A High-temperature High-salinity and High-pollution Oily Wastewater Treatment

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Abstract

A major challenge in oil and gas production is the treatment and disposal of produced water. Produced water is defined as " the water brought up from the hydrocarbon - bearing strata (geological formation) during the extraction of oil and gas, and can include formation water (the water naturally present in the reservoir), injection water, and any chemicals added downhole or during the oil/water separation processes[1]". It is a complex industrial wastewater typically with high TDS and COD. In many cases produced water also has a high temperature. Discharge of produced water into surface water is limited by regulations designed to protect the environment and human health. The parameters controlled are mandated by laws established by national authorities and vary from country to country. Parameters commonly regulated are: oil & grease, COD/BOD and ammonia-nitrogen content. Finding cost-effective ways to treat such water for discharge and/or water reuse is a major concern to industry, academia and government. The problem is especially challenging when new parameters are added or limits are changed. Frequently there is no standard technology developed to apply to produced water and applications have to be developed and tested during the design process.

This paper presents a case study, which identified state-of –the art methodology and integrated various technologies to achieve the desired discharge water quality. This study is used to guide the entire process in treating such complex wastewater for a surface discharge in the People's Republic of China. To comply with environmental regulations, a major oil company in China has been searching for an effective means to treat some of their produced water containing oil & grease of 42 ppm and COD of 800 ppm down to discharge levels mandated by the Chinese EPA. After several unsuccessful attempts made during the last a few years a United States based environmental firm -- HGL International and its associates (HGL Group) submitted a proposal in late 1999. HGL Intl. has conducted a large pilot test on the site during the spring -summer of 2000. Several months of on-site testing have shown the pilot test to be very successful. During this pilot test removal rates of 98% for BOD and oil and grease were achieved and removal rates for COD were 75-87%; Ammonia-nitrogen removal was satisfactory.

These removals were achieved using a series of innovative processes in sequences for:

- oil/water gravity separation,
- oil/water separation through a well-designed DAF,
- sorption/filtration of organic substances through MOC multi-media (MOC S-F) filter/adsorbers,

- biological treatment using bio-film technology –Rotating Biological Wheel (RBW) reactor. Special bacteria training/testing in the lab and field was used to select bacteria for the process.

The process sequence for the pilot plant includes:

1. Produced Water Influent (after Primary Oil/water Separation)
2. Chemical Addition
3. Dissolved Air Flotation
4. Multi Media Sorption/Filtration
5. Rotating Biological Reactor
6. Clarifier
7. Discharge to a River

The specially developed bacterial were selected and dried in the USA and shipped to the job-site in China. Those organisms were able to successfully biodegrade the organic contaminates, even the ones having a low-decay rate, under conditions of temperature over 60°C and chloride concentration similar to the seawater (22,000 ppm level range). High chloride concentration is toxic to many microorganisms, which makes it more difficult for biological treatment. The large-scale pilot test has demonstrated that high-temperature, high-salinity and high-polluted industrial wastewater can be treated in a cost-effective way. More importantly, many engineering parameters and design criteria for the full scale wastewater treatment plant have been optimized through this large scale pilot plant operating in the summer of year 2000.

Introduction

About 110,000 barrels/day of produced water coming from more than 200 wells needs to be treated on daily basis to meet the discharge standard set by the NEPA of China. A large-scale pilot plant was built and had been operated for over 100 days to treat up to 3,500 barrels water per day during summer of 2000. Some of inlet water quality data are as follows (Table 1.).

Table 1. Influent Water Quality and Discharge limit

Parameters	Unit	Influent	Discharge Limit
Temperature	F	145	N/a
pH		6~9	6-9
COD cr	mg/L	803	150
BOD_5	mg/L	302	30
Oil and Grease	mg/L	72	10
Cl^-	mg/L	21,000	N/a
Ca^{++} & Mg^{++}	mg/L	820	N/a
TDS	mg/L	33,000	N/a
TSS	mg/L	132	100
NH_3-N	mg/L	61	25

To successfully build the full-scale water treatment plant in a cost-effective way and at a tight schedule, a pilot plant was a very important step to find the feasible means and engineering parameters needed for the full scale plant A view of the pilot unit equipment is shown below in Figures 1 and 2.

