Temporary Phenol Oxidation Program to Support a Refinery Aeration Basin Turnaround – Lab Treatability Testing Through Successful Full Scale Implementation – A Case Study

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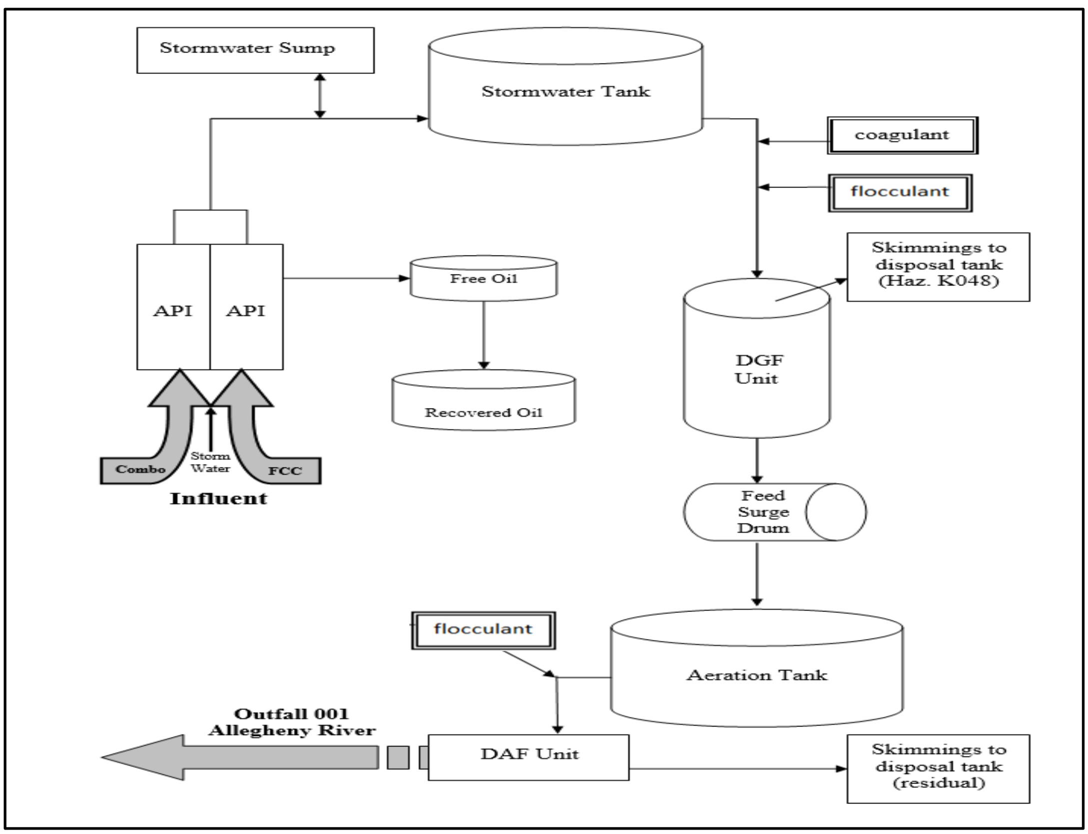
ABSTRACT

In 2015, a maintenance turnaround of the wastewater aeration tank was undertaken at United Refining Company in Warren, PA. During the planned 70 day turnaround, the refinery needed a temporary chemical oxidation program to maintain compliance with permitted effluent phenol levels. This paper will present data and key learnings from all phases of this successful project, including laboratory treatability testing, process design, full scale implementation and successful completion.

United Refining Company (refinery) operates a 92-acre petroleum refinery in Warren, Pennsylvania. The refinery has been in operation since 1902 and processes approximately 70,000 barrels of crude oil per day. The refinery's primary emphasis is placed upon producing gasoline and distillate fuels for retail sale at outlets throughout Pennsylvania, Ohio and New York.

The refinery's wastewater treatment system consists of a sour water stripper, collection sumps and conveyance systems, API separator, slop oil recovery system, storm water equalization tank, dissolved gas floatation (DGF) unit, aeration tank (biological treatment), dissolved air flotation (DAF) unit, sludge holding tanks and a diversion system. On average, approximately 900,000 GPD (625 GPM) of wastewater is processed and discharged to the Allegheny River. The treatment plant outfall is sampled twice a week for NPDES permit compliance. The layout of the individual units is illustrated in the schematic drawing of the wastewater treatment plant in Figure 1 (below).

