point that HCL (hydrochloric acid) levels are too high and corrosion begins. If sufficient contact time can be arranged, there is no need to apply hypochlorite in excess of 10 ppm.