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Peroxide Destruction Testing for the 200 Area Effluent Treatment Facility

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
under Contract DE-AC06-08RL14788

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Peroxide Destruction Testing for the 200 Area Effluent Treatment Facility

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D. L. Halgren
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Date Published
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EXECUTIVE SUMMARY

The hydrogen peroxide decomposer columns at the 200 Area Effluent Treatment Facility (ETF) have been taken out of service due to ongoing problems with particulate fines and poor destruction performance from the granular activated carbon (GAC) used in the columns. An alternative search was initiated and led to bench scale testing and then pilot scale testing. Based on the bench scale testing three manganese dioxide based catalysts were evaluated in the peroxide destruction pilot column installed at the 300 Area Treated Effluent Disposal Facility.

The ten inch diameter, nine foot tall, clear polyvinyl chloride (PVC) column allowed for the same six foot catalyst bed depth as is in the existing ETF system. The flow rate to the column was controlled to evaluate the performance at the same superficial velocity (gpm/ft^2) as the full scale design flow and normal process flow. Each catalyst was evaluated on peroxide destruction performance and particulate fines capacity and carryover. Peroxide destruction was measured by hydrogen peroxide concentration analysis of samples taken before and after the column. The presence of fines in the column headspace and the discharge from carryover was generally assessed by visual observation.

All three catalysts met the peroxide destruction criteria by achieving hydrogen peroxide discharge concentrations of less than 0.5 mg/L at the design flow with inlet peroxide concentrations greater than 100 mg/L. The Sud-Chemie T-2525 catalyst was markedly better in the minimization of fines and particle carryover. It is anticipated the T-2525 can be installed as a direct replacement for the GAC in the peroxide decomposer columns. Based on the results of the peroxide method development work the recommendation is to purchase the T-2525 catalyst and initially load one of the ETF decomposer columns for full scale testing.

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1.0 INTRODUCTION

1.1 Purpose

Pilot scale testing of several manganese dioxide catalysts was conducted as part of the development of options to replace the existing 200 Area Effluent Treatment Facility (ETF) granular activated carbon (GAC) fluidized bed process for destruction of residual hydrogen peroxide in the process wastewater. The objective of this testing was to demonstrate if the catalysts could meet the original process design requirement for hydrogen peroxide destruction capabilities. That criterion is reduction of the peroxide concentration from more than 100 mg/L to 0.5 mg/L at a maximum superficial velocity of 12.7 gpm/ft^2 (a 3.5 minute nominal residence time). One notable difference in the manganese dioxide (MnO_2) catalysts versus the GAC is the higher density prohibits fluidizing the bed at the system design superficial velocities. Ensuring that the catalysts can still meet the performance requirements with potentially reduced active surface area is one aspect of this testing. Another important factor observed during the testing was any indication of particulate fines in the column headspace or the pilot column discharge. Part of that observation was to see if the static catalyst bed state may be beneficial in regards to reduced fines generation. No quantitative criteria were applied to fines generation due to equipment limitations but several qualitative observation methods were used. The ability of the selected catalyst to directly replace the GAC without significant modification to the system was also a consideration. Evaluation of the test data and observations was expected to lead to a recommendation on a catalyst for use in the ETF peroxide destruction system.

1.2 Background

The 200 Area ETF is a wastewater treatment facility that employs a series of unit operations to treat wastewater generated from Hanford Site cleanup activities. The ETF is a RCRA permitted facility capable of treating hazardous wastewaters including those with low levels of radioactive contamination. The main treatment train includes the peroxide destruction module (PDM) where the hydrogen peroxide residual from the upstream ultraviolet (UV) light/hydrogen peroxide oxidation unit is destroyed. Removal of the residual peroxide is necessary to protect downstream reverse osmosis membranes from the strong oxidizer. The main components of the PDM are two decomposer vessels currently utilizing GAC as the catalytic media.

The PDM has experienced a number of operability problems, including frequent plugging, and has not been utilized since the ETF changed to groundwater as the predominant feed source. The unit seemed to be underperforming in peroxide removal during early periods of operation as well[1]. The epoxy coated steel vessels have corroded due to failure of the epoxy coating.

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[1] *Activated Carbon Testing for the 200 Area Effluent Treatment Facility*, R. N. Wagner and J. B. Duncan, HNF-SD-LEF-TI-004, January 1997

The facility has tried several different types of GAC, modified the inlet and outlet headers in the decomposer vessels, and added filters downstream of the PDM in an effort to make the system useable. These things did not sufficiently mitigate the underlying GAC fines problem. Once groundwater treatment commenced the reduced organic constituent concentration did not require peroxide concentrations high enough to significantly affect the reverse osmosis membranes so the PDM was bypassed.

The pilot scale testing of the candidate catalysts is part of the effort to return the PDM to functional service. It is forecast that peroxide destruction capabilities will be critically needed to adequately treat anticipated organics new waste streams from Hanford waste tank remediation activities. Providing an alternative that could be implemented within the same footprint of the existing PDM would be desirable from a simplicity and cost standpoint. Given the condition of the existing decomposer columns they will require replacement so a different configuration within the footprint bounds would be acceptable.

2.0 Bench Scale Testing Summary

Bench scale testing was conducted on approximately 15 initial candidate catalysts to determine their viability. These included the GAC used at the ETF used as comparison point to relate the current performance. In general, the MnO_2 mineral type media, MnO_2 engineered catalysts, and precious metal catalysts performed as well or better than the GAC for peroxide removal in the jar and column tests. The MnO_2 catalysts definitely had fewer fines than the GAC and were cleaner at every phase of operation. The MnO_2 mineral catalysts appeared somewhat improved over the GAC for fines generation. None of the MnO_2 or precious metal catalysts fluidized even at the higher backwash flow rates which would be anticipated to reduce the fines generated during ongoing service. The alumina and iron based catalysts were eliminated from further consideration by this testing based on performance and fines generation. The performance of the precious metal catalysts did not warrant further consideration given the significantly higher catalyst costs.

Destruction of the hydrogen peroxide (H_2O_2) using a reducing agent was also included in the bench testing. Sodium sulfite was used and rapidly reduced the H_2O_2 below the target concentration with a 10% stoichiometric excess determined to be optimal.

A letter report was prepared at the conclusion of the bench scale testing and includes additional details on the testing and some analysis of the potential peroxide destruction methods. It is attached as Appendix A. The testing was conducted according to a prepared test plan[2].

3.0 Pilot Scale Testing

Pilot scale testing was recommended from the bench scale testing to confirm the catalyst performance for H_2O_2 destruction and particulate fines potential in a column of full scale equivalent bed depth so both the superficial velocity and residence time can be duplicated at the same time. Testing in a larger diameter column would also reduce wall effects of a small column and better simulate the flow regime in the column which could impact fines carryover from the column.

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[2] *Effluent Treatment Facility Peroxide Destruction Catalyst Testing*, D.L. Halgren, HNF-38408, July 2008

Information from the bench scale testing provided the basis for selecting the catalysts to be tested. The following three MnO_2 catalysts were selected for testing, two engineered catalysts and one MnO_2 mineral based catalyst.

- SudChemie T-2525, MnO_2 on alumina, 1/16" CDS extrusion
- Carus® Carulite® 200, MnO_2/CuO, 4 X 8 mesh granular
- High Purity MnO_2, 75 X 150 granular.

Testing was conducted at the 300 Area Treated Effluent Disposal Facility (TEDF). The TEDF process includes the same UV oxidation unit operation but the reduced radiological conditions and flexibility considerations made installation of the peroxide destruction pilot (PDP) column there more attractive. Actual testing time was less than anticipated due to delays in column installation, operation resource availability, and the pending permanent shut down of the TEDF. Sufficient test runs were made to assess each of the catalysts in both an upflow and downflow configuration. Testing was conducted according to the operating procedure included in Appendix B.

3.1 Testing Equipment

The PDP column was constructed from a ten inch diameter clear PVC pipe with flanges installed on the top and bottom (Figure 1). A tee was installed at the bottom of the nine foot column to provide access to the bottom of the column. The tee branch stub was filled with inert material to avoid filling with catalyst. Wastewater entered and exited the column through the upper and lower distribution headers which were horizontal ¾" pipes with approximately 20 holes at 1/8" diameter. An air release valve was installed at the top of the column to provide venting for the gas generated during operation. Two nozzles were added to the column for transferring catalyst and the top nozzle was fitted with a pressure indicator for use during column operation.

Installing the column at the 300 Area TEDF to operate off a slipstream while recirculating wastewater between the IX Feed Tank through the UV unit to the Effluent Tank was the safest and most efficient approach (See Figure 2). Acid addition for pH control and H_2O_2 addition utilized the normal plant systems. Flow to the column was manually controlled by the valve at the point the slipstream branched from the recirculation line using a portable ultrasonic flow meter for monitoring. A pressure gage was also installed on the slipstream instrument line. Hoses were used for connection to the column so the configuration could easily be changed between upflow and downflow.