Figure 1 – Refinery IWWTP Schematic

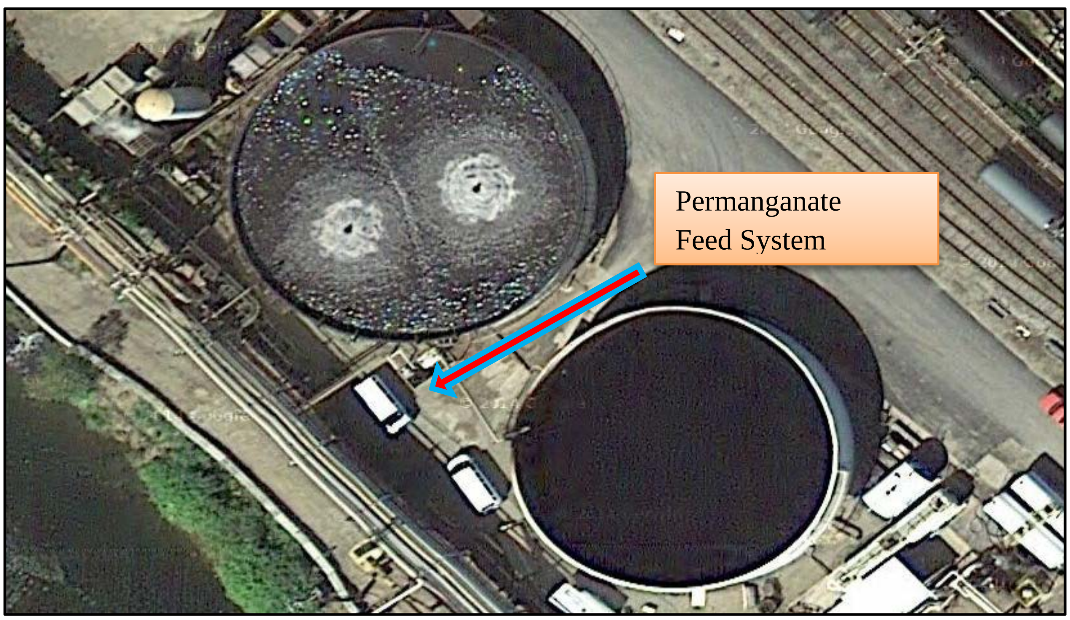


A maintenance turnaround of the wastewater aeration tank was scheduled to begin on May 2015 to remove the aging liner material, spray coat and reseal the aeration tank walls, replace the baffle curtain and perform other tank upgrades. With the aeration tank out of service for an estimated 70 days, the refinery needed a temporary treatment system to oxidize wastewater phenols to maintain compliance with NPDES discharge permits. With the exception of phenol, refinery personnel determined the existing physical/chemical treatment processes would achieve all other wastewater discharge parameters within permit.

In early 2015, the refinery issued a Request for Proposal (RFP) and subsequently awarded the project to USP Technologies (treatment contractor). The RFP required a turn-key, temporary phenol oxidation process that could consistently achieve effluent phenol levels below the permitted discharge concentration of 1.2 mg/L (one time maximum). The RFP specifications included supply of the chemical oxidant technology, bulk chemical storage equipment, explosion proof (Class 1, Division 2) chemical feed equipment and equipment installation and maintenance as well as project startup and operational support, remote monitoring and chemical inventory management. Likewise, pre-project laboratory testing was required to confirm treatment process effectiveness and overall project economics.

One of the many challenges of this project was the available space in the refinery. The refinery's property runs parallel to the Allegheny River, with the wastewater treatment area immediately adjacent to the river, leaving little room available to store temporary treatment equipment. An aerial shot of the refinery wastewater treatment area and proposed location for the temporary treatment equipment is shown (below) in Figure 2.

Figure 2 – Refinery Wastewater Treatment - Google Earth



The refinery had initially considered several chemical oxidation technologies including ozone, chlorine dioxide, Fenton's Reagent (iron catalyzed hydrogen peroxide) and permanganate. The treatment contractor and refinery personnel conducted laboratory treatability testing to evaluate both Fenton's Reagent and permanganate oxidation of phenols. Both oxidizers proved to be very effective, meeting the refinery's internal target of 0.5 mg/L phenol in 60 minutes. Fenton's Reagent's is an established and well documented industrial wastewater treatment technology. Its best technical fit, however, is in lower flow and higher concentration streams. This is due to the requirement for pH adjustment to the acid range and the need for an iron based catalyst (e.g. ferrous sulfate). The practical and operational challenges of feeding multiple chemicals and maintaining proper pH control in a 625 GPM (900K GPD) wastewater flow is apparent.

