Zinc Removal From Produced Water

12th Annual Produced Water Seminar
January 16-18, 2002
Houston, Texas

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ABSTRACT

One of the principle challenges in the completion of "High Pressure" wells are the completion activities associated with an over balanced situation. Normally, when an overbalanced situation occurs, the potential to loose high-density completion fluids such as zinc bromide, into the formation can quickly become a reality. The loss of high density completion fluids into the formation results in 1) an adverse economic impact due to reduced "buy back" of the completion fluids and 2) potential to discharge priority pollutants into receiving waters.

The United States Environmental Protection Agency (USEPA), in accordance with the Federal Register NPDES Permit GMG290000, regulates the discharge of produced water into federal waters. For well treatment, completion and work over fluids, the discharge of priority pollutants is prohibited except in "trace amounts". Toxicity testing determines if a known priority pollutant causes a specific discharge failure. In the event of such failures, the most common cause is a completion fluid, such as zinc bromide. Regrettably, nominal loses of zinc bromide result in toxicity discharge failure, thus violating environmental discharge regulations.

This paper presents data generated from an offshore treatment process, which incorporates a unique treatment technology involving selective precipitation, flocculation and filtration of contaminated waste fluids. To comply with current environmental regulations, the operator performed bench test and evaluated various contributing factors to determine an acceptable total zinc concentration in the effluent prior to discharge.

INTRODUCTION

Kerr McGee Oil and Gas Corporation's daily production on the Main Pass 108-A platform exceeds 40 MMCF of gas, 1,400 barrels of oil/condensate and 240 barrels of produced water. Due to a loss of approximately 1,200 barrels of 17.9 ppg zinc bromide completion fluid into the formation, the produced water contains varying concentrations of total zinc. The concentrations of zinc in the produced water ranges from greater than 100,000 ppm to 800 ppm depending on water production, commingling of produced fluids and/or production volumes. Currently, approximately 230 barrels of produced water are generated on a daily basis from five (5) wells. The produced water requires treatment and processing in order to meet the NPDES Permit GMG 290000, specifically priority pollutants (total zinc). Zinc concentration analyses are conducted at various sample points throughout the production facilities vessels. Listed below are the main sample points for collection and analysis of zinc in the produced water:

- Wellhead
- Low Pressure Separator, High Pressure Separator or Test Separator
- Skimmer
- Floatation Cell

The on-site zinc test employed is the "EM Quant Zinc Test" methodology, which is an orientating rapid test for the semi-quantitative determination of zinc ions. This is a field test method that allows for immediate results. Periodic samples are collected and sent to a third party laboratory to independently confirm the treated produced water is in full compliance with discharge standards.

PROCESS DESCRIPTION

The treatment objective consists of treating produced water containing varying concentrations of zinc below current NPDES discharge criteria, currently established at "trace amounts". For the purpose of setting a quantitative zinc concentration, Kerr McGee completed a study of the zinc concentrations in the produced water and the toxicity factors. The study revealed that many factors (water flow rate, zinc bromide concentrations, etc.) are required to establish a maximum zinc discharge concentration.

The treatment process was designed to accommodate for variations in produced water volumes and varying influent zinc concentrations. Effluent from the well(s) is directed into the operator's separator system and the resulting produced water stream is retrieved from the separator water leg. Produced water containing varying concentrations of zinc is diverted into a chemical mix tank, which consist of two (2) compartments equipped with hydraulic operated mixers. The chemical mix tank is also equipped with a chemical injection manifold system allowing the operator to inject treatment chemicals without direct personnel contact. The initial treatment phase involves the addition of 25% sodium hydroxide, which allows the pH of the produced water to increase to 9.0, which is the prescribed level for optimal selective precipitation of zinc ions. During the addition of sodium hydroxide the produced fluids are constantly agitated to ensure a thorough reaction. The sodium hydroxide is introduced to the produced fluids using a chemical resistant diaphragm pump equipped with a flow meter in order to optimize the chemical usage requirements. A proprietary zinc polymer is then added to enhance flocculation of the zinc precipitant and further precipitant any residual soluble zinc ions.

The specific chemical reaction that occurs in the "Zinc Removal From Produced Water" process is neutralization of the dilute hydrobromic acid (HBr) with sodium hydroxide (NaOH) and the precipitating reaction of zinc (Zn) with NaOH.

