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Enhancing Sustainable Oil and Gas Operations: Produced Water Treatment Using Biological Oxidation

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Abstract

In navigating the imperative of sustainable practices, the oil and gas industry faces a growing need for efficient and environmentally conscious produced water management. Challenges in produced water disposal encompass regulatory compliance, environmental considerations, induced seismicity risks, and the pursuit of economically sustainable solutions. There is a compelling need to explore efficient treatment methods that encourage the reuse of produced water while simultaneously providing long-term storage solutions to alleviate the strain on freshwater resources.

Biological oxidation, employing microorganisms to metabolize organic pollutants, has emerged as a promising and sustainable approach for produced water treatment. Applied at the secondary treatment stage, this technology significantly reduces contaminant and suspended solid concentrations post-primary treatment in the tank battery. The aim of this treatment method is to decrease the biological load in the produced water by introducing facultative microbes that prevent the pit from souring and halting H2S production. Additionally, aeration of the produced water impoundment is essential to introduce dissolved oxygen (DO) and enhance the performance of robust microbial strains.

The introduction of aeration proved instrumental in enhancing produced water treatment, facilitating the efficient dispersion of chemical amendments within impoundments through enhanced recirculation and mixing. Biological oxidation treatment resulted in below detection levels (BDL) of H2S, and post-treatment analysis revealed the absence of sulfate-reducing bacteria (SRB) activity, preventing souring in saltwater disposal (SWD) compared to conventional biocide or flop and drop treatments. Key indicators, such as dissolved oxygen and oxygen reduction potential (ORP), crucial for water stabilization, remained consistently stable over a six-month period without requiring further intervention.

The introduced biological oxidation process represents a cost-effective solution for treating produced water from diverse oil and gas extraction operations. A notable advantage is the absence of chemical or polymer sludge residue in the water impoundments, contributing to a cleaner treatment outcome. Beyond immediate benefits, biological oxidation plays a pivotal role in achieving long-term stabilization, fostering an efficient reuse program, and presenting a viable alternative to conventional water disposal methods.

Introduction

Produced water, a byproduct of oil and gas extraction, is a complex mixture containing suspended solids, hydrocarbons, diverse chemicals, and a range of degradable organic compounds. These constituents can potentially lead to significant quality and stability issues if not adequately managed (Veil et al., 2004). The composition of produced water varies significantly by formation, within plays, from well to well, and over time as new wells clean up from completion operations. Consequently, these components need to be treated or managed to improve water quality and stabilize the water for reuse. Produced water disposal by injection is a common method for produced water management in oil and gas production, but it presents several environmental challenges. Improper well integrity or mechanical failures can lead to groundwater contamination due to the high salinity of produced water. Furthermore, large volume injection can induce seismicity in geologically susceptible regions (Ellsworth, 2013). Surface spills from well sites or during transportation pose a significant risk of soil and freshwater contamination. Additionally, if not properly handled, volatile organic compounds and other contaminants present in produced water can contribute to air and water quality degradation.

Advancements in cost-effective produced water treatment technologies have enabled the oil and gas industry to utilize produced water for hydraulic fracturing, enhanced oil recovery, waterflooding, and drilling operations. However, secondary treatment is often necessary before using produced water for any application beyond re-injection. The level of treatment required depends on the intended use and the specific characteristics of the produced water itself. Environmental regulations play a crucial role in determining how produced water can be managed and reused. Additionally, the economic feasibility of treatment and transportation also influences the ultimate use of produced water.