FIGURE 1 – PEROXIDE DESTRUCTION PILOT TEST COLUMN

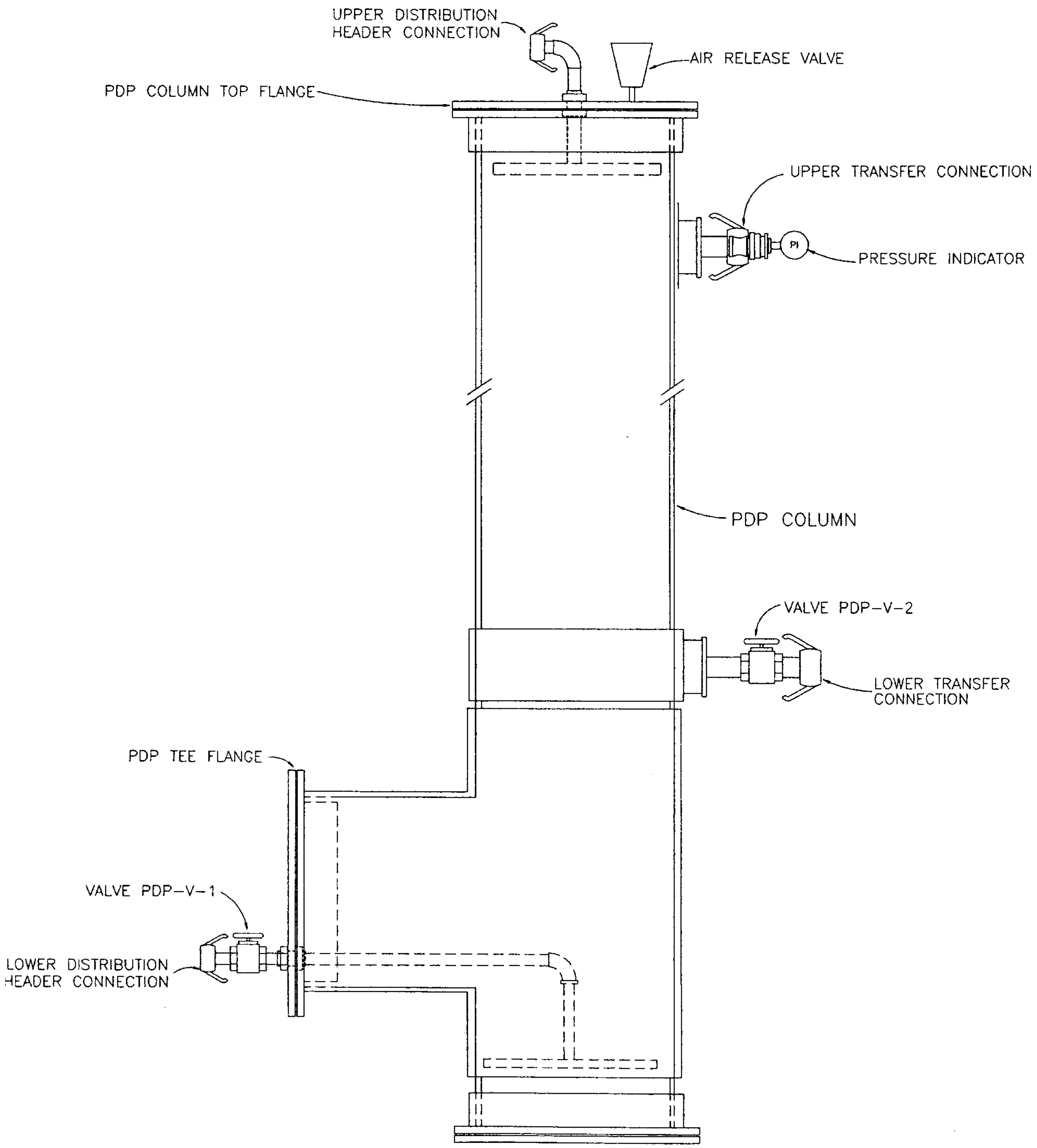
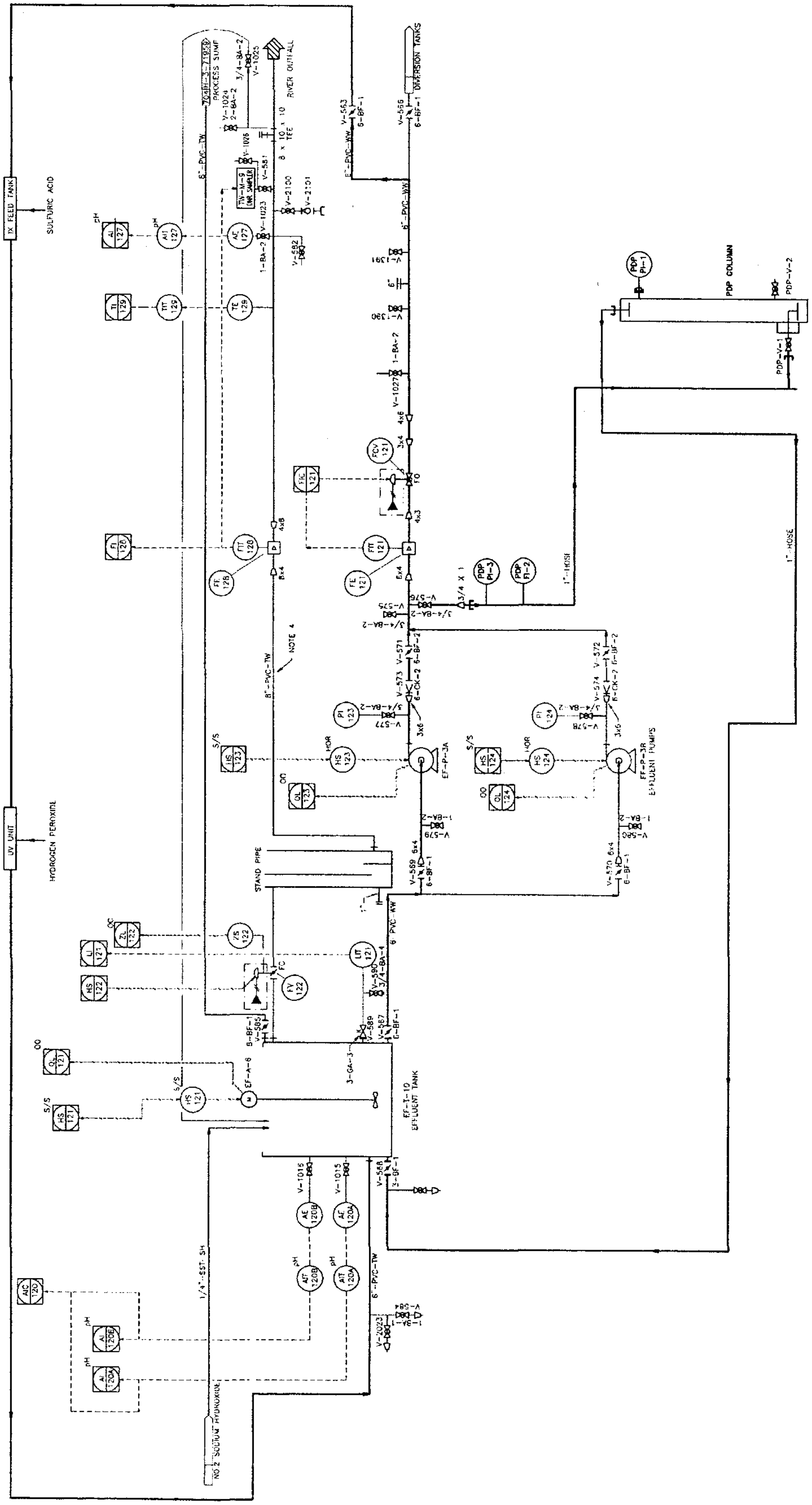


Figure 2 – Peroxide Destruction Pilot Flow Diagram



3.2 Testing Description

Testing included three main parts for each of the catalysts; bed washing, upflow configuration operation, and downflow configuration operation. Refer to the test operation procedure in Appendix B for details of how the testing was conducted. Generally the operating setpoints and conditions were specified on the test datasheet form exhibited in the procedure.

The column was loaded to the six foot level with the catalyst to be tested. There were some fluctuations in bed height throughout the testing but the changes were within several inches and any loading height differences were not significant enough to impact the performance results. Washing was done with plant sanitary service water up through the lower distribution header. The initial bed washing flow rate target was set to match the ETF PDM washing flow rate criteria of 20 gpm/ft^2 or 11 gpm in the PDP column. In each case wash flow rates were raised from the initial target to observe additional fines release and bed behavior since these catalysts do not fluidize like GAC. The target wash time was 30 minutes but in practice was varied depending on observed conditions. Visual observations were made at the wash discharge and column head space on solids presence and water coloring.

For the peroxide destruction testing the column was operated at flow rates that included the maximum PDM design flow equivalent, 7 gpm in the PDP column, and a more normal process flow rate equivalent, 4 gpm in the PDP column. Since the test system was operated in a recirculation mode the H_2O_2 addition rate had to be monitored and adjusted to try and match addition rate with steady state losses. The H_2O_2 concentration in the column influent was generally maintained in the 100 to 150 mg/L range but was as high as 200 mg/l during part of the T-2525 catalyst testing. Peroxide concentration sampling was done at the inlet to the UV unit, the inlet to the column, and the discharge from the column. Peroxide analysis was done using the CHEMet® and VACUettes® colorimetric test kits. The wastewater pH setpoint was adjusted to 5.5 for these tests by addition of sulfuric acid at the IX Feed Tank. There was no temperature control for the wastewater.

Upflow is considered the standard flow path for this process due to the gas generation during H_2O_2 destruction. This configuration allows the gas bubbles to go out the vent at the top of the column with minimal air carryover in the discharge. This is the configuration most likely to allow fines to escape the column. These two conditions were determined using visual observation of the column headspace and discharge.

