

Treatment of Refinery Wastewater Containing High Concentrations of Chemical Oxygen Demand and Total Sulfides for Low Odor Processing through a Capacity-Challenged Bioreactor

Rich Clasen^{1*}, Stan Heimburger², Mike Fagan², Mostafa Jahanian²

¹Shell Oil Company, Puget Sound Refinery, Anacortes, WA

²US Peroxide, Atlanta, GA

*Email: rich.clasen@shell.com

ABSTRACT

Shell Puget Sound Refinery (PSR) is a fully-integrated production facility that first went on stream in September 1958, initially processing up to 45,000 barrels of crude oil per day. Currently, the plant processes up to 145,000 barrels (6.1 million gallons) of crude oil per day producing many useful products -- including several grades of gasoline, fuel oil, diesel fuel, propane, butane, petroleum coke.

The Effluent Plant's Bioreactor at Shell PSR is a three channel oxidation "ditch" style biotreater (a.k.a. Racetrack) built in the early 1990's. The Bioreactor is a concrete basin with three 14' deep channels. While the Bioreactor has gone through several upgrades over the years, including the addition of boat-type aerators and the recent addition of steel brush-type aerators, it was limited in aeration capacity to treat peak load, non-routine wastewater while maintaining target dissolved oxygen. Bioreactor aeration capacity required processing peak load wastewater at reduced rates and led to storage issues. The lack of dissolved oxygen in the first stage of the Bioreactor led to odors and subsequent complaints from neighboring communities. In an effort to process wastewater without odors, Shell would store (divert) the peak load material and process it back to the Bioreactor slowly.

In the summer of 2012, Shell PSR had accumulated a large amount of peak load, high sulfur wastewater that was being stored in a storage tank. PSR needed find a quick solution to expedite the treatment of this high Chemical Oxygen Demand (COD), high total sulfides wastewater because it was limiting the refinery's operational flexibility. Shell partnered with US Peroxide (USP) to develop a project that would allow the processing of the stored wastewater and provide the desired dissolved oxygen to eliminate odors. The injection of hydrogen peroxide (H₂O₂) into Bioreactor influent provided an immediate source of supplemental dissolved oxygen (DO) to support biological treatment of this inventoried wastewater.

Since the successful completion of that project in late 2012, US Peroxide (USP) and Shell PSR have continued to work cooperatively to further optimize pretreatment ahead of the Bioreactor to improve COD removal and minimize odors from the refinery wastewater treatment plant to the nearby community of Anacortes, WA. Efficiencies in treatment of high-COD wastewater spikes

have been achieved by developing and optimizing an upstream treatment program utilizing H_2O_2 and ferrous chloride ($FeCl_2$) added ahead of the Dissolved Nitrogen Flotation (DNF) units, along with varying H_2O_2 addition at the Bioreactor to maintain 2-4 ppm target DO levels in the outlet (i.e. inner) track.

KEYWORDS: Bioreactor, DO, sulfides, VOC, COD, hydrogen peroxide, ferrous chloride

INTRODUCTION

Shell PSR processes 2,500 gallons per minute of refinery wastewater through the Effluent Plant (EP). The PSR EP includes an API Separator, DNFs, an equalization (EQ) tank, an activated-sludge Bioreactor, secondary clarification with Recycled Activated Sludge (RAS) recycle back to the Bioreactor and Waste Activated Sludge (WAS) to aerobic digestion, an aerated pond and polishing ponds prior to discharge to outfall as shown in Figure 1.

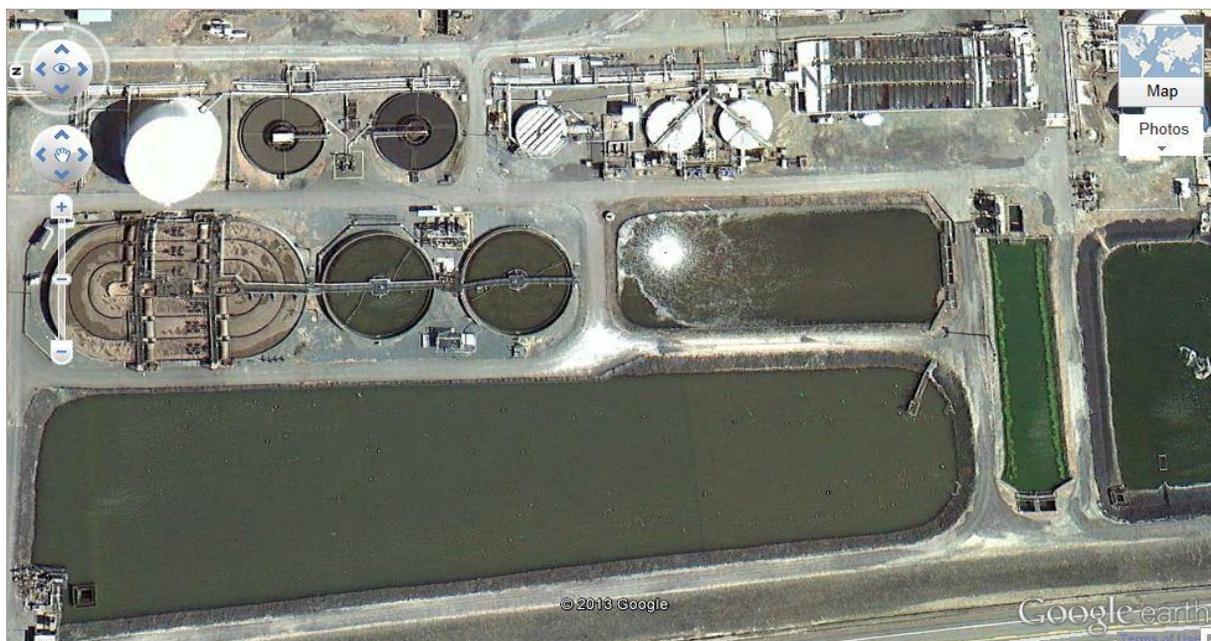


Figure 1. Shell PSR Effluent Treatment Plant

The Bioreactor at Shell PSR is a three-stage oxidation channel (a.k.a. Racetrack) built in the early 1990's. While the Bioreactor has gone through several upgrades over the years, including the addition of boat-type aerators and the recent addition of steel brush-type aerators, it lacks aeration capacity to quickly treat significant quantities of peak load, non-routine wastewater while maintaining target dissolved oxygen. The Bioreactor has a calculated detention time of 5.2 hours at average wastewater plus recycled RAS plus fire water flows.