As shown in **Fig. 1**, typical produced water treatment can be divided into primary (1º), secondary (2º) and tertiary (3º). Primary treatment involves removing oil and total suspended solids (TSS) from the water phase in the tank battery utilizing either mechanical or chemical separation techniques. TSS are suspended particles in produced water of microscopic and macroscopic sizes that consist of either organic or inorganic matter. At this stage, an emulsion breaker is often introduced chemically to accelerate the separation process (Jiménez et al., 2018). Mechanical treatment employs equipment like hydrocyclones, desanders, and plate pack interceptors (Gamwo et al., 2022). A further stage of separation aims to remove impurities that could cause scaling in the wellbore during re-injection in SWD wells. Secondary treatment focuses on reducing the chemical and biological load in produced water through various remediation processes, such as using oxidizers, biocides, aeration, and biological clarifying agents. Oxidizable matter in produced water is measured by chemical oxygen demand (COD) or biological oxygen demand (BOD). COD reflects the total oxygen needed to chemically break down all organic materials, while BOD focuses on the oxygen consumed by microbes during biodegradation Usage of oxidizers or providing additional aeration increases the dissolved oxygen (DO) concentration in the produced water, which aids in degrading the organic load. In the oil and gas industry, tertiary treatment (like filtration using membranes and filter media) to reduce the total dissolved solids (TDS), is often avoided due to the costly nature of these treatments. Produced water's TDS include dissolved salts and organic matter, which can lead to scaling, corrosion and reduce treatment effectiveness. However, new and promising technologies are emerging that may make these methods more economically feasible in the future.

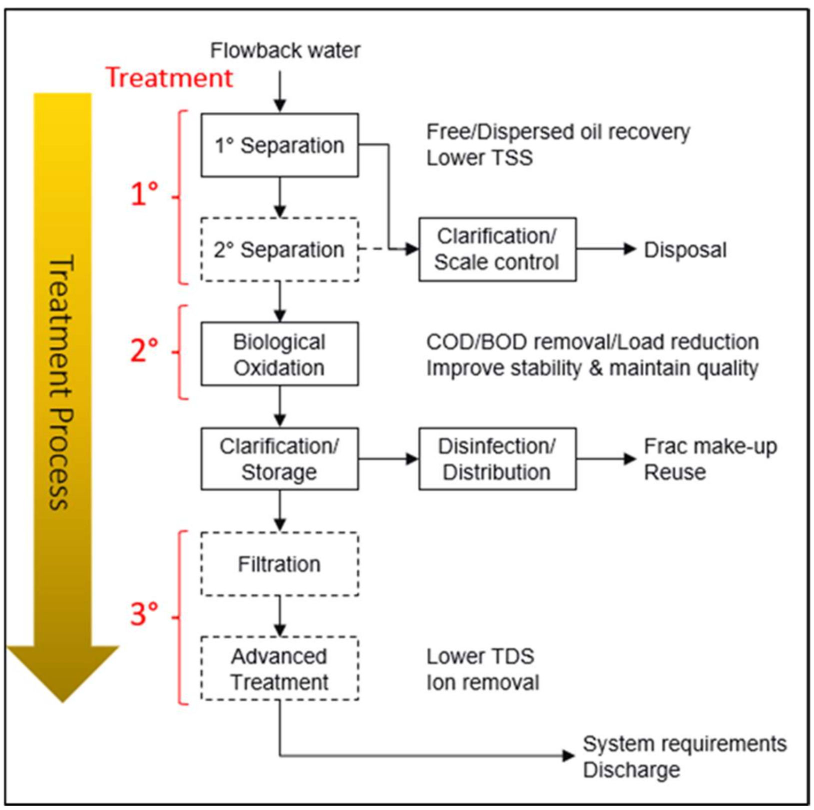

Fig. 1—Typical treatment process for produced water (modified from (Bailey, 2015)).

The scale of produced water treatment varies depending on the composition of the water and management needs (Lin et al., 2020). Proper treatment allows for recycling and reuse, addressing challenges like increased disposal costs and reduced freshwater availability in drought-prone regions (Kondash et al., 2018). Currently, large water recycling facilities can treat and store millions of barrels of produced water. However, concerns about long-term storage and potential fouling during storage often lead to saltwater disposal instead of recycling.

This paper discusses biological oxidation technology, which degrades organic matter and contaminants in produced water. This treatment stabilizes the water for long-term storage and reuse. Biological treatment effectively removes a variety of contaminants, including hydrocarbons, metals, and nutrients, and adapts to various environmental conditions like salinity, pH, and temperature ((Sholtes et al., 1997), (Katsoyiannis & Zouboulis, 2004)). The economic benefits and ability to handle diverse contaminants make biological treatment an attractive option (Lusinier et al., 2019).