Operation of the catalyst bed in a downflow configuration was tested to assess the impacts of gas generation on the operation of the column and identify potential impacts to the downstream equipment. The commercially available MnO_2 mineral media units for use in drinking water treatment operate in downflow mode to provide filtering as well as iron and sulfide treatment. They are then backwashed to remove collected fines and solids. There is no significant gas generation in that service however. Important observations during this testing were the fate of the gas bubbles generated during the H_2O_2 reaction, the presence of any particulate in the discharge, and changes in the system pressures during operation.

4.0 Data and Results

There are two main properties of the catalyst systems evaluated by this testing that will drive the decisions made on replacement of the existing GAC media in the ETF PDM. The catalyst must be capable of achieving destruction of the residual H_2O_2 given the prescribed concentration and flow conditions. Use of the catalyst should result in minimal particulate fines leaving the catalyst bed. An assessment of the catalyst performance in regards to these criteria follows. A more detailed summary of data and test notes for the three catalysts is in Appendix C.

4.1 Peroxide Destruction Performance

All three catalysts performed well in destroying the H_2O_2 from the post UV unit wastewater. All sample sets taken showed a peroxide destruction factor greater than 99% and there was just one sample that did not meet the less than 0.5 mg/L H_2O_2 criteria, a 0.6 mg/L result. If any differentiation could be made from the data the T-2525 catalyst did not have any results less than 99.8% even though the highest H_2O_2 concentrations occurred during one of the T-2525 test runs. The MnO_2 mineral catalyst may perform better in the downflow configuration with a slightly higher H_2O_2 destruction factor, 100% versus 99.6%. There was no difference identified for the flow configuration for the other two catalysts. The pH was controlled at 5.5 to match the ETF process pH. Temperature was not controlled and the ambient wastewater temperature varied between the mid-60's °F to the mid-70s °F. With so little difference in the destruction factor for the different flow and H_2O_2 concentration parameters tested the only observation is that all three catalysts would be expected to meet the peroxide destruction criteria for the design flow and H_2O_2 concentration design ranges.

One test observation important to H_2O_2 destruction is the presence of hydraulic channeling in the catalyst bed. There was visual indication that some channeling was taking place in the column during upflow operation. It was most notable at the apex of the column tee opening. This observation underscores the importance of effective flow distribution in the column. It appeared to be most pronounced during the T-2525 catalyst testing. It is unclear if that may have had any influence on the T-2525 bed separation situation discussed in the next section.

4.2 Catalyst Fines Observation

The color of all the catalysts was black or dark grey which made the presence of fines fairly easy to detect by observation. During the first test an attempt was made to sample the bed washing stream and analyze it using a transmission reading from a spectrophotometer. While that provided quantified numbers as the stream cleared the difficulty of getting a good sample and other errors made qualitative observation more valuable. Change in wastewater coloring could be observed in the column headspace and in the discharge stream. When the wastewater was generally clear individual particles could be seen in both locations as well.

For this criterion the three catalysts performed at three distinctly different levels. The High Purity (HP) MnO_2 catalyst showed a much higher fines loading. The bed washing discharge was still colored after more than an hour of washing. There were continually particles in suspension in the column headspace from the gas bubble action at the surface of the bed and noticeable particles in the discharge stream during normal operation. Abrupt changes in flow through the column would cause momentary coloring of the wastewater. There was a measureable loss of media over the course of the HP MnO_2 test run.

In comparison the T-2525 catalyst was clear after five minutes of washing. The bed wash flow rate was raised up to 17 gpm from the target 12 gpm with only a momentary coloring and no fines carryover. Gas bubble eruptions caused little disturbance on the bed surface and there was a very minimal number of catalysts particles in the column headspace at the highest flows tested. There was no indication of any catalyst carryover out of the column. The T-2525 was clearly the best candidate in regards to fines generation and particle carryover.

Performance of the Carulite® 200 catalyst was somewhere in-between the previous catalysts in fines and carryover. There were noticeable particles in the column headspace at the higher flow rates and some catalyst carryover out of the column in the discharge as well.

4.3 Other Testing Observations

The fines generation and particle carryover problem could potentially be mitigated by switching the column configuration to a downflow mode instead of the currently designed upflow. The GAC system was designed to operate as a fluidized bed, however, since the MnO_2 catalysts cannot be fluidized at the design superficial velocities downflow mode becomes an option. There several noteworthy observations about downflow operation from the testing. First is that in all cases the gas bubbles dissipated out the discharge line regardless of H_2O_2 concentration (quantity of bubbles) or flow rate. There was an initial buildup of bubbles trapped in the interstitial areas of the catalyst bed then any additional bubbles were carried down the column with the flow and out of the bottom discharge with no countercurrent bubbles being vented out of the top of the column. Impacts of the entrained gas on the function downstream equipment would have to be evaluated before downflow could be considered.

Given the fines problem with the HP MnO_2 the only way that product could be used is in the downflow configuration as it is designed to be used in commercial and residential applications. Another potential problem that was observed during the downflow testing with this media is that as the bed void areas filled with gas pockets the differential pressure (dP) began to rise. The dP rose to the maximum operating pressure of the column and restricted the available flow. When the flow was stopped the gas pockets released up the column and out the vent and the dP returned to normal but started building again on restart of flow. There was no significant dP increase during downflow operation with the T-2525 catalyst even though some gas pockets in the interstitial areas did appear. The gas buildup reached equilibrium after about one hour of operation and stabilized.

During the first T-2525 catalyst test there was a period where the catalyst bed separated and the top portion was suspended by a layer of gas bubbles. Sufficient gas bubbles formed across the entire bed at about mid-column and lifted the top portion of the bed. Individual particles were falling down through the gap formed by the rising segment. This was repeated several times with most of the lifted segments destabilizing and collapsing back to the bed surface before reaching the top, but two slugs reached the discharge header where they broke up leaving particles lodged in the header holes. The particles dislodged from the header by stopping or reversing the flow. This only occurred during conditions of high flow and high H_2O_2 concentration. When either of these parameters was reduced small gaps sometimes appeared in the bed but did not cause separation of the bed. After this first upflow test was completed a downflow test was conducted. When the upflow test was repeated this segmentation phenomena could not be repeated even at high flow (7.2 gpm) and H_2O_2 concentration (200 ppm) conditions. It was noted in the first test there was very obvious channeling above the tee in the column and the notation in the second test was there seemed to be less channeling at the same flow rate.

5.0 Conclusions and Recommendations

This report documents the investigation into the available methods for replacing the existing ETF process wastewater H_2O_2 destruction process. An information search identified a number of potential catalysts and media as well as chemical reduction reaction as potential methods. Bench scale testing on a representative number of catalysts narrowed the candidates down to MnO_2 based catalysts. Pilot scale testing was conducted on selected MnO_2 catalysts as reported in this document and provides the basis for the following recommendations.

Implementation of a chemical reduction system to replace the existing PDM would involve a much more extensive facility modification and introduce another chemical to routinely handle. It would also place some additional load an already burdened ETF secondary waste handling system from the addition of ions that will be removed in the reverse osmosis and ion exchange units. Based on these factors and the positive results of the MnO_2 catalyst testing this option will not be pursued.

The Sud-Chemie T-2525 catalyst is the recommended replacement for the GAC media based on the results of this testing. All the catalysts met the criteria for H_2O_2 destruction capability. It was the second criteria of minimizing generation of fines and particle carryover that separated the T-2525 catalyst from the others. Operational problems caused by fines generation is a very important issue and is the predominant reason the GAC is being replaced. It is anticipated the T-2525 can be operated in the upflow mode which would allow it to be used as a direct replacement for the GAC in the PDMs without additional configuration modification.

The HP MnO_2 media would have to be used in a downflow configuration because of fines carryover problem. Although the MnO_2 mineral type media is less expensive than the other two engineered catalysts that savings would be offset by costs to reconfigure the system for downflow operation. This would include possible modifications downstream to handle the entrained gas and the bed pressure buildup that was observed. In downflow mode regular backwashes would be required. These factors increase the operational burden of the system.

The anticipated replacement of the existing PDM columns should be used to attempt to improve the flow distribution in the column. Flow distribution characteristics will be more important in preventing channeling with the fixed bed instead of a fluidized bed. Observations of channeling in the PDP test column may have been a contributing cause for the T-2525 catalyst bed segmentation irregularity. The full scale column configuration is expected to significantly reduce the likelihood of the bed segmentation and lift reoccurrence. The much larger column diameter, no obstructing tee opening transition, and better flow distribution across the column should mitigate formation of any contiguous gas layer across the bed. If a concern still exists when new columns are designed a simple addition to the discharge header to protect it from a slug may be considered.

The results from this pilot scale testing are considered sufficient to proceed with full scale testing of the recommended T-2525 catalyst. Implementation would involve the following steps.

- Purchase the T-2525 catalyst.
- Remove the GAC from PDM column 60D-CO-1B.
- Perform inspection of column to verify it is fit for service.
- Load T-2525 catalyst into column 60D-CO-1B.
- Perform controlled testing of the catalyst.

Appendix A – Letter Report, *Hydrogen Peroxide Destruction Methods Suitable for the Effluent Treatment Facility*

HNF-45613 Rev. 0

Hydrogen Peroxide Destruction Methods Suitable for the Effluent Treatment Facility

Dale L. Halgren
Fluor Hanford

Graham T. MacLean
Fluor Government Group

September 30, 2008

Introduction

The 200 Area Effluent Treatment Facility (ETF) main treatment train includes the peroxide destruction module (PDM) where the hydrogen peroxide residual from the upstream ultraviolet light/hydrogen peroxide oxidation unit is destroyed. Removal of the residual peroxide is necessary to protect downstream reverse osmosis membranes from the strong oxidizer. The main components of the PDM are two reaction vessels utilizing granular activated carbon (GAC) as the reaction media.