Permanganate is also well known for its chemical oxidation of phenol and can be readily accomplished at neutral to alkaline pH conditions, which was typical of the refinery's wastewater 7-8 pH range. Likewise, permanganate oxidation does not require the addition of a catalyst, therefore providing a single chemical solution for this temporary project. Therefore, this option was attractive to the refinery from an ease of operation perspective as well as being a proven technology. Permanganate oxidation was an ideal temporary phenol treatment option. Due to the refinery's large wastewater flows, however, the relative cost to treat phenols compared to the existing biological aeration system meant the treatment technology was not considered a viable long term option for the refinery. The theoretical ratio of permanganate:phenol for complete oxidation (mineralization) is 15.7:1, as shown below. From a practical standpoint, a permanganate:phenol ratio closer to 6-7:1 is required for oxidation to carboxyl acids.

$$3\ C_6H_5OH + 28\ MnO_4- + 5\ H_20\ \text{-------}\rightarrow 18\ CO_2 + 28\ OH + 28\ MnO_2$$

In March 2015, treatment tests were conducted in the refinery's laboratory using fresh samples of wastewater from the pre-aeration tank and 40% liquid sodium permanganate. Typical phenol concentrations entering the aeration tank range from about 2 – 7 mg/L, the untreated sample in this case was 3.5 mg/L phenol. A range of permanganate:phenol ratios were evaluated, 5:1 – 20:1. Results indicated that a 20:1 ratio (wt./wt.) would be required to achieve the refinery's phenol reduction target of 0.5 mg/L within 60 minutes as shown in Table 1 (below).

Table 1: MnO_4- Oxidation of Phenol

Permanganate:Phenol Ratio (wt.)	Phenol (mg/L)			
	0 min	10 min	45 min	60 min
5:1	3.5	2.25	2	n/a
10:1	3.5	2	2	n/a
15:1	3.5	1.5	1.5	1.25
20:1*	3.5	0.4	0.4	0.3

*Note: 20:1 ratio achieved Refinery phenol target of <0.5 mg/L

All permanganate was consumed at 45 minutes for the 5:1 and 10:1 ratio treatments, so no further phenol oxidation occurred at 60 minutes. Despite a NPDES maximum discharge limit of 1.2 mg/L, the refinery targeted a treatment level of 0.5 mg/L to allow for process variations. In addition to the variability of phenol concentrations indicated above, aeration tank inlet wastewater chemical oxygen demand (COD) can also vary from about 200 – 500 mg/L, depending on operating conditions in the refinery or wastewater pretreatment units. Changes in COD can impact the level of background demand for permanganate, above and beyond the specific requirement for phenol oxidation. A reaction time of 60 minutes was needed in order to minimize phenol oxidation tank footprint, given the refinery's space constraints. The objective was to be able to effectively treat the 625 GPM (37,500 GPH) flow, through two 20,000 gallon frac tanks. In addition, at the end of the reaction, it was critical that residual permanganate leaving the oxidation reaction tanks was minimal or non-detectable. Test results showed that all the permanganate completely reacted in 60 minutes, in all ratios tested. Residual permanganate values for the same test as in Table 2 are shown (below) in Table 2.