At a pH of 4.0, there exists dilute HBr and ZnBr ions in solution. The addition of NaOH creates the following reaction:

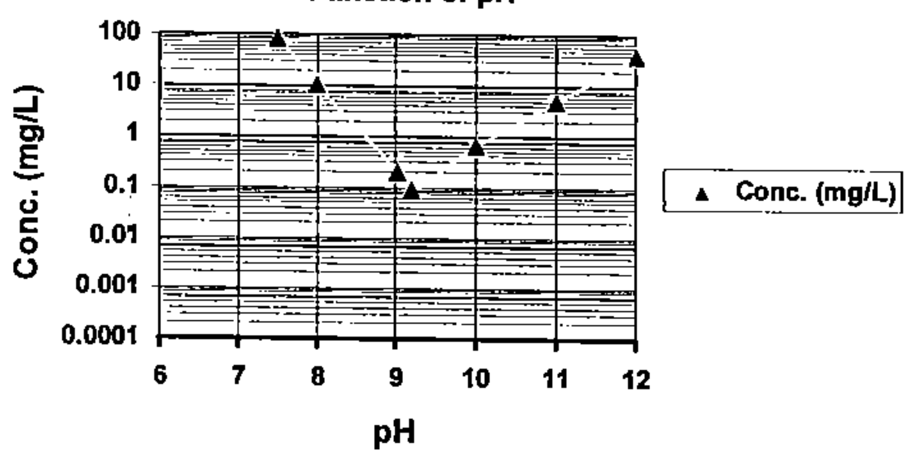
$$ZnBr + HBr + NaOH \longrightarrow NaBr + H_2O + Zn$$

The products of the neutralization reaction are water and a salt (NaBr). Not only must hydroxyl (OH) ions be provided to neutralize the dilute acid HBr, but also OH ions must be provided to form zinc hydroxide. Therefore, at a pH of 8.5 to 9.0 (actually, a pH of 9.2 is the theoretical optimum for zinc hydroxide insolubility), the reaction is:

$$ZnBr_2 + 2NaOH \longrightarrow 2NaBr + Zn(OH)_2$$

Figure 1 illustrates the solubility of zinc hydroxides as a function of pH. Specifically, two (2) molecules of NaOH are required for each Zn ion. Interfering compounds with this reaction are principally organic chelates or complexing compounds such as: ammonia, amines, EDTA, gluconates, citrates, etc. If other metals are present such as iron, copper, aluminum or nickel, additional OH ions are required to form the metal hydroxides of these inorganic constituents as well.

Figure 1 - Solubility of Zinc Hydroxides as a Function of pH

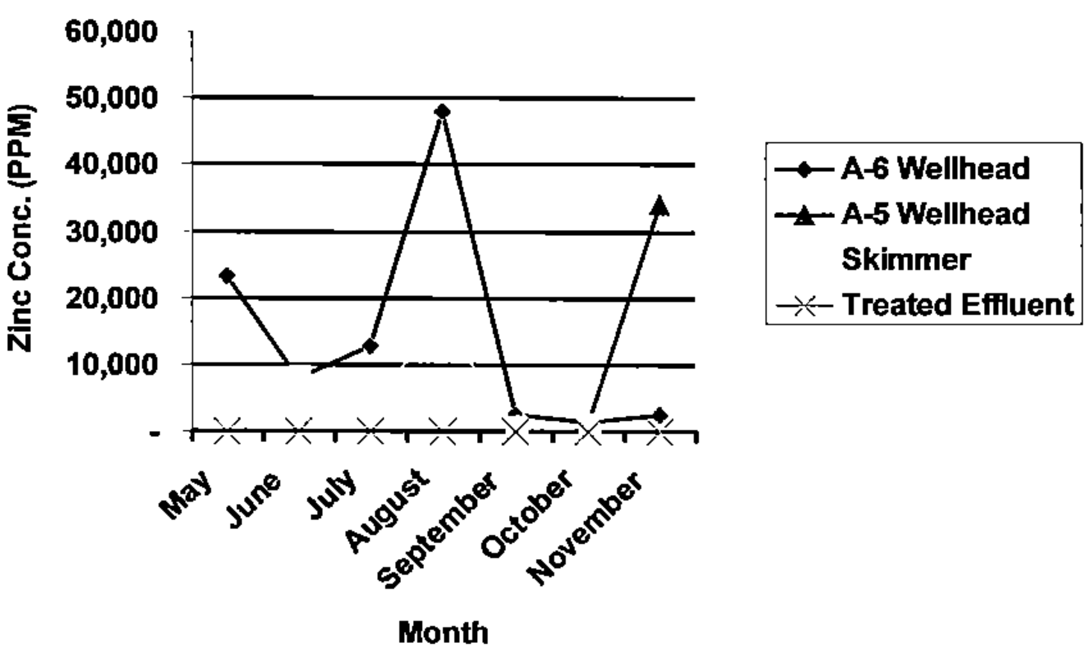


Upon completion of the chemical treatment phase, the treated produced water is flowed to a recessed chamber filter press pre-coated with diatomaceous earth. This step allows removal of the zinc precipitant and forms dry, high solids, zinc filter cake. The resultant filtercake solids are conveyed into cuttings boxes for storage then transported off-site for disposal and/or recycling The treated effluent is discharged into a clean water tank for confirmation that it is below the discharge criteria. Samples of both influent and effluent fluids are collected and analyzed using the EM Quant Zinc Test Method.