The PDM has experienced a number of operability problems, including frequent plugging, and has not been utilized since the ETF changed to groundwater as the predominant feed. The unit seemed to be underperforming in peroxide removal during early periods of operation as well. The current GAC unit has not performed satisfactorily,[3] and the epoxy coated steel vessels have corroded due to failure of the epoxy coating.

It is anticipated that a functional PDM will be required for treatment of wastewater from the vitrification plant and other future streams. An alternate media or method needs to be identified to replace the GAC in the PDMs. Therefore, Effluent Treatment Facility Engineering requested that a study be conducted of possible replacement processes for the PDM. A study was undertaken consisting of a literature survey of all possible technologies, laboratory testing of promising catalysts and reducing agents, and evaluation of equipment and materials needed for the most promising approaches. The results are described in this report.

Literature Search

An exhaustive search of the literature on decomposing hydrogen peroxide in water solution was performed using the Engineering Village literature search engine and the internet. A list of pertinent papers is given in the Appendix. The papers are grouped in the three categories below, based on the number of citations:

1. Immobilized catalase enzyme
2. Ferric oxide/hydroxide catalysts
3. Manganese dioxide, transition metal and precious metal catalysts

A large number of papers were found in which the enzyme catalase was immobilized one way or another and used to decompose peroxide. Catalase is the most active catalyst known for the destruction of peroxide, and is an essential enzyme for protection against oxidation damage in man and animals.

Ferric oxide/hydroxide and manganese dioxide based catalysts are used commercially to catalyze oxidation of iron, manganese, and arsenic in potable and process water. Many references were found for using these materials as catalysts for the decomposition of hydrogen peroxide. Since manganese dioxide powder is well known as a powerful catalyst for this decomposition, it was hoped that manganese dioxide or ferric oxide/hydroxide water treating catalysts would have sufficient activity that one or more products will be suitable to replace the activated carbon in the ETF PDM.

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[3] "Activated Carbon Testing for the 200 Area Effluent Treatment Facility," R. N. Wagner and J. B. Duncan, HNF-SD-LEF-TI-004, January 1997

Other catalysts reported in the literature for peroxide decomposition include transition metals such as copper and nickel, precious metals such as platinum and palladium, and even sand.

Laboratory Tests

A number of potential peroxide destruction catalysts were identified through the literature search and supplier technical information. Materials tested to date included precious metal catalysts, manganese dioxide catalysts, iron based catalysts, and manganese dioxide mineral (purified ore). The GAC currently used at the ETF was included in the testing for comparative purposes. In addition, peroxide reduction with sodium sulfite was tested.

Two types of laboratory testing were performed to provide comparative data for these materials. Jar testing was used to generate hydrogen peroxide reaction kinetics data and a bench scale continuous flow column was used to test dynamic peroxide destruction performance and catalyst behavior.

Jar Tests

In these tests 40 milliliters (mL) tamped volume of the media was covered with 300 mL of pH 5 deionized water, spiked to a target hydrogen peroxide concentration of 200 parts per million (ppm). The mixture was hand swirled for mixing and samples were extracted every 3 minutes and analyzed colorimetrically for peroxide concentration. The water temperature was measured but not controlled during these tests and ranged from 21 to 22°C. From the results, first order reaction rate constants were determined for each of the catalysts.

The media were all washed prior to use. However, during several of the tests, the water had to be filtered prior to performing the peroxide concentration test due to the particulate from the media. The manganese dioxide mineral products (High Purity, LayneOx®), iron compounds, and Carulite® were particularly turbid after swirling. The reaction rates for the iron oxide and activated alumina catalysts were insufficient to warrant any additional testing. The results from the jar testing are summarized in Table 1.

Table 1 - Peroxide Destruction Jar Test Results

Catalyst	Initial H_2O_2 (ppm)	H_2O_2 (ppm) @ t=12 min	Reaction Rate (min^{-1})
Platinum (1%) 8 X 18	220	0.4	0.54
LayneOx® (MnO_2) 20 X 40	190	0.5	0.47
SudChemie T-2550 (MnO_2/CuO) 1/16" CDS	190	2.5	0.34
Carus® Carulite® 200 (MnO_2/CuO) 4 X 8	250	2.0	0.32
LayneOx® (MnO_2 ore) 8 X 20	190	10	0.29
Calgon Centaur® GAC 12 x 40	200	7.0	0.27
SudChemie T-2525 (MnO_2) 1/16" CDS	190	15	0.20
Palladium (1%) 8 X 18	220	25	0.17
High Purity MnO_2	220	25	0.17
SudChemie T-2525 (MnO_2) 1/10" CDS	250	30	0.13
Activated Alumina AAFS-50 28X 48	200	48	0.12
O-P Hydrous Ferric Oxide 30 X 50	220	40	0.10
GFH Iron Hydroxide Oxide	190	60	0.09
Activated Alumina AA-400 28X 48	200	150	0.02
Iron Oxide Pellets 20 X 80	220	175	0.02
BASF DD-6 (peroxide alumina) 28 X 48	200	175	0.01

Column Tests

A one inch diameter clear PVC pipe was used as the test column for the continuous flow catalyst tests (See Figure 1). The column could be configured in either an up flow or down flow configuration. Tests were conducted using a low flow rate to approximate the superficial residence time in the current PDM columns, and a higher flow to approximate the superficial velocity. In order to provide a comparison, the bed depth was generally limited to the smallest media sample size which was 50 mL tamped volume (approximately 3.75 inches of bed depth), but several tests were performed with a 12-inch bed depth.

The results of the bench scale column peroxide destruction tests are summarized in Table 2. In general, the manganese dioxide ore media performed the best with manganese dioxide catalysts and platinum also performing well. The platinum catalyst did not stand out enough to warrant the significantly higher cost. Manganese dioxide ore media is the least expensive but concern remains about the fines from the media based on the turbidity during both the jar testing and some of the column tests. This is supported by the catalyst fines generation test results where only the GAC and the manganese dioxide mineral had measureable TSS in the discharge stream (detection limit 1 mg/L). The tests were all conducted at pH 5.0 to 5.5, which is the bottom of the manufacturer specified operating range for the manganese ores. The low pH may affect the stability of the media adding to the turbidity. Down flow column operation appeared to generate less turbidity/fines.

None of top performing media had any notable bed expansion during up flow operation. Uniform flow distribution is a concern and channeling may account for some of the difference between the rankings from the jar test and results from the column tests. The reaction rate constant reported in the table is for comparison purposes only and should not be used for sizing equipment or calculating bed height.