While other treatment methods like physicochemical treatments, ozonation, and filtration can be effective, they often come with high operational costs or generate residuals that can harm water quality. Additionally, their effectiveness might diminish over time (Abujayyab, 2022). Biological oxidation offers various treatment approaches, including fixed-film, anaerobic, suspended growth, and bioreactor membrane processes. A key challenge for biological treatment in the oil and gas industry is salinity, as brine can hinder microbial activity (Kargi, 1996). For such cases, different nutrient packages are implemented depending on the microbes and condition of the water to aid the microbial organisms for degrading the chemical and biological load. Additionally, if there is a hydrocarbon film present on the top of the water pit acts as barrier for effective atmospheric oxygen transfer that beneficial microbes require to degrade the overall load (Boeglin, 2015). Therefore, additional oxygen needs to be delivered either chemically or mechanically to improve the water DO levels. This oxygen rich environment aids to control the sulfate reducing bacteria and thus prevent water from spoiling during storage (Eyitayo et al., 2023). This paper aims to enhance understanding of biological oxidation treatment and highlight the technology as a solution for recycling, stabilizing, and enabling long-term storage of produced water.

Methodology

Biological aeration process significantly improves water quality by degrading organic matter and contaminants, reducing oxygen consumption, and enhancing storage stability. Pre-treatment water samples are collected to determine the BOD using the standard BOD5 method 5210B. This analysis helps establish the initial biological load and the time required for its degradation (**Fig. 2**). Sequential testing during treatment monitors changes in oxygen demand, allowing for the estimation of total oxygen needs and the degree of reduction necessary for long-term storage. Throughout the treatment process, technicians perform on-site and laboratory monitoring to assess treatment performance and ensure effectiveness. To understand biological oxidation treatment, it is important to know the role of the components involved in the process.

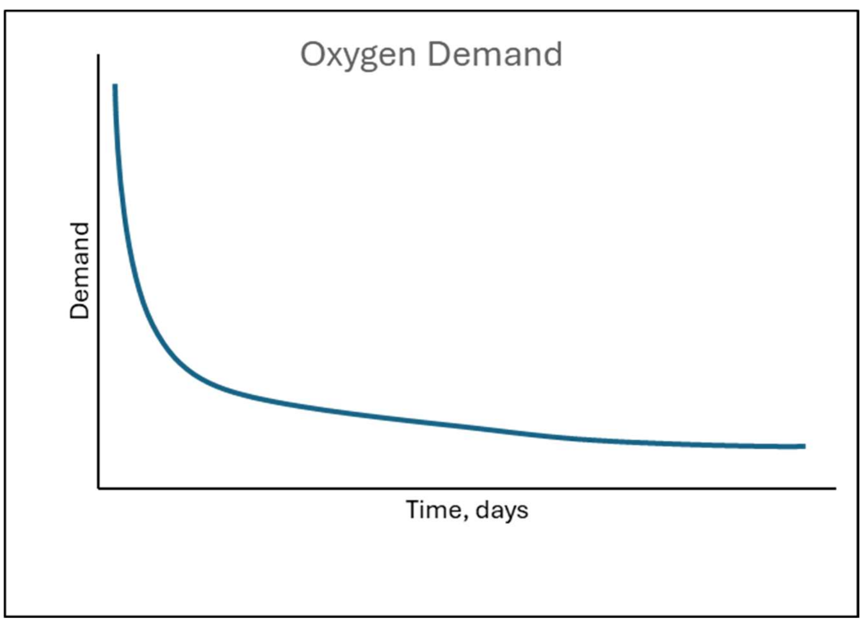

Fig. 2—Oxygen demand vs. Time.

Microbial Bioremediation

Flowback and produced water exhibit variations in both total microbial load and types of microbes present. These variations may reflect the effectiveness of the biocide program in controlling bacteria introduced during well completion and any prior interventions. Some degradable chemicals in the water can potentially stimulate bacterial growth. If not managed, this can lead to problems like blooms of sulfate-reducing bacteria (SRB), production of hydrogen sulfide (H_2S), and a phenomenon known as souring. SRB are anaerobic bacteria, meaning they thrive in oxygen-depleted environments. They utilize sulfate instead of oxygen for anaerobic respiration to degrade organic matter.