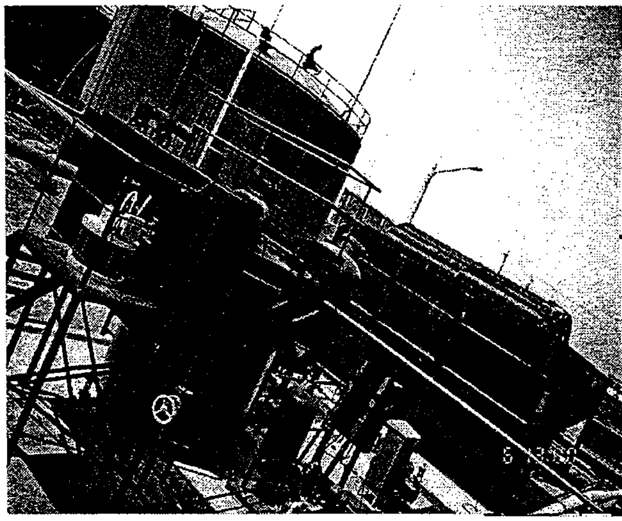

Figure 1. Outlook of the pilot plant

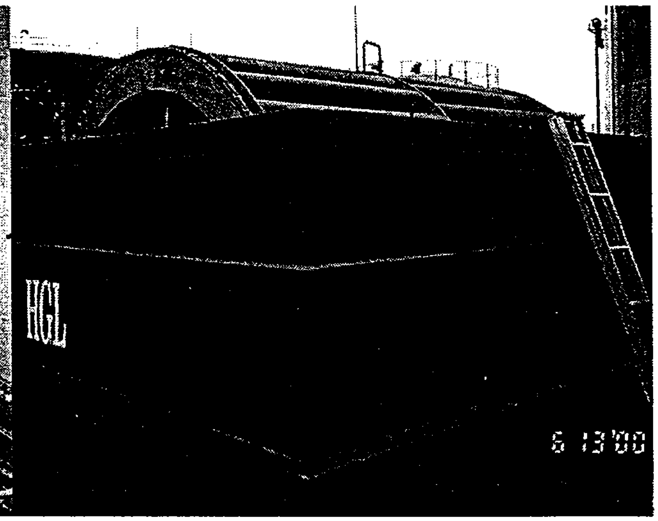

Figure 2. Outlook of the Bioreactor

The paper is discusses the individual processes and their features of the system in terms of their design and operation.

Optimization of the Integrated System Is a Top Priority

To meet the discharge standards shown in Table 1 is not an easy task based on the influent water quality especially within limited budget. It is also a challenging technically speaking. Oil and grease, COD and BOD are all related and share some common causes. But they are separate entities that each has features not included in the others. Oil and grease values may be as low as 2 ppm but COD can be as high as several hundred to a thousand ppm.

For this treatment purpose, we think the whole process consists of two portions: oil removal portion and COD/nutrient removal portion. There are several alternatives for reducing COD/nutrient levels including chemical oxidation, distillation and biological treatment. The influent water quality data and the discharge limits indicate that biological treatment is the less expensive way to. However, biological treatment is limited by high temperature, high salinity and high pollutant load. There is no established existing engineering technology developed for this case available for us to apply and one had to be adapted. Obviously all process units must be integrated and optimized to achieve final goal—a cost-effective way to treat the water. In the oil removal portion, the system is to predominantly remove oil and grease even though COD will also be reduced, but more often than not, COD reduction is not significant during the secondary oil/water separation phase for the most produced water cases. From this point of view, we can discuss the oil removal and COD/nutrient removal separately.

In the oil removal phase, there are several factors that affect the downstream processes that must be taken into account. The plan for the system included:

1) Control of pH lowering during well treatments or in attempting to separate dissolved,
2) Use of dissolved air flotation (DAF)
3) Use flotation aid chemical, but minimize the chemical usage, and find the chemical which has the least COD contribution.
4) Apply multi-media sorption/filtration (MOÇ S-F) to remove dispersion oil further and some dissolved oil especially for those with bigger molecular size and harder decayed biologically from the water. Ordinary filter media does not do this.
5) Apply biological degradation.

For biological treatment we considered factors such as high temperature (145° F),high salinity, heavy loadings of COD and NH3-N, and etc., and elected to use a biological rotating reactor, which has the features of bio-film and activated sludge in one, as the COD and NH3-N removal tool. Special developed bacteria are also an important factor because of the toxicity of the water to normal bacteria. With all of those factors in mind, we found that the present process is about 20-50% less in capital cost, and about 40-60% less in operating cost comparing with alternatives.