Since its refinery's original construction the crude slate of the refinery has changed. Shell PSR is now processing higher sulfur crudes and has seen generally increasing loading on the Bioreactor.

In June 2012, Shell PSR had begun accumulating a significant quantity of high-COD, high-total sulfide wastewater as a result of a series of operational upsets. While there were no issues treating this inventoried water to meet outfall permit requirements, a solution to treat the wastewater without impacting the community from odors was needed. Shell PSR had earlier equated low DO in the Bioreactor to odors emanating from it. By August, 2012, Shell partnered with USP and a quick, low-capital solution to temporarily expand the Bioreactor capacity was proposed. Using this approach, H₂O₂ would be fed into Bioreactor influent, providing an immediate source of supplemental DO to support the biomass and minimize odor emissions while the high strength, inventoried wastewater was being processed through EP. In September, 2012 the project was implemented and by November 15, the inventoried wastewater had been completely processed through the Effluent Plant.

Because of success in odor reduction while operating the Bioreactor with increased COD loading during this project, Shell PSR decided to continue applying hydrogen peroxide to it to control DO level in the inner track between 2-3 ppm. In March, 2013 Shell PSR began dosing H₂O₂ both into the Bioreactor and upstream of it, ahead of the DNFs, to allow for longer contact time with H₂O₂ and greatly improve the ability to process wastewater COD spikes at EP. In June 2013, Shell PSR initiated a demonstration using FeCl₂ as a catalyst for the H₂O₂ to improve wastewater COD reduction capacity through the DNFs.

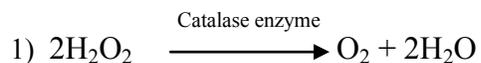
RESULTS AND DISCUSSION

Crude Tank Inventoried Wastewater

By the beginning of the project, Shell PSR had inventoried nearly 160,000 barrels of high-COD, high-sulfide wastewater in one of its crude tanks, making this tank unavailable for normal use. Attempts had been made earlier in the prior few months to “bleed” this water into conventional wastewater being sent to EP, but these efforts were met with increased odor emissions from the Bioreactor that resulted in complaints from the nearby community of Anacortes. The inability to treat this wastewater without odor emissions at the Bioreactor could be traced to inadequate retention time through it, incomplete oxidation and stripping of Reduced Sulfur Compounds (RSC) at the Bioreactor due to the type of aeration devices in use there.

In September, 2012, a US Peroxide turn-key H₂O₂ storage/handling system was installed and treatment began a few weeks later on October 8th.

The conversion of hydrogen peroxide to DO in an activated sludge mixed liquor proceeds according to reaction 1):



Catalase enzyme is a natural decomposition catalyst for H₂O₂ and is found in all activated sludge mixed liquors, being produced by many aerobic organisms. Because this enzymatic decomposition of H₂O₂ is extremely rapid, the oxygen supplied by H₂O₂ is immediately available for uptake by the aerobic organisms. This approach met Shell PSR's operational criteria, and provided very predictable performance as shown in Figure 2.

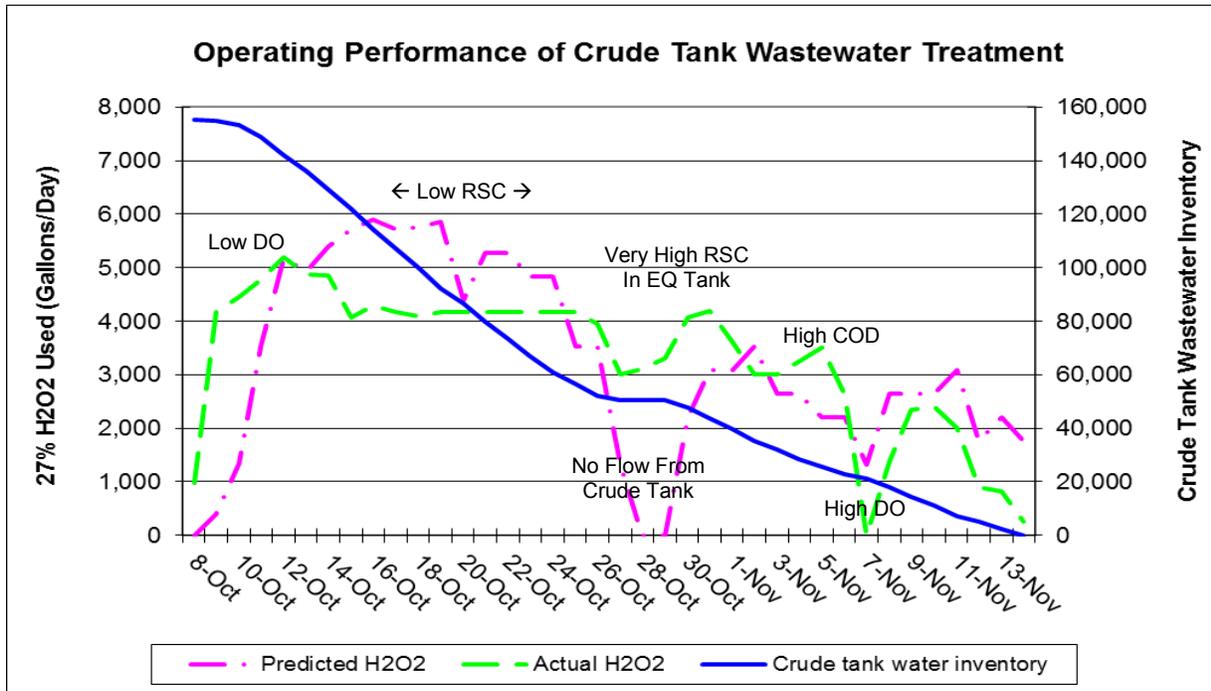


Figure 2. Operating Performance of Crude Tank Wastewater Treatment

Specifically, the requirements of the Crude Tank treatment project were to:

1. Supply additional dissolved oxygen to effectively increase the capacity of the Bioreactor to meet the demand of up to 300 GPM of high-COD wastewater
2. Continue to meet all effluent permit limits during the duration of the project.
3. Execute project without odor impact to the community.
4. Implement treatment within two weeks of project contract signing.
5. Complete treatment of inventoried wastewater within 45 days of project start up.