The **Eq. 1** below illustrates sulfate reduction, a process undergone by SRB. In this process, they utilize sulfate as an electron acceptor and organic matter as an electron donor, ultimately producing hydrogen sulfide (H_2S). H_2S is a toxic and foul-smelling gas responsible for the characteristic odor of rotten eggs, commonly encountered in oil and gas wells or produced water storage tanks due to SRB activity.

$$SO_4^{2-} + \text{Organic matter} + \text{SRB} \rightarrow H_2S + CO_2 + H_2O + \text{other byproducts} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

The observed Oxidation Reduction Potential (ORP) of untreated produced water typically falls within the range of -300 mV to -100 mV (as seen in **Fig. 3**). These conditions favor microbial sulfate reduction of aromatic compounds, leading to increased H_2S production by SRB. This biological oxidation treatment aims to counter this by raising the ORP to positive values, creating an unfavorable environment for SRB to thrive. They achieve this by using their proprietary biological product, BSP-1622. BSP-1622 contains naturally occurring facultative anaerobic species selected for their ability to reduce Chemical Oxygen Demand (COD) and raise ORP. These beneficial microbes degrade the organic load in the water, which is the primary food source for SRB. This creates a hostile environment, making it difficult for SRB to survive.

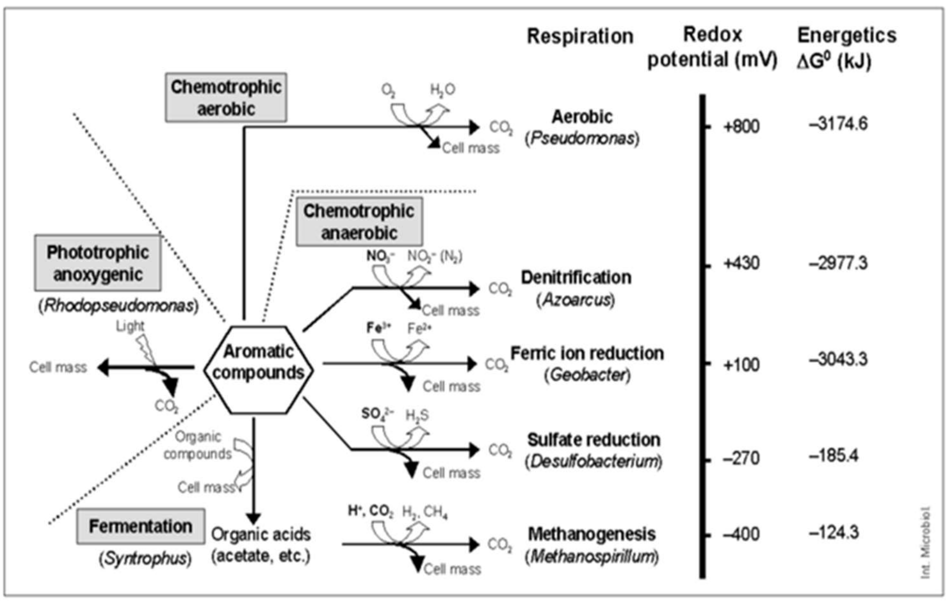

Fig. 3—Microbial utilization of Aromatic compounds with corresponding redox potentials (Díaz, 2004).

Building upon the below **Eq. 2**, we can see how the beneficial microbes break down the organic load in produced water into carbon dioxide and water. This reduces the overall chemical and biological load without generating harmful biofilms. Additionally, these microbes produce biosurfactants that improve water injection rates and remove oil from solid surfaces. Biosurfactants achieve this by reducing surface and interfacial tension in the fracturing fluid (frac water).

$$\text{Organic matter} + O_2 + \text{Beneficial microbes} \rightarrow CO_2 + H_2O + \text{other byproducts} \dots\dots\dots\dots\dots\dots\dots (2)$$