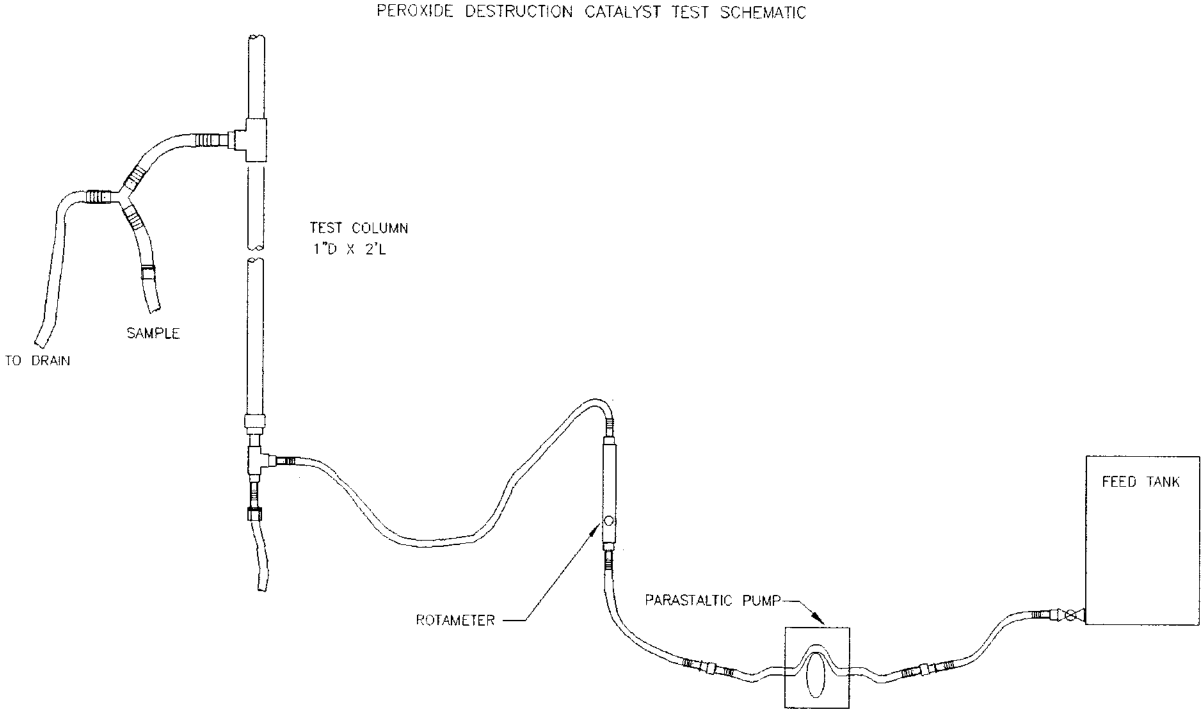

Figure 1

Table 2 - Peroxide Destruction Column Test Results

Property	Flow	Bed Ht.	H_2O_2 in	H_2O_2 out	Flow Direct.	k*
Catalyst	mL/m	in	ppm	ppm	Up/Dwn	min^{-1}
Residence Time Equivalent to Full Scale						
Calgon Centaur® GAC 12 x 40	44	12	200	0.1	U	2.17
SudChemie T-2525 (MnO_2) 1/16"	44	12	190	0.1	U	2.15
O-P Hydrous Ferric Oxide 30 X 50	44	12	200	0.2	U	2.07
SudChemie T-2525 (MnO_2) 1/16"	44	12	240	0.4	D	1.90
LayneOx® (MnO_2) 8 X 20	44	12	190	0.3	U	1.84
SudChemie T-2550 (MnO_2/CuO) 1/16"	44	12	100	0.4	U	1.84
Calgon Centaur® GAC 12 x 40	14	3.75	95	0.2	U	1.79
High Purity MnO_2	32	8.75	215	0.7	U	1.63
LayneOx® (MnO_2) 20 X 40	44	12	175	0.8	U	1.54
Carus® Carulite® 200 (MnO_2/CuO) 4 X 8	44	12	185	1.0	U	1.49
Palladium (1%) 8 X 18	13	3.375	200	1.3	U	1.45
High Purity MnO_2	14	3.875	185	1.5	U	1.35
SudChemie T-2550 (MnO_2/CuO) 1/16"	14	4	200	1.5	U	1.33
Platinum (1%) 8 X 18	14	3.75	185	7	U	0.95
LayneOx® (MnO_2) 20 X 40	14	4	190	7	U	0.94
LayneOx® (MnO_2) 8 X 20	14	4	190	7	U	0.90
SudChemie T-2525 (MnO_2) 1/10"	44	12	200	12	U	0.80
Carus® Carulite® 200 (MnO_2/CuO) 4 X 8	13	3.5	185	25	U	0.58
O-P Hydrous Ferric Oxide 30 X 50	14	3.75	190	30	U	0.54
SudChemie T-2525 (MnO_2) 1/10"	14	3.875	200	30	U	0.53
Superficial Velocity Equivalent to Full Scale						
LayneOx® (MnO_2) 20 X 40	260	4	100	30	D	6.08
High Purity MnO_2	260	3.75	100	35	D	5.66
LayneOx® (MnO_2) 8 X 20	260	4	100	35	D	5.30
High Purity MnO_2	260	3.875	80	30	U	5.12
LayneOx® (MnO_2) 8 X 20	260	4	95	35	U	5.04
LayneOx® (MnO_2) 20 X 40	260	4	80	30	U	4.96
SudChemie T-2550 (MnO_2/CuO) 1/16"	260	4	90	40	U	4.88
Platinum (1%) 8 X 18	260	3.75	105	50	D	4.00
O-P Hydrous Ferric Oxide 30 X 50	260	4	100	50	D	3.50
Platinum (1%) 8 X 18	260	3.75	90	50	U	3.17
Carus® Carulite® 200 (MnO_2/CuO) 4 X 8	260	3.5	100	60	U	2.95
Calgon Centaur® GAC 12 x 40	260	12	95	17	U	2.92
Carus® Carulite® 200 (MnO_2/CuO) 4 X 8	260	3.5	115	70	D	2.87
SudChemie T-2525 (MnO_2) 1/10"	260	3.875	120	80	D	2.84
Calgon Centaur® GAC 12 x 40	260	3.75	200	120	U	2.75
SudChemie T-2550 (MnO_2/CuO) 1/16"	260	4	90	60	D	2.05
Palladium (1%) 8 X 18	260	3.375	100	75	U	2.01
SudChemie T-2525 (MnO_2) 1/10"	260	3.875	100	70	U	1.86
Calgon Centaur® GAC 12 x 40	260	3.75	200	90	D	1.66
Calgon Centaur® GAC 12 x 40	260	3.75	200	150	D	1.55
O-P Hydrous Ferric Oxide 30 X 50	260	3.5	110	95	U	1.17
Palladium (1%) 8 X 18	260	3.375	100	75	D	0.63

*Reaction rate based on first order reaction with the time equal to the contact time in the bed (bed vol/flow). For comparison only.

Chemical Reduction Tests

Chemical reduction of hydrogen peroxide was tested using sodium sulfite as the reducing agent. Jar tests were conducted at various sodium sulfite concentrations. The reaction appeared to be complete in a well stirred flask by the time the first sample was taken at 15 seconds. Testing showed that at a 10% stoichiometric excess of sodium sulfite the H_2O_2 was reduced from 195 ppm to 0.1 ppm, while at 5% excess the residual peroxide concentration was 30 ppm.

Testing Recommendations

Pilot scale tests are recommended to determine the most suitable catalyst or media type for the peroxide destruction system. Based on the results from the bench scale testing the pilot testing should focus on the manganese dioxide ore media and manganese dioxide catalysts. The pilot column should be tall enough to allow a full six foot bed height so the testing can be conducted at flows that will replicate both the superficial velocity and residence time. Given the concern over the impact of fines in the system, the potential for fines generation from the manganese dioxide media needs to be more completely assessed before a selection is made. Pilot testing should be sufficient to provide information for sizing of a full-scale unit and selecting the best flow configuration. It is anticipated that at a minimum the following media would be planned for evaluation in a pilot unit.

- SudChemie T-2525 (MnO_2) 1/16" CDS
- Carus® Carulite® 200 (MnO_2/CuO) 4 X 8
- High Purity MnO_2
- Filox-R® (MnO_2 ore) 12 X 40

Process Design and Cost Evaluation

Hydrogen peroxide decomposes spontaneously to the more thermodynamically stable compounds water and oxygen. However, this reaction takes place very slowly, and requires a catalyst to take place sufficiently fast for water treatment purposes. An alternative to catalytic decomposition is chemical reduction by any of a number of reducing agents.

Catalytic Decomposition

The enzyme catalase by far the most effective material for catalytically decomposing H_2O_2, but costs for the material are prohibitive at about $10/g in powdered form. Although there are several commercial manufacturers of the enzyme and a number of references in the literature to immobilizing it, no commercial manufactures of an immobilized product have been located. Therefore, the use of a process utilizing catalase was not developed or evaluated further.

A number of metal oxide catalyst products are commercially available, and have been tested for catalytic activity as discussed in the testing section. All of these products are intended to be used in beds such as used for granular media filtration. The differences are in catalytic activity or efficiency of decomposition, cost, and suitability for use in a granular media bed. The details of testing to evaluate the activity/efficiency and suitability are found in the previous section.

Since the most promising catalysts appear to be the manganese dioxide ores, manufacturer data for one of these products, LayneOx®, was used to evaluate design and cost information for this class of catalysts. Layne recommends a specific flow rate (flux) of 8-15 gpm/ft^2 (1.1-2.0 ft/min) and a bed height of 3–4 ft. for use in oxidizing and removing Fe, Mn, As and H_2S from water. The current GAC column beds in the ETF are 3 ft. in diameter with a 6 ft. bed height, or a volume of 42 ft^3. They are designed to operate at up to 88 gpm, giving a maximum specific flow rate of 12 gpm/ft^2 (1.6 ft/min), in the middle of the range recommend by Layne. The superficial residence time (bed height divided by superficial velocity) at the maximum rate is 3.7 min.

The laboratory column tests were conducted with a superficial flow rate of 0.6 to 12 gpm/ft^2, and superficial residence times of 0.2-4.0 min. The highest superficial flow rate is the same as the maximum design rate for the PDM. The highest superficial residence time is slightly higher than the design for the current PDM columns. The lab column was too short to allow testing at both the same superficial flow rate and residence time as the existing PDM columns. Therefore, tests were conducted at lower flow rates to give approximately the same residence times, and tests were also conducted at the same superficial flow rate with a resulting residence time much shorter than the PDM columns.

Lab column performance was in general good at the long residence times, but as expected, poor at the short ones. The short residence time tests were designed to evaluate the media behavior such as expansion, carryover, bubble buildup. Column performance is generally very much a function of residence time, but not much of rate (i.e., the peroxide decomposition is reaction rate limited rather than mass transfer limited). Therefore, since the residence times that resulted in good peroxide removal (3.7-3.9) are very close to the current PDM column operating residence time, it is assumed the current geometric design (3 ft. diameter by 10 ft. high) is suitable for the replacement decomposition catalyst.

The current columns, which are constructed of epoxy coated carbon steel, are failing by corrosion due to leaks in the coating. These columns need to be replaced with a more corrosion resistant material to endure the lower pHs that may be encountered – as low as 5. The recommended material of construction is 316 stainless steel, which is good for very dilute sulfuric acid (5% at ambient temperatures), and fine for the low chloride levels found in the processed waters (less than 500 ppm). Type 304 stainless steel may be acceptable, and some current piping is 304, but it is marginal for both the pH and possible chloride concentrations that may be encountered. An alternative material is a fiberglass reinforced plastic (FRP), which would not be effected by corrosion, but would not be as resistant to abrasion from the catalyst medium as would be the stainless steel.