To maintain the dissolved oxygen (DO) levels, a ratio of 1.5 lb. H₂O₂-100% for each additional lb. of COD entering the Bioreactor was initially estimated. The hydrogen peroxide addition rate and overall treatment time was dependent on the flow (“bleed”) rate of Crude Tank wastewater into the Bioreactor as indicated in Table 1.

Table 1. Demand for H₂O₂ at Bioreactor based on Crude Tank Wastewater Flow and COD

Crude 4 WW, GPM	Additional COD, lb/day	27% H ₂ O ₂ Rqmt., GPD	Days of Treatment
50	1,948	1,146	70
100	3,896	2,292	35
200	7,792	4,584	18
300	11,688	6,876	12

Laboratory testing was also conducted to determine the “background” demand for H₂O₂ attributable to inorganic RSC (i.e. sulfides (S⁻) and sulfites (SO₃⁻). These compounds react rapidly with hydrogen peroxide and exert an immediate demand which must be accounted for when estimating H₂O₂ requirements to increase DO in biological treatment systems. Lab testing prior to the project start up showed that 2.8 lb. H₂O₂-100% was required for each additional lb. of inorganic RSC in the inventoried wastewater. Thus, hydrogen peroxide feed rates required to account for inorganic RSC across varied Crude 4 wastewater flow rates are indicated in Table 2.

Table 2. Demand for H₂O₂ at Bioreactor based on Wastewater Flow and Inorganic RSC

Crude 4 WW, GPM	S ⁻ +SO ₃ ⁻ , lb/day	27% H ₂ O ₂ Rqmt., GPD	Days of Treatment
50	180	203	70
100	360	406	35
200	720	812	18
300	1,080	1,218	12

During the project, feeding Crude Tank wastewater into the Bioreactor increased overall influent COD concentration by 15-30%, while total sulfides increased by 100-2,400%. H₂O₂ addition rate was adjusted during the project by measurement of dissolved oxygen (DO) in the three tracks of the Bioreactor (see Figure 3). In particular, DO measurements in the outer track and the inner track were found to be most important to utilize for control of H₂O₂ addition which was done by use of a rotometer on a feed line into each track of the Bioreactor that branched off of a discharge header from the hydrogen peroxide feed system.

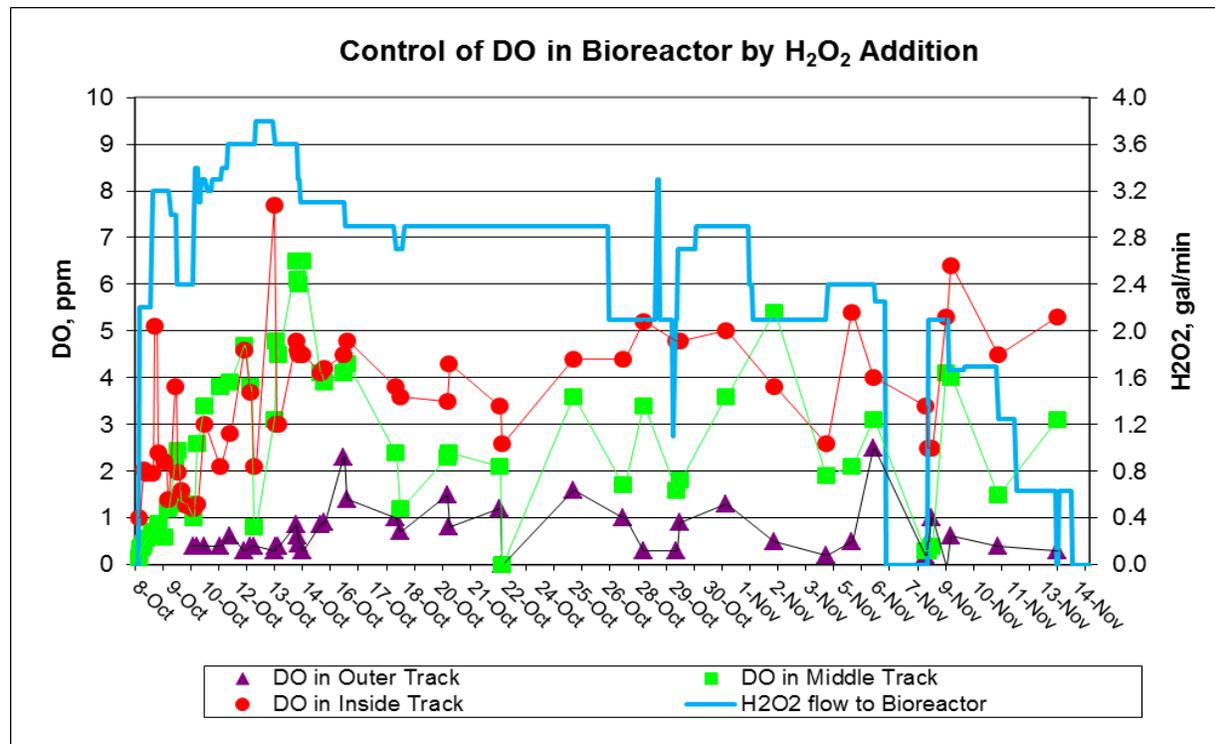


Figure 3. Control of DO in Bioreactor by H₂O₂ Addition

As a result of close monitoring of DO in the Bioreactor and adjustment of hydrogen peroxide feed rates, clarifier effluent COD was consistently maintained within permit limits, despite the variation in Bioreactor influent shown in Figure 4.