Biological Oxidation process

Flowback and produced waters contain various oxidizable organic compounds, some readily metabolized by bacteria. If left untreated, these biodegradable components can fuel the growth of sulfate-reducing bacteria (SRB), leading to H_2S production and sulfide solids formation during storage. Sulfide solids can cause problems like pipe corrosion and equipment damage. In this study, ORP and DO are used extensively to perform qualitative analyses of produced water apart from the other parameters monitored. ORP measures a substance's capacity to either gain or lose electrons. A positive ORP indicates an oxidizing agent, while a negative value suggests a reducing agent (Horne, 1994). Essentially, it reflects a solution's tendency to accept or donate electrons. ORP is commonly used in fields like water treatment and environmental monitoring to assess water quality and disinfection effectiveness. A higher ORP value indicates that the bacteria can effectively degrade and decompose the organic matter as well as other contaminants present in the water body. DO refers to the amount of oxygen gas present in water. Factors such as temperature, atmospheric pressure, and microbial activity influence DO levels. High DO levels generally indicate good water quality, while low levels can signal potential environmental issues.

During the initial stages of the biological treatment, the initial ORP reading can be high while DO levels are low. This occurs because the microbes are rapidly consuming oxygen to degrade the organic matter and reduce the biological load in the water. Once the majority of the biodegradable load is removed, the oxygen demand and degradation rate slow down significantly. Complete degradation of all organic material can take a very long time.

To address low DO levels, Flex-Chem has designed MOXI-AIRE (shown below in **Fig. 4**), a portable aeration unit that delivers supplemental oxygen crucial for microbial activity. This aeration unit has a capacity to process approximately 65,000 barrels of process fluid and can be easily scaled to accommodate larger volumes.

Fig. 4—MOXI-AIRE modular water conditioning unit and typical setup.

This type of secondary treatment for water recycling utilizes biological oxidation to eliminate degradable fractions and enhance water quality. Complete removal of all oxidizable organics is not necessary; some residual organics cannot be utilized by microbes and remain as residual oxygen demand. To overcome challenges associated with brine, which hinders microbial activity, a customized nutrient package is used to boost microbial activity. This nutrient package also contributes to mitigating H_2S production and increasing DO levels in produced water. The biological water treatment process creates unfavorable conditions for SRB growth and removes the biologically degradable portion of the oxidizable organics. This treated water achieves stability for storage in pits, enabling reuse.

Results and discussions

The results discussed in this paper are from a biological oxidation treatment (in **Fig. 5**) supplemented with continuous aeration, implemented at a produced water recycling facility in Kingfisher County, Oklahoma, during the summer months (treatment start date mid-June). Aeration plays a crucial role in the treatment process by providing recirculation and ensuring sufficient mixing of the microbial amendment package with the produced water in the treatment pit. In the following results, we will discuss the effects of DO, ORP, rain events, and temperature on the key parameters for produced water storage: BOD, oil and grease content, and H_2S concentration.

(a)

(b)

Fig. 5—(a) Aerial view comparison between pre-treatment (left) and 4th day of treatment (right) showing the surface condition of the pit. (b) Glass bottle visual comparison between pre-treatment (left) and 4th day of treatment (right) samples, highlighting changes in color or clarity of the water.

DO and ORP stabilization

Pre-treatment samples indicated that the DO level in the produced water was less than 1 ppm. During the initial treatment stage (**Fig. 6**), DO levels rose to 2 ppm and remained stable as the microbes consumed the organic matter (oil and grease microemulsions) present in the water. This stable DO consumption suggests a consistent breakdown of degradable organic compounds. By the end of the treatment stage, the biological load in the produced water had decreased, allowing DO levels to rise closer to 3 ppm. Even after treatment, the beneficial microbes and residual nutrients likely continued to contribute to improved water quality. The final stage, where DO levels stabilized between 4-6 ppm, suggests a significant reduction in the degradable organic load, minimizing the risk of future water spoilage.