One difficulty with the current ETF process equipment arrangement is that the pH Adjustment Tank 60C-TK-1 is located before the PDM. Therefore, the low pH (generally about 5) needed to protect the reverse osmosis units is marginally below the desired operating pH of most of the catalysts (generally 6 or higher). Since the UV/H_2O_2 organic destruction units are operated with a water pH of about 6, it would be advantageous to relocate the pH Adjustment Tank to be after the PDM in the flow scheme. This would be feasible if the Surge Tank Pumps 60A-P-1A/B/C can provide enough head to move the water through the PDM. Vendor specifications for the LayneOx® medium give a pressure drop of 2 psid for a bed height of 3-4 ft. and a flux of 9-15 gpm/ft^2. The Surge Tank Pumps are rated at 100 psid for 175 gpm, and should have enough capacity to handle the extra load, but this will have to be determined from operating data, testing, and/or calculation.

A preliminary estimate of the total installed cost to replace the existing columns with 316 stainless steel columns is summarized below:

Two vessels (columns)	$40,000
Removal of old columns	12,000
Installation of new columns	21,000
Overhead, profit, taxes	22,000
Engineering	20,000
Project/Construction management	32,000
Other overhead	24,000
Subtotal	$171,000
Contingency (30%)	51,000
Cost of initial charge of new media	10,000
Total $232,000	

The estimate above does not include costs to rearrange piping (and equipment, if necessary) so that the pH Adjustment Tank follows the PDM rather than precedes it in the process flow. This would require redesign of the process, and there was not sufficient time to complete this task. A rough estimate is that is would cost about the same as installation of the PDM columns plus some engineering and management, totaling about $50,000. This assumes no new pumps would be required.

Chemical Reduction

Commercially available reducing agents that can be used for peroxide reduction include hydrazine, hydroxylamine, sulfur dioxide, sodium sulfite and bisulfite, sodium thiosulfate, sodium hydrosulfite, sodium hydrosulfide, etc. Of these, hydrazine and hydroxlamine have the advantage of not directly adding sodium or other cations to the water, but can decompose violently and are considered too hazardous for use at the ETF. Sodium hydrosulfide, though probably the least expensive reducing agent, can release hydrogen sulfide. This is a very dangerous toxic gas, so it was not considered further.

Liquefied sulfur dioxide gas is frequently used as a reducing agent in water treatment, but since it is a toxic gas there are some hazards associated with using it. The other sulfur based chemicals are also commonly used in water treatment, and are less dangerous to handle than sulfur dioxide. Use of any of the sulfur-based reducing chemicals produces some sulfuric acid when reacting with peroxide, so caustic addition is necessary to bring the pH value back up to between 5 and 6.

All of these sulfite-based chemicals were considered for use in the ETF for peroxide destruction. The peroxide reducing reactions are shown below:

$SO_2 + H_2O_2 = H_2SO_4$
$NaHSO_3 + H_2O_2 = NaHSO_4 + H_2O$
$Na_2S_2O_3 + 4H_2O_2 = Na_2SO_4 + H_2SO_4 + 3H_2O$
$Na_2S_2O_4 + 3H_2O_2 = Na_2SO_4 + H_2SO_4 + 2H_2O$

Process simulations were performed using the Environmental Simulation Program (ESP, Version 8) to predict the amount of reducing agent and caustic needed to destroy 200 ppm of hydrogen peroxide and then raise the pH to 6, with a flow rate of 175 gpm. The results are shown in the table below. The rates predicted by ESP are based on thermodynamic equilibrium calculations. The test data using sodium sulfite to reduce peroxide indicate that about a 10% excess over the stoichiometric amount is required, so 10% was added to the calculated (stoichiometric) value to arrive at the values in the table.

Prices were obtained from one supplier for sodium bisulfite and from ICIS (www.icis.com) for all other chemicals. Shipping costs are assumed to be \$0.07/lb of liquefied gas or solution based on a quote for sodium bisulfite shipped by 5000 gal. truck from Green River, Wyoming. The caustic price used is \$.030/lb on a 100% NaOH basis, with no addition for shipping. No capital or operating costs are included for new storage tanks, pumps, piping, etc. Also, the cost of processing and disposing of the added sodium sulfate to the secondary waste was not determined and thus not included.

Peroxide Reduction Chemical Costs
(200 ppm residual H_2O_2, Flow = 175 gpm)

Reducing Chemical	Form Chemical Supplied and Used	Chemical Cost $/lb dry	Chemical Usage lb/hr as is	Chemical Usage lb/hr dry	50% NaOH lb/hr	Annual Cost $/yr
SO_2	Liquefied Gas	0.15	36.2	36.2	1.37	72,000
$NaHSO_3$	40% Solution	0.25	147	58.9	0.685	220,000
$Na_2S_2O_3$	30% Solution	0.25	74.6	22.4	0.343	95,000
$Na_2S_2O_4$	45% Solution	0.78	73.3	33.0	0.457	271,000

SO_2 = sulfur dioxide
$NaHSO_3$ = sodium bisulfite
$Na_2S_2O_3$ = sodium thiosulfate or hyposulfite
$Na_2S_2O_4$ = sodium hydrosulfite or dithionite

The cost of the caustic is less than $2,000/yr in all cases, so it can be neglected. The estimated shipping costs are substantial, as much as a third or more of the total reducing agent cost. Notice that the table is based on a residual hydrogen peroxide concentration of 200 ppm, which is the upper limit of what is expected. Actual peroxide concentrations will likely average more like 50 ppm, which would give an annual cost of about $24,000/yr for sodium thiosulfate. A word of caution: costs for the reducing chemicals and particularly shipping are not based on firm quotes, with the exception of the sodium bisulfite; what is presented in the table is a preliminary estimate.

Conclusion and Recommendations

One thing clear from this study is that the choice between installing new PDM columns, or using a reducing agent such as sodium thiosulfate, will be determined by the frequency that the residual H_2O_2 concentration exceeds roughly 50 ppm. If it is not expected to be very often, then chemical reduction may economically be the preferred choice. The chemical solution is likely available in totes, such as 400-500 gal. size, which would alleviate the need for a storage tank. The chemical solution could be metered directly out of a tote to the process. The chemical cost, however, will be somewhat higher in totes than delivered in bulk by tanker truck.

If the peroxide concentration is expected to routinely be greater than 50 ppm, replacing the PDM columns and using a new catalyst will be the likely choice. The preferred catalyst will be determined from pilot scale testing, as mentioned previously in the Testing section. The catalyst route to peroxide destruction may require rearranging the process so peroxide destruction comes before pH adjustment.

Appendix

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Appendix B – Procedure 310-OP-039, *Peroxide Destruction Pilot Unit Operation*

310/340

Operating Procedure

310-OP-039

Peroxide Destruction Pilot Unit Operation

Revision: 0
Change: 1

Approval Designators: I, R

Procedure Use Level: Reference

Hazard Analysis: AJHA #3T3D-308

Release Date: March 11, 2009

Note

Management will direct which of the two methods of filling the column to use.

5.0 INSTRUCTIONS

5.1 Fill Column with Catalyst

5.1.1 Sluicing Method

a. DON PPE (half mask with P-100 filters, goggles, coveralls).

b. POUR the catalyst into a drum or other container that allows water to be added, if necessary.

c. CONNECT the 2" discharge hose from the jet eductor to the upper transfer connection on the PDP column.

d. CONNECT the 1" service water supply hose from the jet eductor to a utility station water connection.

e. OPEN the lower distribution header valve PDP-V-1.

f. CLOSE the lower transfer valve PDP-V-2.

g. PLACE jet eductor suction hose into the catalyst container.

h. ADD water to the container as needed.

i. OPEN the service water supply valve to begin transfer.

5.1.2 Top Fill Method

a. DON PPE if required.

b. CLOSE the lower transfer valve PDP-V-2.

c. CLOSE the lower distribution header valve PDP-V-1.

d. REQUEST pipefitters remove the PDP column top.

e. FILL the column half full of water.

f. DUMP the catalyst containers into the column.

g. REQUEST pipefitters replace the column top.

Note

Management will direct which of the two methods of filling the column to use.

5.0 INSTRUCTIONS

5.1 Fill Column with Catalyst

5.1.1 Sluicing Method

a. DON PPE (half mask with P-100 filters, goggles, coveralls).

b. POUR the catalyst into a drum or other container that allows water to be added, if necessary.

c. CONNECT the 2" discharge hose from the jet eductor to the upper transfer connection on the PDP column.

d. CONNECT the 1" service water supply hose from the jet eductor to a utility station water connection.

e. OPEN the lower distribution header valve PDP-V-1.

f. CLOSE the lower transfer valve PDP-V-2.

g. PLACE jet eductor suction hose into the catalyst container.

h. ADD water to the container as needed.

i. OPEN the service water supply valve to begin transfer.

5.1.2 Top Fill Method

a. DON PPE if required.

b. CLOSE the lower transfer valve PDP-V-2.

c. CLOSE the lower distribution header valve PDP-V-1.

d. REQUEST pipefitters remove the PDP column top.

e. FILL the column half full of water.

f. DUMP the catalyst containers into the column.

g. REQUEST pipefitters replace the column top.

5.2 Column Backwash

5.2.1 CONNECT a 1" hose from the lower distribution header connection to a service water supply through the PDP instrument line.