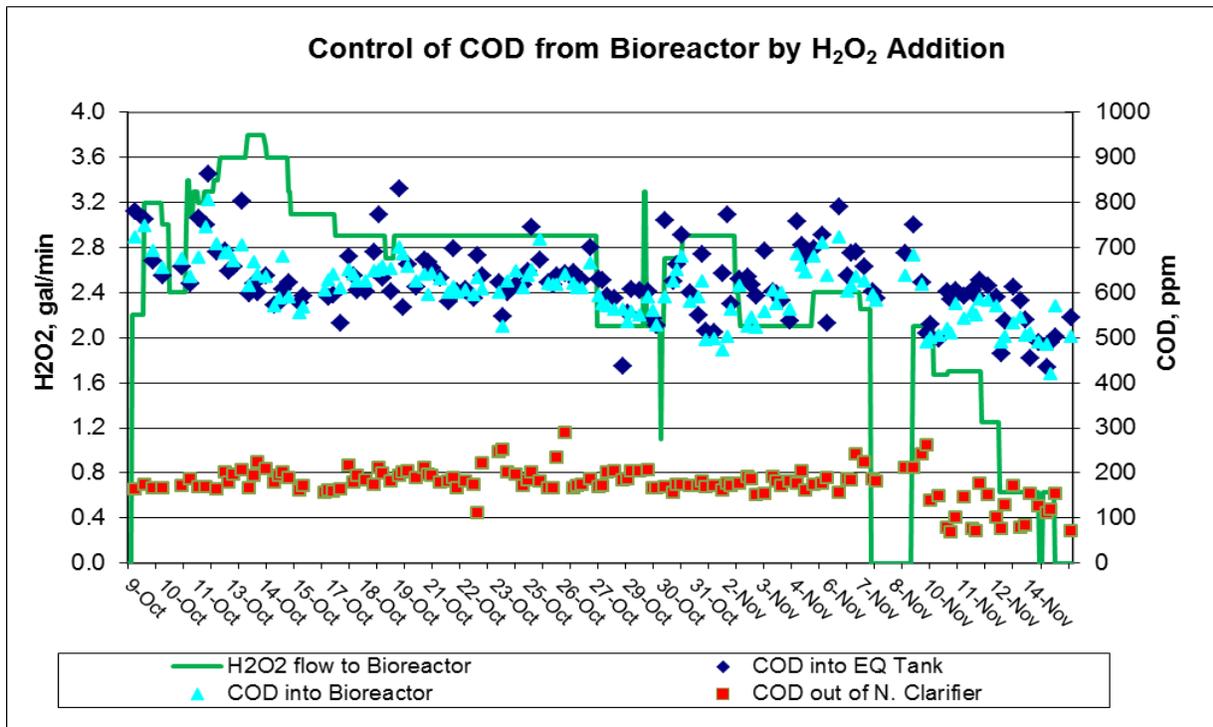


Figure 4. Control of COD from Bioreactor by H₂O₂ Addition

The cost for the turnkey H₂O₂ program (chemical, storage/handling equipment, services) to successfully treat the entire volume of inventoried Crude Tank wastewater through the biological treatment system resulted in an average additional cost of \$2.10/barrel or 0.05/gallon. The daily cost did vary considerably through the project as H₂O₂ addition was adjusted to maintain DO levels, which were in turn affected by incoming wastewater COD and RSH as shown in Figure 5.

One unrelated observation from the hydrogen peroxide injection activity was that the aeration of wastewater near its injection point into the Bioreactor needed to be kept to a minimum to prevent the stripping of RSC into the atmosphere. Shell PSR determined that the Bioreactor did not have enough reaction time to consume the RSC and volatile organics and therefore they were being stripped. As a result, Shell PSR and USP agreed to study adding an upstream H₂O₂ injection point to more thoroughly oxidize these compounds, prior to the Bioreactor.

In summary, this project demonstrated that the effective treatment capacity of a refinery wastewater bioreactor could be temporarily expanded to allow processing of inventoried, high COD wastewater. Ultimately this was accomplished with minimal capital expenditure, while meeting effluent permit requirements and minimizing odors.

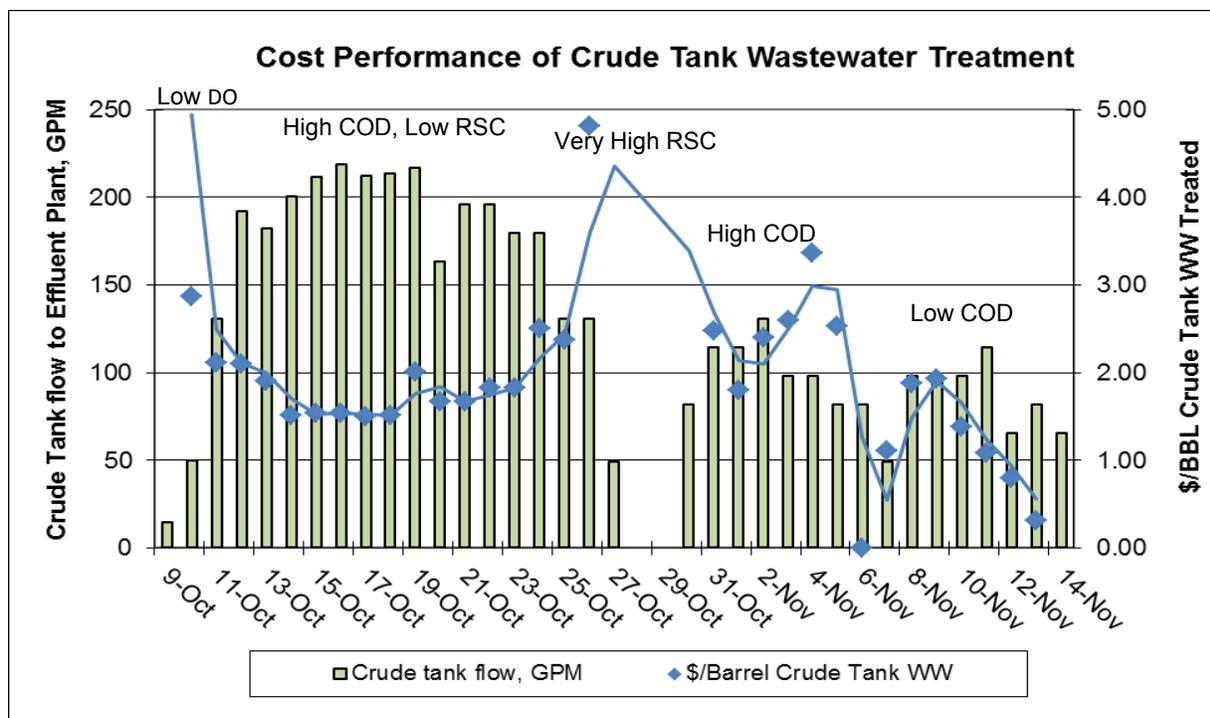


Figure 5. Cost Performance of Crude Tank Wastewater Treatment

As a result of the activity, Shell PSR was able to process the inventory in the Crude Tank in thirty-six days at a total cost of US \$350,000. This cost was well justified by getting this tank back into crude service and the cost per gallon of wastewater treated was 5% below that predicted by US Peroxide.