Gravity Separation and Sorption/Filtration

Since the oil content in the inlet water has been through a preliminary oil/water separation, the oil concentration is about 70 ppm . Flotation gravity separation is easy to handle and cost-effective way for removal to about 10-15 ppm level. DAF provides a good oil removal rate and the best oxygen level comparing with other applicable oil/water systems available in the market. By minimizing the chemical usage, we saw a reasonable COD reduction (30%) happened in DAF system. But when the chemical dosage or the chemical itself is not right, we did see the COD level was actually increasing rather than decreasing even though the oil removal rate was higher. Average inlet of water to the DAF system was 71 ppm and an average effluent concentration of 11 ppm was achieved in the 100 days pilot test run.

To further reduce the biological loading sorption/filtration was also applied. The media used was mostly organically treated clay. After 100 days testing, the there was no need for the media change. The average oil removal result is very good (80%) and COD removal rate is also reached the acceptable level (50%-60%) even considering for stand-alone.

Biofilm and Activated Sludge Combined

The unit used for biodegradation was a combination of biofilm reactor and activated sludge treatment in one unit, a rotating biological reactor. It has the following advantages for the this type of produced water:

- High process efficiency for COD/BOD and nitrification as well, especially good for high loading rate
- Cools efficiently without any extra disadvantage (See Figure 3)
- No "dead zone" in center of drum, eliminating weight build-up, a major cause of RBC failure.
- Capital costs are cut by one-third.
- Operational costs are typically cut by half.
- Small footprint and great flexibility.
- Low maintenance because of the material of the system in composite materials or stainless steel where contact with wastewater occurs.
- Promotes high dissolved oxygen levels, eliminates the need for supplemental forced air systems.
- Equipment is manufactured of composite materials – minimizing the wastewater's corrosive effects.
- Wastewater treatment occurs by both fixed film and activated sludge processes.
- No costly aeration facilities are needed for oxygen transfer into the water.
- The ability to support a wider, more diverse climate of microorganisms effectively increases the efficiency of the treatment process.
- Provides for aeration of wastewater with the lowest electrical power consumption.

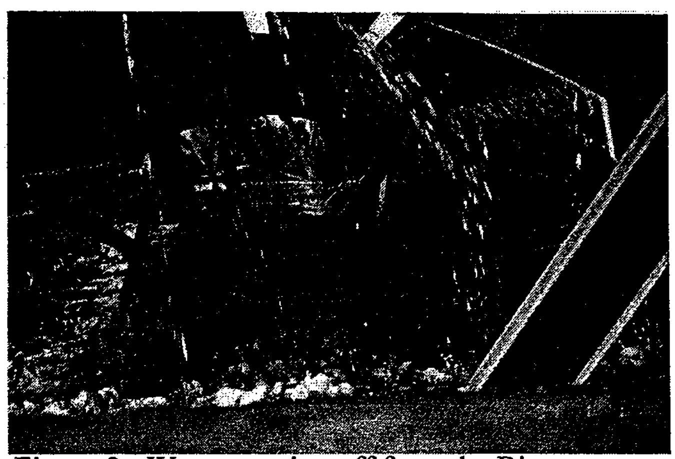
Figure 3. Water running off from the Bioreactor

Bacteria type: The *Bacillus-X6-10 type.* Those bacteria are not grown in pharmaceutical environment. If they were no one would be able to afford them for our use. The bacteria are grown in a food grade fermenter and are heat and moisture treated to force the majority of them to form Spores. Because of the method of growth it is possible for non-pathogen contamination from time to time which we do not bother to test for. We do however test for pathogen contamination on every lot at least twice. Once with the pure bacteria after it is dried the other time is the final product after it has been formulated. This type of bacteria can live in this type of water and grow consuming the COD/BOD and nutrient in the water.

Summary of Test Results

The water treatment results are shown as the Table 2.

Table 2. Water Data at the Inlet and Outlet of Each Unit

Parameters	DAF (mg/L)		MOC S-F (mg/L)		Bio-R (mg/L)	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Oil	72	11	11	2	2	0.2
COD	802	557	557	304	304	121
BOD	304					3
NH_3-N	61	55	55	53	53	31

Conclusions

The present system works very efficiently for this produced water application based on the pilot test. The results as shown in Table 2. were based on 10 days of 24 hours/day monitoring designated lab appointed officially by the client, the oil company in China. COD is not low compared with removal rate for BOD and this is probably due to the high salinity which can impact the COD measurement done using Cr oxidation. BOD levels indicate that the water is almost organic free. BTEX and phenols are all below the discharge level.

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