5.2.2 CONNECT a 1" hose from the upper distribution header connection to the Sludge Thickener Tank.

5.2.3 ENSURE the pressure gage PDP-PI-1 fitting is in the upper transfer connection.

5.2.4 ENSURE the flow meter PDP-FI-2 is on.

5.2.5 OPEN the lower distribution header valve PDP-V-1.

5.2.6 OPEN the service water supply valve and adjust to the flow rate specified on the PDP Test Datasheet.

5.2.7 RUN for the time specified in the datasheet or as directed by PIC.

5.2.8 CLOSE the service water supply valve.

5.2.9 CLOSE the lower distribution header valve PDP-V-1.

5.2.10 DISCONNECT hoses from the service water supply and Sludge Thickener Tank.

5.3 Operate PDP Column

5.3.1 IF the plant is operating,
THEN SHUT DOWN the plant in accordance with 310-OP-27.

5.3.2 ENSURE the IX Feed Tank and Effluent Tank levels are between 60 and 80%.

5.3.3 OPEN the IX Tank diversion inlet valve WW-V-563.

5.3.4 CLOSE diversion line valve WW-V-566.

5.3.5 BYPASS the IX Columns as follows:

a. SET switch HS-270 to Local on Panel LP-2.

b. VERIFY the column C/D isolation valve WW-V-522 is open.

c. SET switch HS-271 to Local on Panel LP-2.

d. OPEN column A/B bypass valve WW-V-555.

e. VERIFY the column A/B outlet valve WW-V-524 is open.

5.3.6 CONNECT a 1" hose from the effluent diversion line connection at valve WW-V-576 to the PDP instrument line inlet.

Note

The column will be operated in either an upflow or downflow configuration as specified on the PDP Test Datasheet.

5.3.7 IF upflow operation is specified,
THEN PERFORM the following:

a. CONNECT the 1" supply hose from the instrument line outlet to the lower distribution header connection.

b. CONNECT the 1" discharge hose from the upper distribution header connection to the Effluent Tank and secure.

5.3.8 IF downflow operation is specified,
THEN PERFORM the following:

a. CONNECT the 1" supply hose from the instrument line outlet to the upper distribution header connection.

b. CONNECT the 1" discharge hose from the lower distribution header connection to the Effluent Tank and secure.

5.3.9 **SET** the hydrogen peroxide concentration at the level specified in the datasheet.

5.3.10 **PUT** the effluent diversion flow rate controller WW-FCV-121 in Auto mode.

5.3.11 **SET** the effluent diversion flow rate controller WW-FCV-121 setpoint to 100 gpm.

5.3.12 **VERIFY** the IX Feed Control is set to Manual (on the IX pump system screen).

5.3.13 **SET** the IX Feed Tank level control WW-LIC-238 to Cascade mode and 63% setpoint.

Note

Step 5.3.15 should be performed immediately after step 5.3.14 to avoid emptying the Effluent Tank and filling the IX Tank to the overflow drain.

5.3.14 **START** effluent pump EF-P-3A/B.

5.3.15 **START** IX feed pump IX-P-2A, B or C.

5.3.16 **START** the sulfuric acid feed system as follows:

a. **OPEN** valve SA-V-1501 at the IX Feed Tank.

b. **PUT** IX Feed Tank pH control AIC 255 in Auto mode.

c. **SET** IX Feed Tank pH control AIC 255 setpoint at the level specified in the datasheet.

d. **PUT** the sulfuric acid feed system in Manual (on the sulfuric acid feed system screen).

e. **START** the lead pump CF-P-15A or B.

5.3.17 **START** UV/Ox on one chamber with no lamps.

5.3.18 <u>WHEN</u> flow has stabilized,
<u>THEN</u> **OPEN** valve PDP-V-1.

5.3.19 **OPEN (slowly)** valve WW-V-576.

5.3.20 **ADJUST (manually)** valve WW-V-576 so that the flow reading on PDP-FI-2 is as specified on the datasheet.

Note

- Discharge samples are taken from the end of the discharge hose.
- Supply samples are taken from valve WW-V-579 or 580 (depending on pump in use).

5.3.21 **PULL** samples as directed on the datasheet to verify hydrogen peroxide concentration using the colorimetric test kit.

5.3.22 **ADJUST** the hydrogen peroxide concentration as directed by PIC.

5.3.23 <u>WHEN</u> the run time specified on the datasheet is reached, or as directed by PIC,
<u>THEN</u> **PROCEED** with shut down of the column operation.

5.4 Shut Down PDP Column

5.4.1 **STOP** the sulfuric acid feed pump CF-P-15A/B.

5.4.2 **CLOSE** valve SA-V-1501 at the IX Tank.

5.4.3 **STOP** the UV/Ox system.

Note

Step 5.4.5 should be performed immediately after step 5.4.4 to avoid emptying the IX Tank and filling the Effluent Tank to the overflow drain.

5.4.4 **STOP** the effluent pumps EF-P-3A/B.

5.4.5 **STOP** the IX feed pumps IX-P-2A/B/C.

5.4.6 **CLOSE** valve WW-V-576.

5.4.7 CLOSE valve PDP-V-1.

5.4.8 IF the TEDF process is to be restarted,
THEN GO TO Section 5.5.

5.4.9 IF the catalyst is to be changed and another run performed
THEN GO TO Section 5.6.

5.4.10 IF the run is to be continued,
THEN RETURN to Section 5.3 when directed by PIC.

5.5 System Drain

5.5.1 CLOSE the IX Tank diversion inlet valve WW-V-563.

5.5.2 OPEN diversion line valve WW-V-566.

Note

During the pump down draining of the tanks the IX and Effluent Tank low and lolo tank level alarms will activate.

5.5.3 SET the IX flow controller WW-FIC-245 to Auto.

5.5.4 ENTER a flow setpoint from 150 to 200 gpm.

5.5.5 START IX feed pump IX-P-2A/B/C.

5.5.6 START effluent pump EF-P-3A/B.

Note

Draining is complete when pumps stop at the lolo level alarm.

5.5.7 WHEN draining is complete,
THEN RETURN the IX columns from bypass as follows:

a. SET switch HS-270 to Remote on Panel LP-2.

b. SET switch HS-271 to Remote on Panel LP-2.

c. CLOSE column A/B bypass valve WW-V-555.

5.5.8 PUT the IX flow controller WW-FIC-245 in Manual mode (on the IX pump system screen).

5.5.9 RESET IX Feed Tank pH AIT 255 to the normal setpoint according to the Process Direction.

5.5.10 RESET hydrogen peroxide concentration to the normal setpoint according to the Process Direction.

5.5.11 PUT the effluent diversion flow rate controller WW-FCV-121 in Manual mode.

5.5.12 IF the plant will not be started by the next shift,
THEN ADD service water to the Effluent Tank until the pH probes are covered.

5.6 Remove Catalyst from Column

Note

Management will direct which of the two methods of removing catalyst to use.

5.6.1 Sluicing Method

a. STAGE the receiving container over a sump leaving it on the drum dolly.

b. CONNECT the 2" discharge hose from the jet eductor to the receiving container.

c. CONNECT the 1" service water supply hose from the jet eductor to a utility station water connection.

d. CONNECT the jet eductor suction hose to the lower transfer connection on the PDP column.

e. CONNECT a hose from the service water at a utility station to the lower distribution header connection.

f. OPEN the lower transfer valve PDP -V-2.

g. OPEN the service water supply valve to the jet eductor to begin transfer.

h. OPEN PDP -V-1 to add water to the column as needed.

i. CLOSE the service water supply valve to stop the transfer.

j. CLOSE valve PDP-V-1.

k. IF additional catalyst remains below the lower transfer connection
THEN perform the following to attempt removal:

   1. CONNECT a 1" hose to the jet eductor suction.

   2. INSERT the hose through the lower transfer valve PDP-V-V2 into the remaining catalyst.

   3. OPEN the service water supply valve to begin the transfer.

   4. OPEN valve PDP-V-1 to add water to the column as needed.

5. REMOVE as much catalyst as possible.
6. CLOSE the service water supply valve to stop the transfer.
7. CLOSE valve PDP-V-1.

5.6.2 Manual Removal Method

a. CONNECT a drain hose to the lower distribution header connection.

b. OPEN the lower distribution header valve PDP -V-1 to drain the column.

c. PLACE a container under the tee.

d. REQUEST pipefitters remove the PDP column tee flange.

e. SCOOP and FLUSH out the media.

f. REQUEST pipefitters replace the column tee flange.

6.0 RECORDS

Completed Document	Destination	Disposition	Inactive Records Storage Area
Attachment 1 - PDP Test Data Sheet	310/340 records file	Maintain 1 year	RHA

7.0 BIBLIOGRAPHY

310-OP-009, "Operate UV System"

310-OP-027, "Plant Shutdown/Restart"

8.0 CHANGE SUMMARY

Change Document	Pages Changed	Summary of Changes
15440	4	Edit step 5.3.5 and substeps for bypassing the IX columns.
	7	Edit substeps to 5.5.7 for returning IX columns from bypass.