Upstream H₂O₂ to Further Minimize RSC and VOC Odors at the Bioreactor

By early March 2013, H₂O₂ was being injected as required into Bioreactor influent to maintain DO of 3-4 ppm in the inner track as determined by an in-line DO analyzer. This process had been successful over the previous 2-3 months in minimizing odor complaints from the nearby Anacortes community. However, H₂O₂ demand at the Bioreactor was at times high and it was believed that this was due to variable levels of RSC and VOC in wastewater coming to EP.

From laboratory treatability studies previously completed on Shell wastewater, direct oxidation of RSC had been quite successful at deodorizing (and decolorizing) these samples (Figure 6). To allow for more complete oxidation and odor control of these compounds prior to the bioreactor, injection of H₂O₂ upstream, just ahead of the dissolved nitrogen flotation units (DNFs) was evaluated.

The key chemical reactions associated with direct oxidation of total reduced sulfur compounds are summarized in reactions 2), 3), 4) and 5).

- 2) $S^{2-} + H_2O_2 \rightarrow S_0 + 2H_2O$ (Sulfides at acidic-neutral pH)
- 3) $S^{2-} + 4H_2O_2 \rightarrow SO_4^{2-} + 4H_2O$ (Sulfides at alkaline pH)
- 4) $SO_3^{2-} + H_2O_2 \rightarrow SO_4^{2-} + H_2O$ (Sulfites)
- 5) $2RSH + H_2O_2 \rightarrow RSSR + 2H_2O$ (Mercaptans)

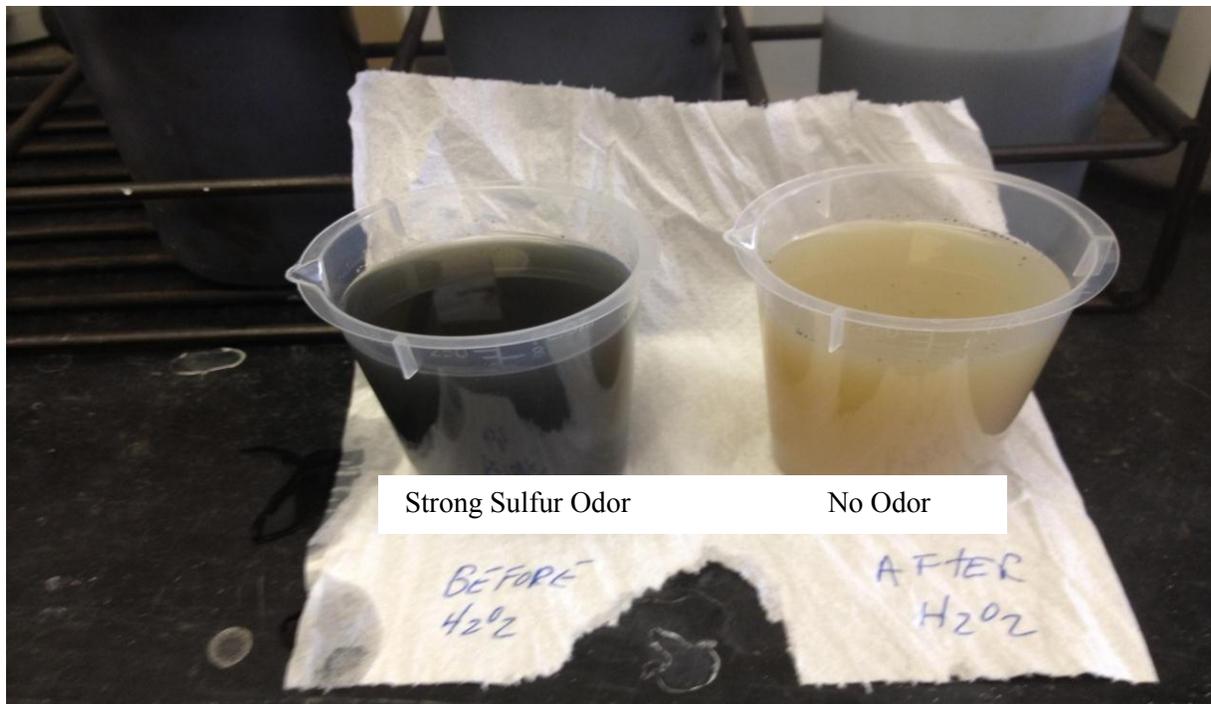


Figure 6. Direct Oxidation of RSC in Wastewater with H₂O₂

A 30-day demonstration period of upstream H₂O₂ addition to wastewater between the API separators and the DNF's began on March 8. Significant reductions in liquid and vapor Total Sulfide levels and VOC vapor level were observed, and are summarized in Tables 3-5.

