

Selection, Screening and Field Trial of Calcium Hypochlorite to reduce bacteria population in freshwater storage tanks in Williston, North Dakota, USA

James R Fajt
Schlumberger Production Chemicals
6350 W. Sam Houston Parkway N
Houston, TX, 77041 USA

Stephanie Iwuala
M-I SWACO Production Technologies
12 E Dakota Parkway
Williston, ND 58801USA

Alyn Jenkins
Schlumberger Production Chemicals
Pocra Quay, Aberdeen,
AB11 5DQ, United Kingdom,

Jarrod Hastie
M-I SWACO Production Technologies
12 E Dakota Parkway
Williston, ND 58801USA

ABSTRACT

Fresh river water is used to flush production lines to control halite deposits in unconventional carbon steel wells near, North Dakota, USA. Raw river water is stored in 400 (bbl) fiberglass tanks and is treated with oxygen scavenger before injection. Quarterly testing showed high levels of bacteria. The remote location, cold seasonal temperatures, tank design, USA EPA regulations and restricted access limit treatment options to biocide application in solid form added to tank tops. To cover all reasonable product candidates, range of both liquid and solid biocides were tested on site to determine an effective formula and dose. Selection was based on multiple factors including, effect on bacteria, compatibility with water, worker safety, product label restrictions and cost. Based on the results, calcium hypochlorite was selected for tank treatments. Hypochlorite is corrosive, however testing showed acceptable corrosion rates (<3mp/y) against carbon steel at target treatment rates for extended periods of time. Tanks were dosed not to exceed 3 ppm free available chlorine residual. Bacteria monitoring showed that bacteria levels in the tank were reduced by as much as 5 log to non-detectable levels post quarterly treatments with calcium hypochlorite.

Key words: Bacteria, hypochlorite, corrosion, production, biocide, non-oxidizing, oxidizing,

INTRODUCTION

This study describes an effort to find a method to control bacteria in 130 remote freshwater fiber glass storage tanks with an effective low-cost, convenient treatment method. Freshwater, in this application, is being used to control halite scale formed in the production from unconventional oil wells in the Williston, North Dakota, USA area. The water is sourced from local freshwater rivers and trucked to location and stored in 400 barrel (bbl) freshwater tanks. The water stored in the tanks is injected continuously, and the tanks are refilled on a variable schedule. This results in the tank volumes being

replaced every 3-5 days. Bacteria population in the water storage tanks have increased over time and range from tens of thousands (4 log) to hundreds of millions of (9 log) living bacteria per milliliter. Bacteria growth in the tanks is a concern for the production operator. Bacteria population reduction and control is conducted to reduce the occurrence of microbial induced corrosion and valve failure from biofilm or water injection line clogging.

All reasonable methods of chemical bacteria management of the freshwater tanks were considered including: sighting totes of biocide for continuous injection, water source and water delivery truck treatment, and tank batch treatments. The number of tanks, limited resources, limited access, remote location, and tank operation made the selection, supply, and application of a biocide to control bacteria challenging. The fields are in an area that has winter temperatures of -40C and each tank requires 30 to 90 minutes travel time to access. The remote, unattended tank sites require that the tank treatments be automated or have minimal working hours on site. The cost and tank design does not allow for the placement of liquid biocide totes and meter pumps to apply biocide. Additionally, any liquid product needs to be freeze protected. The only access to apply biocide is via a catwalk to a hatch at the top of the tanks. All the site-specific factors lead to the conclusion that a solid biocide or concentrated liquid be applied by hand to the top of the tanks.

EXPERIMENTAL PROCEDURE

Tank Biocide Selection

The options for a potential biocide treatment of the tank water are regulated by USA Federal Insecticide, Fungicide, and Rodenticide Act.¹ This law requires that biocides used in the USA must have an approved USA environmental Protection Agency label. Furthermore, the application to the environment must appear in the "Direction for Use" section of the biocide label. The biocide must also be chemically compatible with the physical asset when in contact with oil and gas production streams. Biocides formulated with glutaraldehyde or tetrakis hydroxymethyl phosphonium sulfate (THPS) were considered and rejected because both are liquid and would require repeat application to control high numbers of bacteria. The options for product formulation were limited to DBNPA (2,2-dibromo-3-nitrilopropionamide), calcium hypochlorite and quaternary ammonium-based products.

After the candidate biocides were selected, tests were conducted to determine if they would be effective on tank bacteria. To determine the amount of biocide needed to control tank bacteria an onsite biocide kill study was conducted. The corrosion risk of calcium hypochlorite was also assessed.