Attachment 1 – PDP Test Datasheet

Catalyst: ______________________________

MSDS #: ____________________________________

Bed Height: ___________ ft

Backwash Flow: __________ gpm

Backwash Time: _________ min

Column Configuration: upflow / downflow (circle one)

Hydrogen Peroxide Concentration Setpoint: ___________ ppm

pH Setpoint: ___________

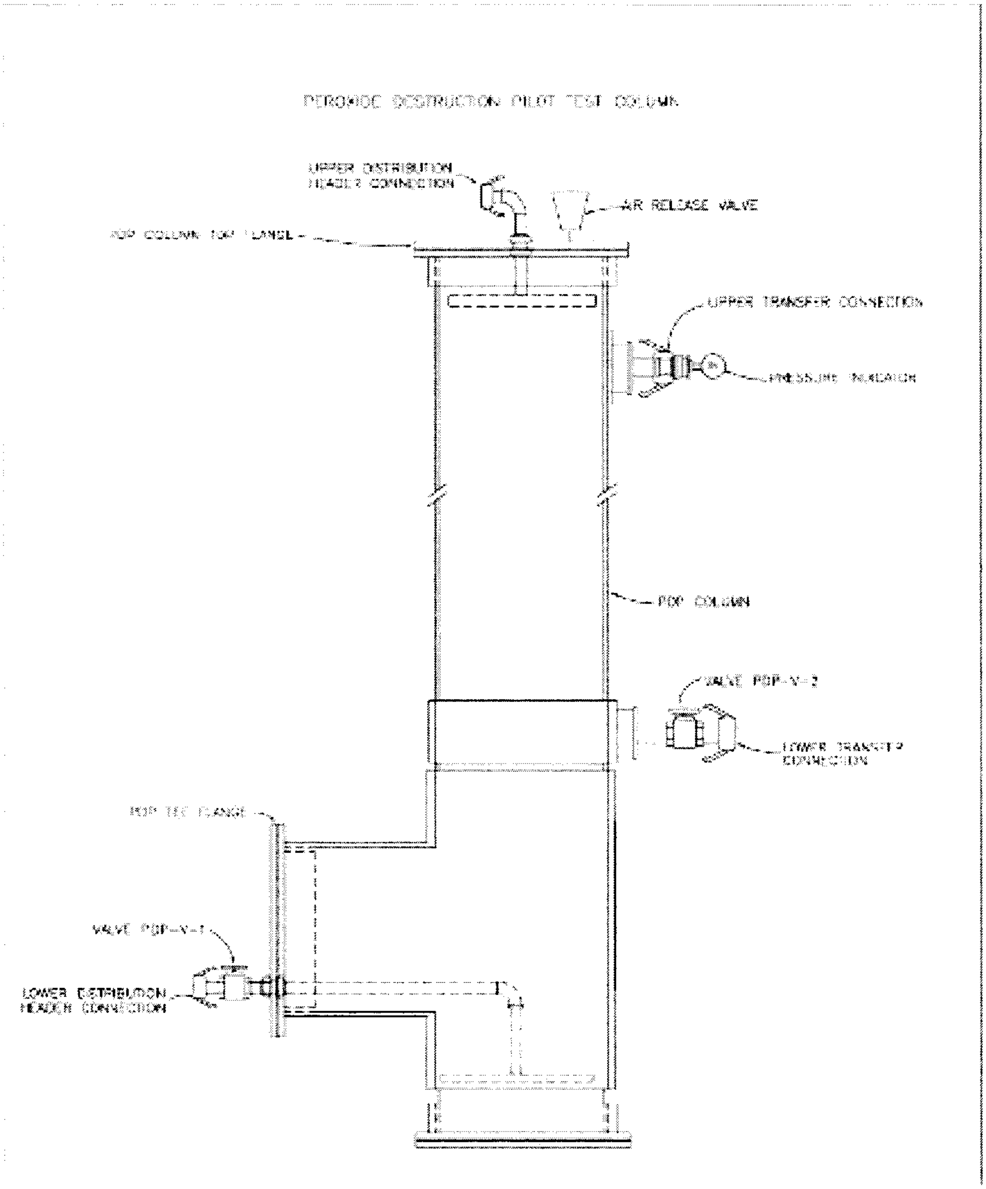
PDP Operation Flow: __________ gpm

Test Time: _________ hours

Samples: Take at least _____ samples each day shift of operation as direct by the PIC.

Date	Time	Sample Point	Result

Attachment 2 - Peroxide Destruction Pilot Test Column



Appendix C – Catalyst Pilot Test Results Data and Notes

High Purity Manganese Dioxide Mineral

HP MnO_2 Peroxide Destruction Data Summary

Flow (gpm)	H_2O_2 In (mg/L)	H_2O_2 Out (mg/L)	Direction	Rxn Time (min)	H_2O_2 Destruct (%)
3.6	25	0.2	Up	6.8	99.2
4.0	130	0.6	Up	6.1	99.5
4.5	130	0	Down	5.4	100.0
6.7	150	0	Down	3.7	100.0
7.0	100	0.1	Down	3.5	99.9
7.2	100	0	Down	3.4	100.0

Catalyst Washing

Washing flows were approximately 12 gpm. At the half hour duration the discharge was still black with fines so washing continued for more than one hour with the discharge still cloudy dark. Three inches of bed expansion from the load-in bed height. There was goopy foam at the top of the water.

Upflow

Some bed expansion (3.5 in.) at 7 gpm. Bubbles of gas releasing from the bed were ejecting significant amount of surface media into the water and there was frequent venting from the column. Liquid/foam coming out of the air release valve contained very fine black particulate. Any little disturbance made the headspace dark. There was significant carryover of media out of the column. The head space of the column between the upper header and the column top was filled with particulate carried up. Even after the flow stabilized down at 3.8 – 4.0 gpm putting the outlet hose in a bucket revealed media particles and significant cloudiness. Appeared to have lost approximately 1 inch of the bed to carryover.

Downflow

Bubbles were carried out with the discharge and not going up the column. Small gas pockets developed in the bed interstitial areas. Pressure built up across the bed as the amount of retained gas increased. After 2 hours the control valve was full open to get 7 gpm flow with 22 psig dP. After 4 hours the max pressure was reached 23 psig and the flow was 6.7 gpm. When flow stopped there was a large release of gas bubbles up and out the top of the column. Discharge was clear and clean.

Sud-Chemie T-2525 Catalyst

T-2525 Catalyst Peroxide Destruction Data Summary

Flow (gpm)	H_2O_2 In (mg/L)	H_2O_2 Out (mg/L)	Direction	Rxn Time (min)	H_2O_2 Destruct (%)
3.6	180	0	Up	6.8	100.0
5.9	110	0.1	Up	4.1	99.9
7.0	110	0	Up	3.5	100.0
7.2	180	0.2	Up	3.4	99.9
7.2	200	0.1	Up	3.4	100.0
7.0	90	0	Down	3.5	100.0
7.0	135	0	Down	3.5	100.0

Catalyst Washing

Washing flows were approximately 10-12 gpm. The discharge water had minimal fines and was clear in less than 5 minutes. No bed fluidization or lift. The washing rate was raised to 17 gpm. Some more color on increase but it cleared right away. The bed lifted 5 inches with some channel fluidization and a dP increase from 8 to 21 psig.

Upflow

There was no evidence of any particulate in the discharge. The vigorous gas bubble generation did not entrain or propel catalyst particles into the head space. Visual inspection of captured discharge was clean and clear even at the highest flow and H_2O_2 concentration. During the initial run the bed settled 3 inches from post-washing level at flow start then no movement. Shortly after startup of the initial run bands of gas bubbles formed across the column at about mid-column and began lifting bed leaving band of water with a thin layer of bubbles collected on the bottom of this bed segment. Individual catalyst pieces dropped through the band moving reducing the segment size as it floated upward. The gap was noted as large as 10 inches. Some segments dissipated on their own but two reached the distribution header and broke up. Segments that hit the header caused partial plugging that was cleared by shutting off flow or reversing flow through the header. This only occurred with the combination of high flow, >6 gpm or the full scale equivalent of 150 gpm, and high H_2O_2, >110 ppm during the initial test run. If the flow was lowered or the H_2O_2 concentration reduced some small gaps appeared but did not cause separation. When the upflow test was repeated after running the downflow test this segmentation phenomena could not be repeated even at high flow (7.2 gpm) and H_2O_2 concentration (200 ppm). It was noted on the datasheet there appeared to be less channeling at the tee during this run. There were also notes in both tests of bed height settling. This appeared to happen more rapidly in the first test before the gap formation but that was apparently more gradual in the second upflow test.

Downflow

Bubbles were carried out with the discharge in a steady stream and not going up the column. Small gas pockets developed in the bed interstitial areas. Discharge was clear and clean. There was no significant dP rise like occurred in the HP MnO_2 media.

Carulite® 200 Catalyst

Carulite® 200 Catalyst Peroxide Destruction Data Summary

Flow (gpm)	H_2O_2 In (mg/L)	H_2O_2 Out (mg/L)	Direction	Rxn Time (min)	H_2O_2 Destruct (%)
5.0	180	0.4	Up	4.9	99.8
6.5	130	0.1	Up	3.8	99.9
9.5	150	0.2	Up	2.6	99.9
5.5	100	0.1	Down	4.5	99.9
8.8	30	0.1	Down	2.8	99.7

Catalyst Washing

At washing flows of approximately 8-12 gpm the discharge was initially very black but cleared in 5 minutes. The washing rate was raised to 12-15 gpm and the discharge was black again. No bed lift was noticeable. During the initial wetting of the catalyst with water for loading into the column it generated significant heat to the point of producing vapor.

Upflow

Flow was difficult to control in this test. The pressure drop was slightly higher with this bed than the T-2525 test bed. There were noticeable fines erupting off the top of the bed with bubbles with most observed to settle back down. Visual observation of captured discharge showed some fines carryover at the higher flow and particularly at flow changes.

Downflow

Bubbles were visible coming out with the discharge and not going up the column. There were dP fluctuations causing flow fluctuations and the dP was higher than the T-2525 test but still lower than in the HP MnO_2 media. Again the dP changes tend to follow the observed buildup of gas pockets in the bed.