Table 3. March 8-April 7 – Total Sulfides in Liquid (mg/L)					
	Average	Minimum	Maximum	Std. Dev.	% Oxidation
API Out	1.9	0.2	5	1.7	
DNFs Out	0.3	0	1.0	0.4	84*
EQ Tank Out	0	0	0		100

* baseline data suggests that 38% of RSC in liquid was being transferred to gas phase and removed in carbon filters

Table 4. March 8-April 7 – Total Sulfides in Vapor (mg/L)					
	Average	Minimum	Maximum	Std. Dev.	% Oxidation
API Out	82.4	16.5	132	46.6	
DNFs Out	2.3	1.5	4.5	1.0	97
Tank 74 Out	0	0	0		100

Table 5. March 8-April 7 - VOC in Vapor (mg/L) (30-40 GPH 27% H₂O₂)					
	Average	Minimum	Maximum	Std. Dev.	% Removal
API Out	929	300	1,500	481	
DNFs Out	343	90	1,140	372	63

VOC are not directly oxidized by H_2O_2 alone at a significant rate, however, USP had recently demonstrated at another refinery that up to 92% of hydrocarbon (oil) soluble benzene present in wastewater to the DNF units could be removed by addition of H_2O_2 with performance achieved by formation of microbubbles that “physically” improved oil removal across the DNFs. An analysis of wastewater to Shell PSR DNFs just ahead of the demonstration showed BTEX levels at Benzene – 4.4 mg/L, Toluene – 20 mg/L, Ethylbenzene – 2.6 mg/L and Xylenes – 15.6 mg/L.

Though it was expected that H_2O_2 demand for DO control at the Bioreactor would be decreased during the demonstration of upstream H_2O_2 addition due to the toxic attributes of RSC toward biology, this was not observed. In fact, during the demonstration, an increase in H_2O_2 demand at the Bioreactor was observed. After an evaluation of other operating parameters including wastewater flow rate and concentration, it was found that wastewater temperature was elevated above a typical range during much of the demonstration and that this related well to increasing demand for H_2O_2 at the Bioreactor as shown in Figure 7.

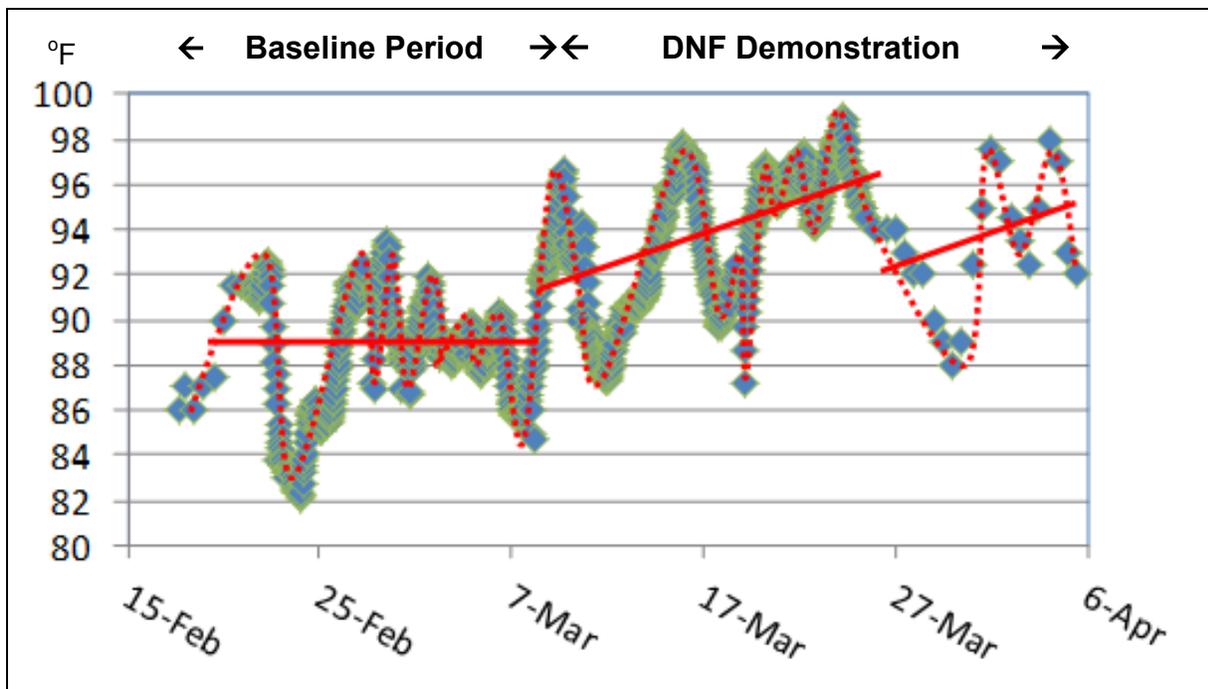


Figure 7. Temperature of Wastewater to Bioreactor

This result would be expected due to the increasing difficulty of maintaining an aerator-provided DO level in wastewater above 92 °F due to the reduced solubility of oxygen as temperature increases (due to decreased transfer efficiency from gas to liquid). However, Bioreactor DO target levels could be maintained by addition of H_2O_2 , since its enzyme catalyzed decomposition to oxygen occurs in the liquid phase versus in a gas to liquid transfer with mechanical aeration.

Upstream H_2O_2 + $FeCl_2$ to Eliminate RSC, VOC Odors and Reduce COD at the Bioreactor

Additional laboratory treatability studies were completed in April, 2013 that investigated the enhancement of H_2O_2 performance for oxidizing and/or removing RSC and water insoluble VOC between the outlet of the API Separator and the outlet of the DNFs. The visual success of these studies is summarized in Figure 8.