Six 20-liter samples of tank water were collected in closed containers. The containers were transported to a local laboratory and allowed to come to room temperature of 25 C. Dose rates were selected based on product label rates. The biocides tested were alkyl dimethyl benzalkonium chloride (ADBAC) at 300 ppm active, didecyldimethylammonium chloride (DDAC) at 300 ppm active, DBNPA at 10 ppm active, tributyl tetradecyl phosphonium chloride (TTPC) at 350 ppm active and calcium hypochlorite 150 ppm produced a free chlorine residual (FAC) of 3 ppm. FAC is defined as the concentration of residual chlorine in water present as hypochlorous acid (HOCl), and/or hypochlorite ion (OCl⁻). The presence of an FAC in water indicates that a sufficient amount of chlorine was added initially to the water to inactivate the bacteria and that the water is protected for a short period from recontamination during storage. The untreated endemic population in each container was measured using a bacteria metabolism method.² Bacteria population was measured after 30 minutes, 5 hours, 24 hours, and 72 hours after treatment. The results of the biocide testing on tank water are shown in figure 2.

Bacteria Metabolism Test Method

The method determines total living planktonic bacteria in a sample of water. Samples of fluid to be tested for bacteria are processed with the new method within 8 hours of collection. Samples can be collected and processed aerobically or anaerobically but are required to be cooled to <38°C for analysis. Typically, 50 ml of water is isolated from a sample in a syringe. The sample is then passed through a 0.2-micron filter which captures the bacteria. After the bacteria are captured on the filter, they are exposed to a solution that contains an enzyme substrate dye complex. If the bacteria are living, a phosphorescent dye

will be released. The dye is then extracted by rinsing the filter into a cuvette where dye concentration is read with a fluorometer (Figure 1). The level of fluorescence recorded is directly proportional to the bacteria concentration. The method includes a normalization calculation that adjusts a sample reading value for, an analytical blank, the volume of samples filtered, the exposure time to the enzyme substrate complex and the temperature of the sample. The standardized value is then converted using a propriety algorithm developed from previous method calibrations to either colony forming units / ml (cfu/ml), or equivalent serial dilution bug bottle turns using a mobile application or computer program (Figure 1). Each batch of tests includes a set of control bacteria samples to ensure the method is being performed correctly. Typically, it takes 30 minutes to analyze a water sample but 10 – 20 samples can be analyzed concurrently.

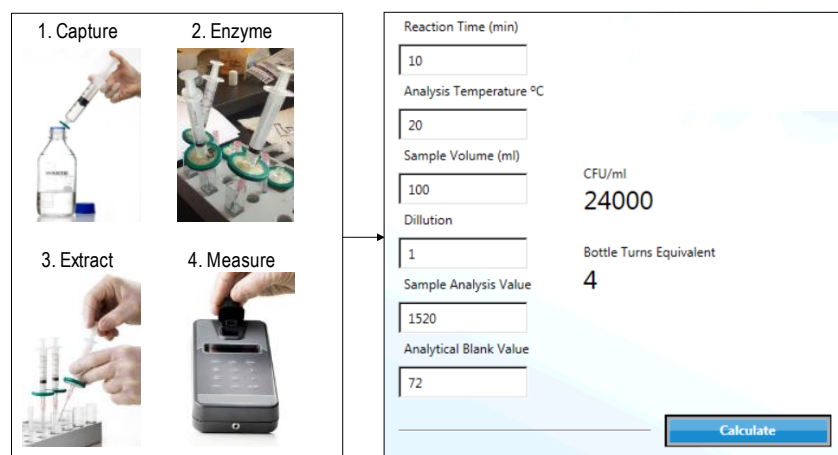


Figure 1: Schematic of Monitoring Method and Conversion Software (Mobile Application)

Evaluation of the Corrosion Risk of Calcium Hypochlorite.

The results of the on-site biocide kill study showed that calcium hypochlorite was effective to rapidly reduce and control bacteria populations. Calcium hypochlorite is the preferred treatment because it is supplied as highly concentrated tablet that is easily stored, transported, and applied. However, calcium hypochlorite is known to be corrosive in freshwater. The fiberglass tanks are not susceptible to corrosion from hypochlorous acid but do have a carbon steel lining and fitting that can be affected by hypochlorous acid. Therefore, a test was conducted to determine the corrosive risk of dosing calcium hypochlorite in fresh river water. Water for the corrosion study was collected from the river water source and stored in five, 5-gallon buckets with lids at room temperature. One additional bucket was filled with municipal drinking water as a control. Five carbon steel corrosion coupons (UNS G10180) were suspended on a monofilament line in each bucket 5 cm from the sides and 5 cm from each other, and in the center of the height of the bucket. Buckets were dosed with calcium hypochlorite to create an instantaneous measured free available chlorine level (FAC) of 0 ppm, 2 ppm, 5 ppm, 20 ppm and 50 ppm. Once per week for 5 weeks one corrosion coupon was removed from each bucket, and in each bucket fresh calcium hypochlorite was added to adjusted FAC to selected dose level. Corrosion coupons were cleaned, inspected, and corrosion rates calculated using ASTM-G1 standard methods according to Equation 1.

$$\text{Corrosion Rate (mm/yr)} = 87563 \times W / (A \times D)^3 \quad (1)$$

Where: *W* is mass loss (grams), *A* is coupon area (cm²) and *D* is coupon density (g/cm³)