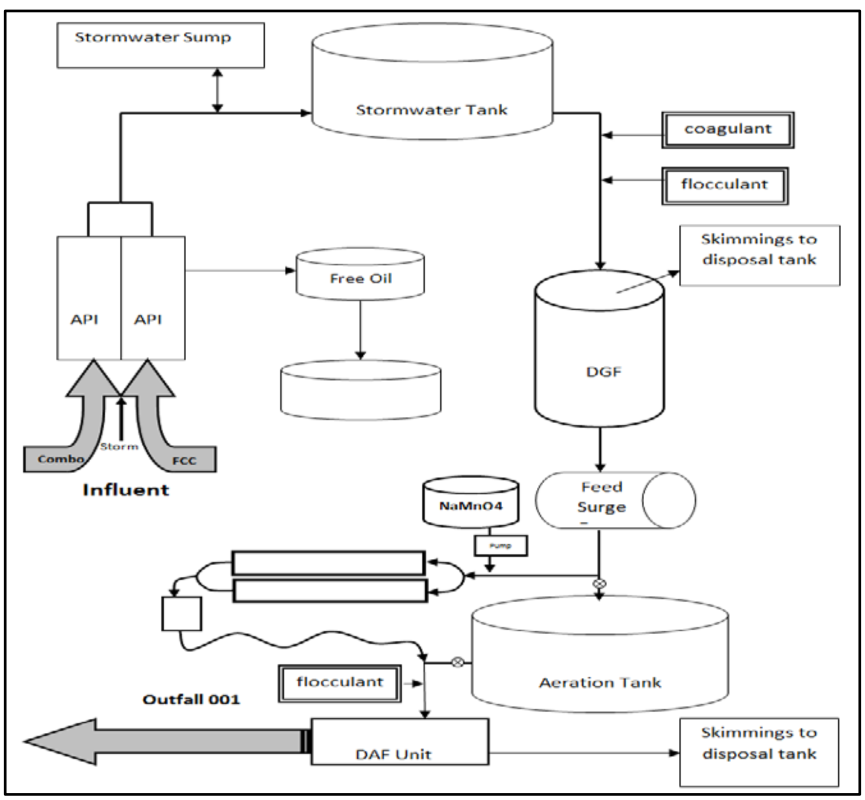
Table 2: MnO_4- Residuals over 60 minutes

Permanganate:Phenol Ratio (wt.)	Permanganate Residuals (mg/L)				
	0 min*	5 min	30 min	45 min	60 min
5:1	17.5	0.75	1	N/D	N/D
10:1	35	1.5	2	N/D	N/D
15:1	52	2	2.5	0.05	N/D
20:1	70	>3	>3	0.05	N/D

*The "0 min" data is the amount of permanganate added for each ratio.

Based on successful lab treatability testing, a process flow diagram for the temporary phenol treatment system was developed. DGF effluent (aeration tank influent) would be rerouted to by-pass the aeration tank and flow through two 20,000 gallon nominal capacity phenol oxidation tanks (frac tanks), run in parallel. The phenol oxidation tanks were outfitted with mixers and baffles to prevent short circuiting of the flow and ensure the required reaction time was provided. Permanganate would be injected into the wastewater flow as it entered the front end of the phenol oxidation tanks. Injection of permanganate upstream of the dissolved air flotation (DAF) units was done to provide removal (flotation) of the manganese dioxide (MnO_2) floc that is a by-product of oxidation, and could potentially contribute to total suspended solids (TSS) in the effluent. The flow diagram of the temporary phenol treatment system is shown in Figure 3 (below).

Figure 3 – PFD Temporary Phenol Treatment System

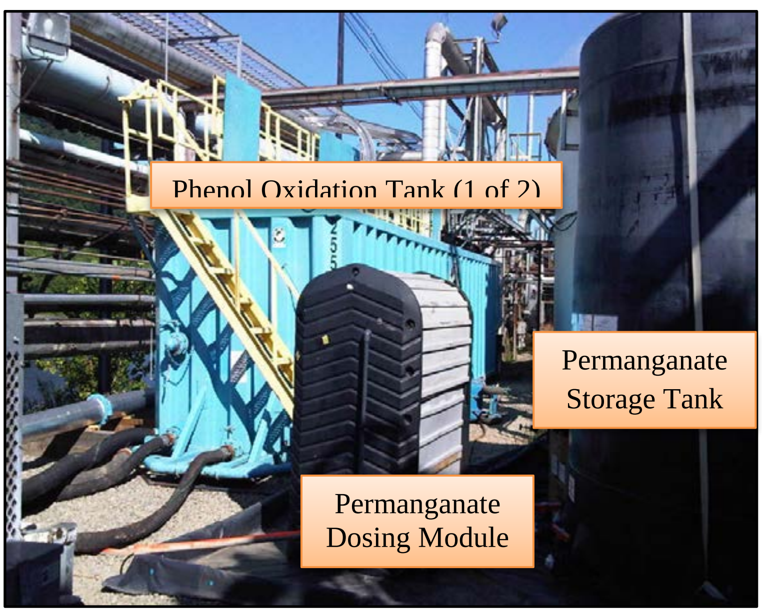


In late April 2015, installation of the required aeration tank bypass piping, phenol oxidation tanks and bulk permanganate storage and feed equipment was installed and tested by refinery and treatment contractor personnel. On May 6th, the wastewater flow was diverted through the oxidation tanks, injection of permanganate was started and the full scale phenol treatment system was launched. In concert with the phenol treatment part of the project, draining of the aeration tank and removal of aging liner material and baffle curtain commenced, as shown in Figure 4 (below). This would later be followed by installation of a more robust curtain as well as sealing and spray coating the aeration tank walls.