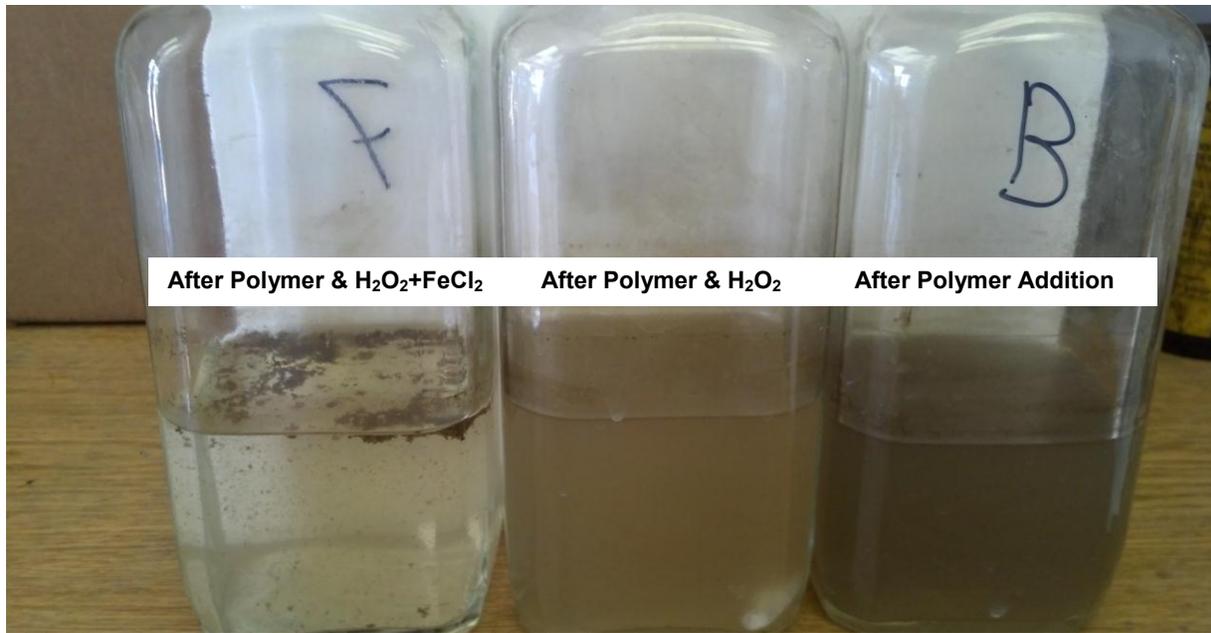
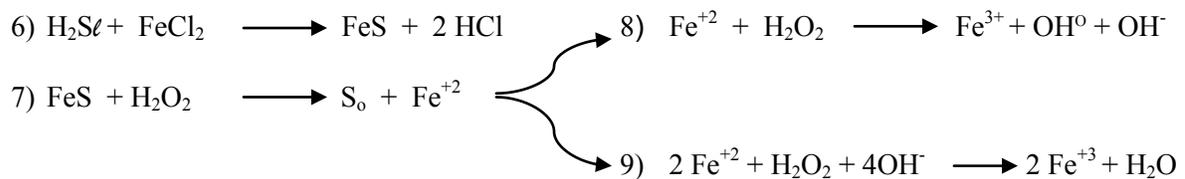


Figure 8. H₂O₂ + FeCl₂ ahead of DNFs Treatability Study Results

The chemistry that occurred during the one-hour simulated detention time through the Shell PSR DNFs is summarized below in reactions 6), 7), 8) and 9).



The important points to conclude from these reactions are that:

- With addition of FeCl₂, H₂O₂ rather than directly oxidizing sulfides, is now oxidizing FeS, producing elemental sulfur (inert precipitate) and regenerating free ferrous iron (Fe⁺²).
- The free ferrous iron produced catalyzes the reaction of H₂O₂ to form the hydroxyl radical (OH[°]), a much stronger oxidant than H₂O₂ by one pathway and simultaneously produces ferric (Fe⁺³) iron by a second pathway.
- The hydroxyl radical is able to oxidize soluble organics, in the process destroying a source of COD and VOC odor emission downstream of the DNFs.
- The ferric iron then neutralizes charge and coagulated suspended materials including Total Suspended Solids (TSS), insoluble VOC and colloidal materials.
- The addition of flocculant (already utilized by PSR) further agglomerates the floc particles, allowing efficient removal by a flotation device, i.e. DNF.
- The HCl generated in reaction 6) lowers the pH of wastewater slightly. In the PSR demonstration, pH of wastewater from the API Outlet to the DNF outlets dropped by 0.5-1.0 unit.

A 30-day demonstration period of both H₂O₂ + FeCl₂ addition ahead of the DNFs began in June. Positive results from the demonstration were achieved and are presented in Tables 6-10 and in Figure 9.

Table 6. June 11-July 10 – Total Sulfides in Liquid (mg/L)					
	Average	Minimum	Maximum	Std. Dev.	% Oxidation
API Out	4.9	0.3	20	6.7	
DNFs Out	0.1	0	0.4	0.1	99

Comparing the results in Table 6 to those in Table 3, it can be clearly seen that though average total sulfides in solution were much higher during this demonstration at 4.9 mg/L than during the H₂O₂-only demonstration earlier in the year (1.9 mg/L), oxidation efficiency through the DNFs was much improved (99% reduction through the DNFS compared to 84% reduction with only H₂O₂). We conclude that this was most likely due to generation of the hydroxyl radical outlined in the reaction chemistry reviewed earlier.

Table 7. June 11-July 10 - Daily Avg. COD <675 mg/L to DNFs					
	Average	Minimum	Maximum	Std. Dev.	% Reduction
API Out	652	630	674	18	
DNFs Out	560	492	609	43	14

Table 8. June 11-July 10 - Daily Avg. COD >675 mg/L to DNFs					
	Average	Minimum	Maximum	Std. Dev.	% Reduction
API Out	740	678	870	59	
DNFs Out	571	506	645	42	23

Results in Tables 7 and 8 demonstrated that H₂O₂ + FeCl₂ were more effective at reducing COD across the DNFs as the incoming COD in wastewater from the API Separator increased.

This conclusion was further supported by a one-day mini-demonstration completed on July 19 when H₂O₂ + FeCl₂ was restarted over a ten-hour period when very high COD “bottoms” water from a crude tank was “bled” slowly into the main covered sewer to EP. The results from this are summarized in Table 9, indicating that with an average wastewater COD concentration from the API Separator of 1,660 mg/L, COD reduction through the DNFs can be expected to be >30%.

Table 9. July 19 Crude Tank Water Bottoms Pretreatment, COD (mg/L)					
	Average	Minimum	Maximum	Std. Dev.	% Reduction
API Out	1,661	953	1,981	380	
DNFs Out	1,088	665	1,290	251	34

Table 10 summarizes the reduction in turbidity of wastewater through the DNFs when H₂O₂ + FeCl₂ chemistry was applied ahead of them. Compared to data from the March-April demonstration of only H₂O₂ applied before the DNFs, turbidity reduction of wastewater was nearly doubled.