The on-site zinc test, with a method detection limit of 5 ppm, is suitable for testing the waste fluids using analytical test strips and reagent for the detection and semi-quantitative determination of zinc ions. The basis of the test methodology is the formation of the red complex from dithizon and hydrozinc cations. The success of the zinc test is attributed to the fact that the dithizon is stable in the test zone. Since dithizon reacts with many other metal ions, sodium hydroxide solution must be added to precipitate any interfering ions and to transfer Zn^{+2} into zincate. The test is relatively simple and quick. The test vessel must be rinsed several times with the test solution and filled with 5 milliliters of test solution. Ten drops of reagent is then added, and the vessel is agitated to ensure a thorough mixing. A reaction zone of the test strip is then immersed in the solution for approximately one (1) second. The excess liquid is removed from the test strip and compared to the color scale to determine the zinc concentration. In the event the zinc concentration is above the color strip scale the solution must be diluted.

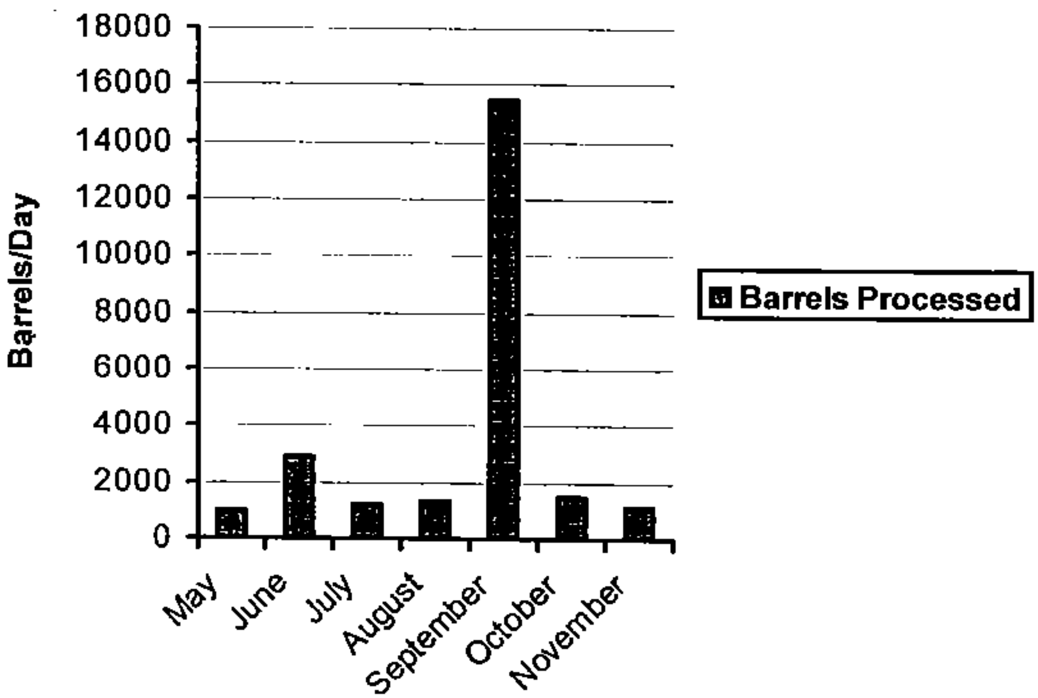
Once the treated water is tested and confirmed that it meets discharge criteria, it is pumped to the floatation cell for disposition overboard. Figure 2 graphically depicts influent concentrations and treated effluent zinc concentrations over the past 195 days.

Figure 2 - Zinc Concentration Levels



The results of the "Zinc Removal From Produced Water" treatment has been highly successful with an estimated 86,000,000 grams of zinc initially lost in the formation and 77,600,00 grams removed from the produced water treated. This correlates to 90.2% of the total quantity of zinc lost being recovered. A total of 24,463 barrels have been successfully processed over the last 195 days as shown in Figure 3.

Figure 3 - Monthly Treated Volumes (bbls)



SUMMARY AND CONCLUSIONS

Treatment of completion fluids/produced water for priority pollutants on the platform has resulted in the accomplishment of several significant objectives. First, the operator has not exceeded discharge criteria as it pertains to priority pollutants regulated under the NPDES General Permit. Second, the platform has been able to operate continuously without interruption due to the Zinc Removal Treatment System and third, cost savings are recognized over the traditional method of transporting and disposing of the waste fluids onshore. The loss of high-density completion fluids is very common in "over balance" situations; however the use of this treatment system allows operators to maintain production while achieving full regulatory compliance.

The above mentioned treatment process was successful even with the presence of varying zinc concentrations and large fluctuations in volumes. In summary, the operator was able to operate within current EPA NPDES compliance guidelines while continuing to maintain maximum production.