Figure 4 – Removal of Liner and Baffle Curtain

As noted previously, space for this temporary phenol treatment project was quite limited. This is evidenced by the photo in Figure 5 (below), showing the treatment contractor's bulk permanganate storage tank and feed system (Class 1, Div. 2) containment berm and one of the two phenol oxidation tanks.

Figure 5 – Treatment Contractor Temporary Systems

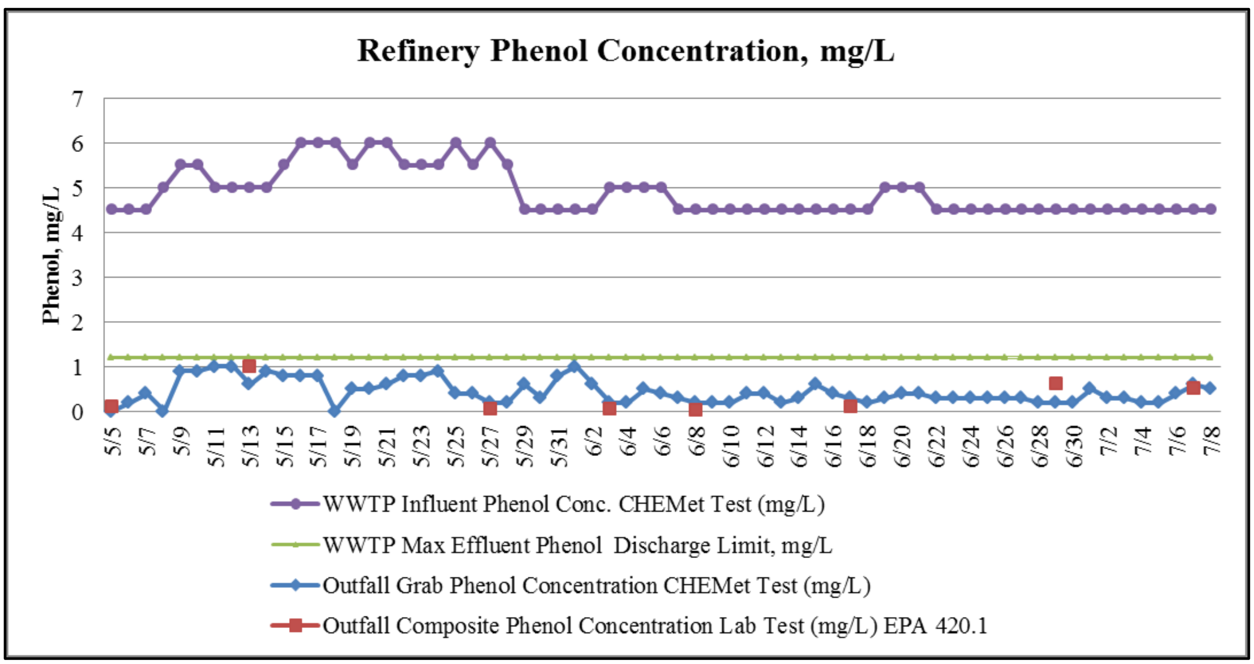


At the start-up of the project and throughout, regular sampling and process monitoring of the DAF effluent was conducted. This included measurement of phenols, using the 4-aminoantipyrine (4-AAP) test method and residual permanganate using low range (0-3 mg/L) permanganate test strips. Phenol data for NPDES reporting purposes used EPA method 420.1. Although wastewater flows were mostly consistent (with exception of significant rain events), this regular sampling was required to make adjustments to the permanganate feed rates, given the variability of wastewater phenol and COD concentrations.

The requirement for liquid permanganate during the project ranged from a low of 125 GPD to a high of 300 GPD (1 day) with an overall average of 174 GPD. Permanganate inventories were remotely monitored by the treatment contractor via cellular based telemetry. Deliveries were scheduled directly with the permanganate manufacturer as soon as the bulk tank could receive a full tanker truck (4,000 gallons). This was needed to ensure sufficient lead times for bulk deliveries so product was always available for this mission critical application.