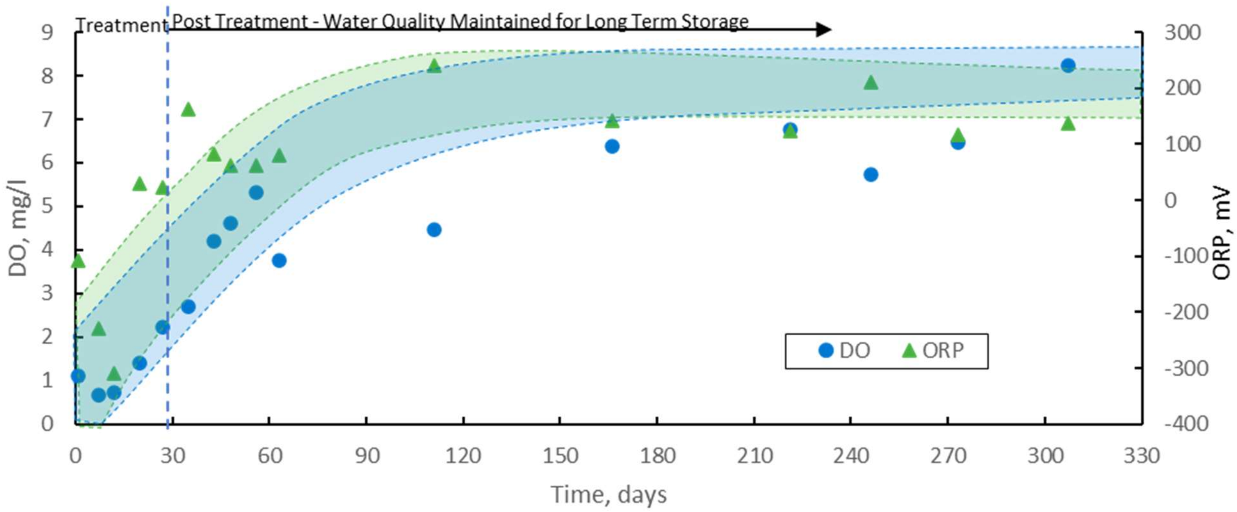

Fig. 6—DO and ORP trends stabilized after biological oxidation treatment for more than 300 days.

As shown in the diagram by Díaz, 2004, a negative ORP (around -200 mV) is unfavorable and promotes SRB growth, leading to H_2S production and water spoilage. Our pre-treatment samples exhibited an ORP below -300 mV, indicating ideal conditions for SRB activity. Introducing beneficial microbes alongside a strategic nutrient selection can curb SRB activity. The addition of the beneficial microbes along with the nutrient package provided the necessary resources for their growth, immediately boosting the ORP to 0 mV and creating favorable conditions for the reduction of organic compounds by the beneficial microbes. Post-treatment, the ORP further increased to +100 mV. As the degradable load reduced over time, there was a noticeable increase in the ORP levels for the treatment pit. Another trend observed is that with the drop in average temperature, the ORP levels improve slightly (from +100 mV to +200 mV). Lower average temperatures can also contribute to a slight increase in ORP levels, possibly due to increased oxygen solubility in colder water. These results suggest that a combination of ORP exceeding +100 mV and DO exceeding 4 ppm can indicate successful biodegradation of organic matter, leading to long-term storage stability (over a year) and potential reuse of the treated produced water.

Effect of Temperature

Data indicates that water quality deteriorates during summer months due to increased microbial activity. Most microbes, particularly SRB, remain dormant in produced water during winter or colder months. As temperatures rise to favorable conditions for SRB growth (between 20°C and 45°C) (68^0 F to 113^0 F) from May to September (**Fig. 7**), coupled with the negative ORP (-200 mV), fouling is observed through H_2S production in the pre-treatment sample. The pre-treatment sample exhibited an H_2S concentration of 16 ppm. However, following treatment, the concentration dropped below the detection limit (BDL) and remained undetectable for the remaining 10 months of storage.