Table 10. June 11-July 10 - Wastewater Turbidity (NAU) using Hach Colorimeter Method					
	Average	Minimum	Maximum	Std. Dev.	% Reduction
API Out	202	153	239	39	
DNFs Out	121	68	171	36	40

Finally, the June-July demonstration provided some very strong evidence of much lowered levels of VOC odor emissions above the Bioreactor.

In the fall of 2012, Shell PSR idled one of its Bioreactor brush type surface aerators in the outer track because it had evidence that the aerator stripped VOCs. After the addition of the FeCl₂, VOC odor measured in this location had been reduced significantly.

During this demonstration, there was a relationship found between COD and turbidity (measured using a Hach colorimeter and test method) in wastewater both to and from the DNFs as clearly shown in Figure 9.

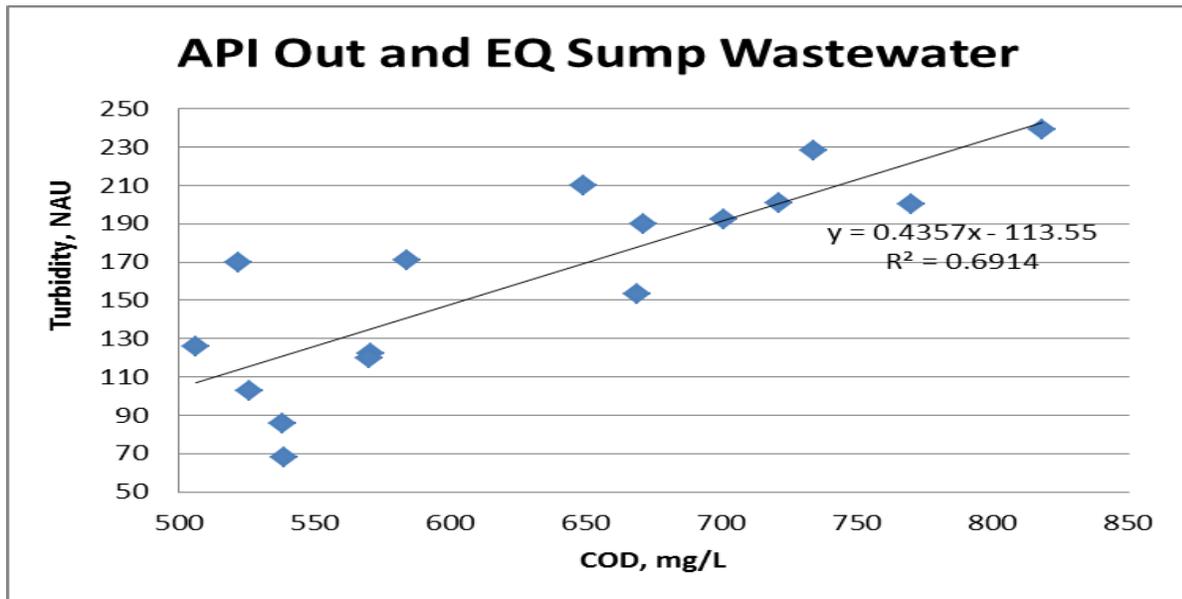


Figure 9. Turbidity vs. COD in Wastewater to and from the DNFs – June 11-July 10

This statistically-valid preliminary correlation between the two variables may allow the Shell PSR EP operators to utilize turbidity testing for predicting COD concentration changes in wastewater coming to the Bioreactor in between their twice-per-shift sampling and in addition to utilizing the in-line TOC analyzer located after the DNFs in the wastewater feed line to the EQ Tank and Bioreactor. Further data collection at variable operating conditions through the DNFs would be required to prove the long-term validity of utilizing wastewater turbidity to predict COD.

In addition to H₂O₂, when applying polymer and FeCl₂ in an upstream application point ahead of a flotation device such as a DNF, chemical application rates need to be tested and optimized based on incoming wastewater toxicant type and concentration and wastewater flow rate.

SUMMARY AND CONCLUSIONS

Hydrogen peroxide alone or in combination with catalysts such as ferrous chloride offers refineries low capital wastewater treatment solutions, especially during periodic spikes in COD, sulfides, etc. including the following practical examples that have been studied and adopted into practice at the Shell Puget Sound Refinery:

- ✓ Supplemental source of dissolved oxygen in a Bioreactor that is lacking in retention time and/or mechanical aeration capacity
- ✓ Oxidation of RSC including sulfides, sulfites and mercaptans during flotation before they can lead to odor emissions in a downstream Bioreactor
- ✓ Improved removal of oil-soluble organic materials (e.g. oil, benzene, toluene) in flotation before they result in VOC emissions and consume DO downstream in the Bioreactor
- ✓ Oxidation of soluble organic compounds upstream of the bioreactor, to reduce the overall COD load and reduce the toxic or inhibitory impacts on the biomass

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the cooperation of operators of the Shell PSR Effluent Plant and management in engineering, operations, maintenance, technical applications and purchasing departments at both Shell PSR and US Peroxide who offered us support and assistance during incorporation and testing of the process changes that became the basis for preparation of this manuscript. We also acknowledge the assistance of the individuals who performed outside laboratory analytical analyses that supported our technology evaluations at Shell PSR.

REFERENCES

- Supplemental Dissolved Oxygen with Hydrogen Peroxide, www.h2o2.com.
Reduced Sulfur Compounds Treatment with Hydrogen Peroxide, www.h2o2.com.
High Strength Wastewater Pretreatment with Hydrogen Peroxide. www.h2o2.com.
BOD and COD Removal Using Hydrogen Peroxide. www.h2o2.com.
Steiner, N.; Gec, R.; (1992) Plant Experience using Hydrogen Peroxide for Enhanced Fat Flotation and BOD Removal. *Environmental Progress, Volume 11, No. 4*.
US Patent #6,773,604 B2 "Method for Reducing Hydrogen Sulfide Emissions from Wastewater"
Walton, et al., August 10th, 2004.
Watson, L.; Neofotistos, P.; Collins, C.; Harshman, V.; Morano, D.; (2007)
Anaerobic Digester Hydrogen Sulfide Removal at the Manatee County, FL Southwest Water Reclamation Facility. *Proceedings of WEFTEC 07, the 80th Annual Water Environment Federation Technical Exhibition and Conference; San Diego, California.*