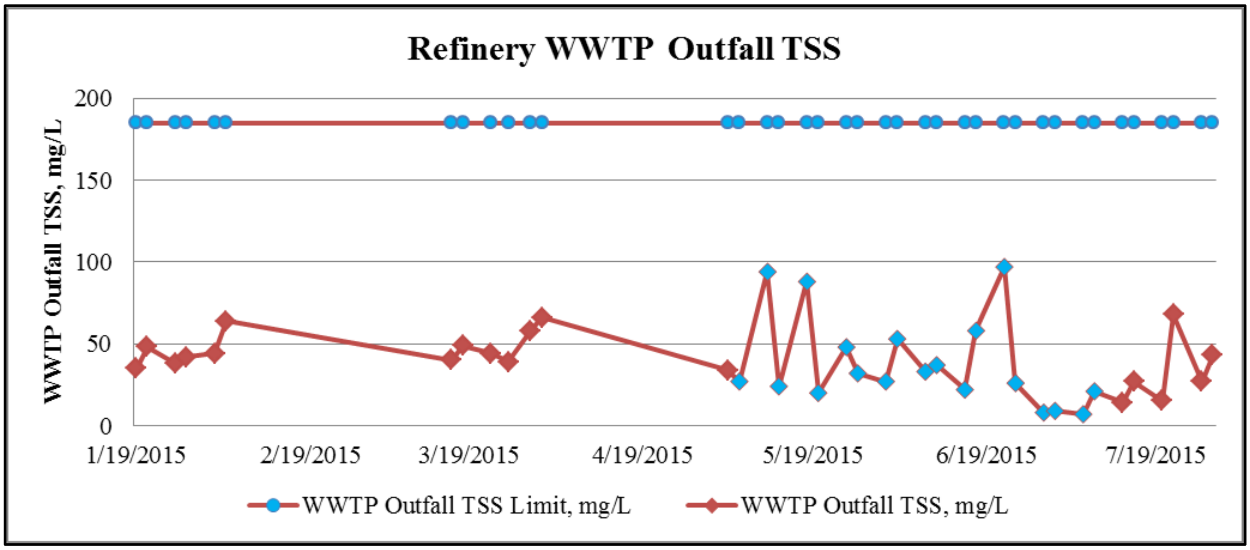
The Key Performance Indicators (KPI's) for this project were the reporting data submitted for NPDES compliance. Figure 6 (below) compares the phenol values for oxidation tank influent, effluent (both 4-AAP test kit values, and EPA method 420.1 values), with the maximum discharge limit of 1.2 mg/L. This data covers the period just before, during and after the temporary treatment system was implemented as part of the aeration tank turnaround project. The highest effluent phenol value recorded during this project was 0.98 mg/L (EPA 420.1), which occurred within the first several days. After gaining more operational experience, the average effluent phenol concentration over the rest of the treatment program was 0.23 mg/L. This data confirmed the effectiveness of the treatment program, maintaining the refinery in compliance with their NPDES phenol discharge permit.

Figure 6 – Effluent Phenol Data



Likewise, NPDES reporting data also documented that the MnO_2 floc formed during the phenol oxidation by permanganate did not have a negative impact on effluent TSS. The MnO_2 was readily removed (floated) in the DAF without the need for any change to the normal flocculant chemistry used. Significantly, effluent TSS values during the majority of project were at or below normal (pre-project) levels. Outfall TSS limits (185 mg/L max.) and NPDES reporting data points during the temporary phenol treatment are noted in blue and shown in Figure 7 (below).

Figure 7 – TSS Reporting Data Points during Permanganate Treatment



Upon completion of the aeration tank upgrades, wastewater flow was returned back to the aeration tank on July 6th and normal operation of the wastewater treatment system was resumed. The two photos in Figure 8 (below) show the newly spray-coated and resealed aeration tank (left) and the fully operational aeration tank (right) with new baffle curtain in the foreground.

Figure 8 – Aeration Tank Completion

PROJECT SUMMARY AND HIGHLIGHTS

- This temporary treatment program successfully met the permitted effluent phenol discharge levels during the entire project, keeping the refinery in compliance with their NPDES permit.
- Discharge limits for TSS and all other effluent parameters were likewise achieved.
- This highly effective temporary treatment program provided the refinery personnel and other contractors involved in this project the time to make the necessary upgrades to the aeration tank.
- The aeration tank turnaround project was completed in 65 days, which was 5 days sooner than the projected 70 days.

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