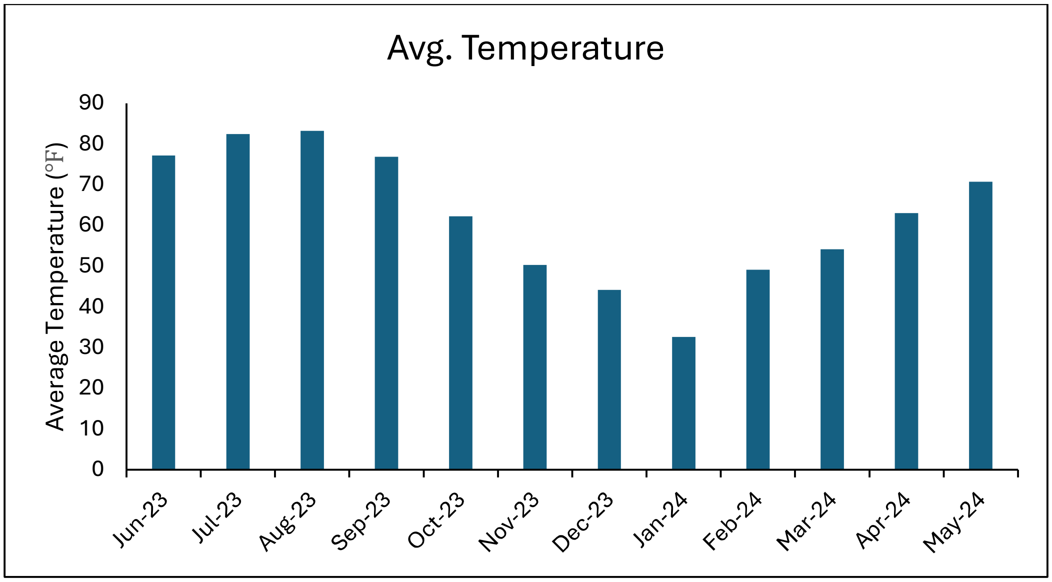

Fig. 7—Effect of Temperature (Mesonet).

BOD5

The BOD5 data revealed a high oxygen demand rate of 230 mg/L in the pre-treatment sample. Within a week of adding the microbial amendment package with the aeration module, the BOD5 rate dropped to half its initial value and continued to decrease at a slower, steadier rate. This reduction in organic load (as shown in **Fig. 8**) aligns with the trends observed in **Fig. 2**, where the steeper slope (M1) represents the faster initial degradation, and the following slope (M2) represents the slower, steadier degradation phase. Therefore, the microbial oxidation treatment effectively lowers the BOD, addressing the root cause of water spoilage as confirmed by the improvements in oil and grease (O&G) and H_2S levels as discussed in the section below.

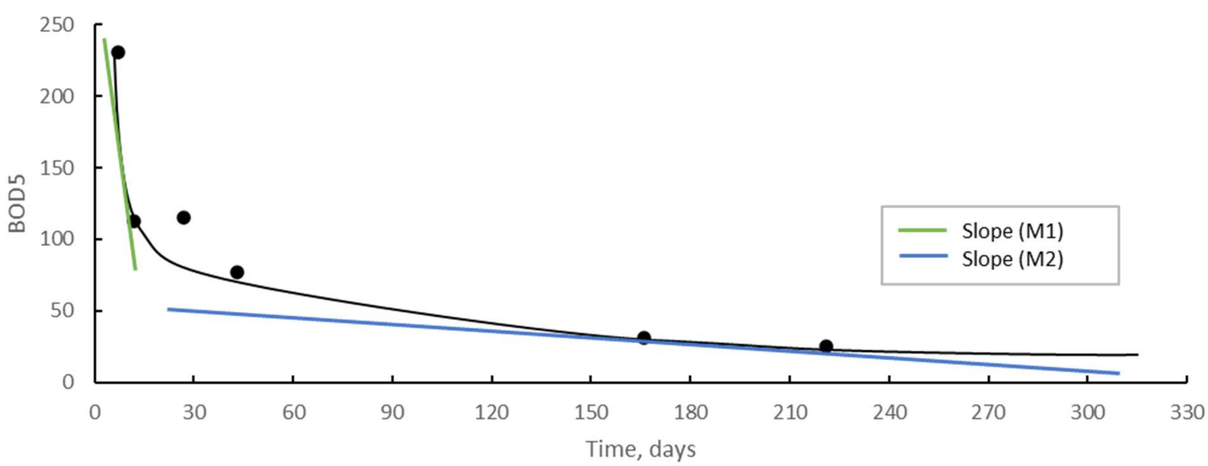

Fig. 8—BOD5 data shows a reduction in BOD following treatment, indicating a decrease in organic matter and improved water quality.

H_2S and oil & grease data

Fig. 9 shows that the initial produced water sample contained a high H_2S concentration (16 ppm), which directly correlates to the amount of oil and grease present (micro-emulsions exceeding 27 ppm). Once the treatment commenced, the oil and grease concentration decreased to BDL. This observation underlines the critical role of organic matter in H_2S production. By effectively degrading these organics through aeration and beneficial microbes, biological oxidation treatment eliminates the SRB's food source, leading to a significant reduction in H_2S levels (below detectable limits). The similar trends observed in Figure 9 for H_2S and oil & grease further emphasize that organic compounds are the main source of oxygen demand in the water impoundment. Targeting these organics with aeration and beneficial microbes effectively stabilizes the treated produced water for long-term storage.

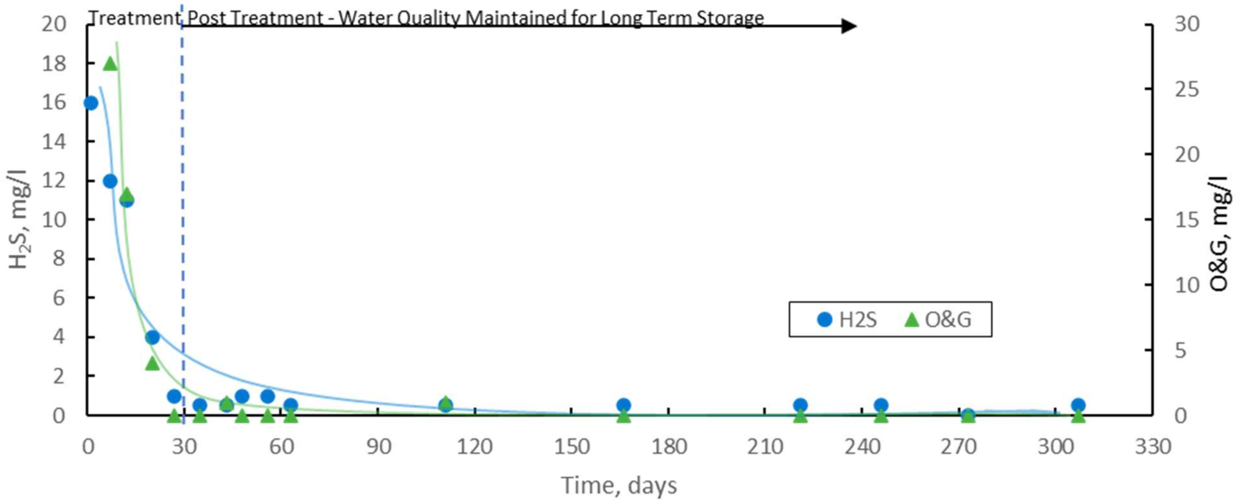

Fig. 9—H_2S and O&G concentrations reduced during treatment.

Conclusion

Biological oxidation technology has proven successful in treating produced water, enabling long-term storage and reuse applications. This technology offers value in regions facing freshwater scarcity, potentially reducing reliance on SWD for produced water reinjection. Key takeaways from this study include:

1) Biological oxidation effectively degrades organic loads in produced water, improving overall water quality.

2) Biological treatment methods enable long-term storage and reuse of produced water without the risk of souring.

3) Economical mechanical aeration to improve DO levels reduces overall chemical consumption, minimizing operational costs and environmental impact.

4) Increasing ORP, introducing beneficial microbes, and reducing SRB activity significantly decrease H_2S production.

5) This treatment technology can be used to effectively mitigate existing concentration of H_2S in the produced water body.

6) The extended period of stable water quality observed during 11 months of storage testing suggests the potential for even longer-term stability, allowing for reuse during fracturing or other activities with lower chemical demand. This translates to reduced costs associated with on-the-fly chemical treatments.

Overall, biological oxidation offers a cost-effective and environmentally friendly approach for treating produced water, enabling long-term storage and reuse. This treatment process avoids generating a sludge layer with residual chemicals and environmentally non-degradable byproducts.

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