

DRAFT

Full Scale Pilot Study Using the VTX Catalyzed Oxidation System for the Destruction of Sulfides Within Wastewater Entering the York River WWTP **Advanced Oxidation Technology, Inc** **H.W. Cox, PhD**

Introduction

An abbreviated pilot study was conducted at York River using the VTX process during February of 2004. The wastewater total sulfide levels for this test could generally be described to be in the range of 6 to 10 ppm. Flows into the plant could be described as normal flows for the York plant in the range of 12 to 14 MGD.

Complete reduction of hydrogen sulfide entering the scrubbers could not be attained during this first study due to a very short reaction period (estimated at less than 30 seconds) before the wastewater entered the aerated grit chambers. Significant amounts of untreated hydrogen sulfide could be readily stripped from the water. However, even with the short reaction period, substantial reductions in hydrogen sulfide were noted at the scrubbers. Additionally, very low levels of total sulfides remained in the water after the grit chamber (retention time within the grit chamber 20-40 minutes) leading investigators to believe that a longer contact time before the aerated grit chambers would result in complete destruction of sulfides within the water resulting in no hydrogen sulfide within the air going to the scrubbers.

Previous studies have indicated that 3 to 5 minutes of contact time is sufficient for the VTX reaction for sulfide destruction.

The dosage of hydrogen peroxide for sulfide destruction in the presence of VTX catalyst generally results in a ratio of 1.5 parts hydrogen peroxide to 1.0 parts sulfide. Hydrogen peroxide alone will oxidize sulfides but the ratio of peroxide to sulfide is higher at 3.0 parts hydrogen peroxide to 1.0 parts sulfide. The time required for oxidation is also extended to about 20 minutes of contact.

Calculations from the February study confirmed that the VTX process approximated the 1.5 ratio. Using this ratio it was determined that a dose rate of about 12.5 gallons per hour of peroxide and VTX would be necessary to treat sulfide entering the York River plant under most normal day-time flow situations.

General Discussion of the Full Scale Pilot Study

Chemical Injection

It was determined that injections of VTX and peroxide could be accomplished from an old hydrogen peroxide injection point located approximately 1000 feet above the plant headworks. Calculations indicated that the retention time prior to entering the bar screens

to be from 10 to 14 minutes from this location. This would allow for adequate contact time for the process to go to completion.

A 'slip stream' of treated wastewater was connected directly to the injection port on the sewer main. Injection lines were connected to the treated wastewater line for VTX and peroxide addition. Walchem metering pumps were attached to each injection line and from totes of VTX and hydrogen peroxide (50%). Chemicals could then be metered into the slip stream of treated wastewater for immediate addition to the primary sewer main entering the plant.

Two time periods were selected for full scale treatment at York River. The first period went from August 31 to September 3 and the second period from September 13 through 17. Seven injection periods were scheduled within these time frames.

Plant Flows and Total Sulfides Entering the Plant

Flows over the test period were generally up from normal flows. Most hourly flows during treatments were above normal levels. Heavy rains from various storm events had driven flows above normal for both study periods.

Total sulfide levels were substantially above the levels noted in the earlier study. Incoming total sulfides were often over 20 ppm. Total daily mass of sulfide for the periods of treatment exceeded 2500 lbs/day of total sulfide. This was substantially above the average mass of sulfide seen in the February study. Total sulfides during the February study approximated 1000 lbs/day of total sulfide.

The significant increase in total sulfide meant that the metering pump system used by AOT would often be limiting for the treatment of all sulfide entering the plant. However, it was possible to obtain good data on the overall efficiency of the system. Importantly, during selected times the system was able to treat almost all of the total sulfides. This resulted in drastic reductions of sulfides entering the scrubber system (zero sulfides during selected periods) with very little sulfide remaining in the water past the grit chamber. During times in which the system did not treat all of the sulfide entering the plant, from 2 to 4 ppm sulfide remained in the wastewater past the grit chamber. These data offered good information for mass balance calculations.

Results and Discussion

Seven tests were conducted over the period of study. Since most of the results indicate similar findings, two days were selected as representative for in-depth discussion. However, all of the data can be reviewed within the Appendix of this paper.

One of the days (September 14th) represented a period of time in which flows were down. This provided a period during which less overall mass of total sulfide entered the plant as compared to other periods. Flows on the 16th were moderate to high initially and were reduced substantially toward the end of treatment.

The treatment chemical dosage rate for VTX and hydrogen peroxide for the 14th and 16th were ~23.6 gallons per hour. Hydrogen peroxide (50%) accounted for ~23 gallons of this total.

Treatments were initiated at 6:17 AM and 5:20 AM for the 14th and 16th, respectively. Treatments were stopped at 2:10 PM and 5:30 PM, respectively, for those dates.

Table 1 depicts the flow and total sulfide concentration data collected on the raw and treated influent. Calculations were made to indicate the total poundage of sulfides within the wastewater before treatment (taken above the injection point) and after treatment (taken at the distribution box just past the aerated grit chamber). Calculations were also made for the total mass of sulfide entering the scrubber during the treatment periods in order that some statements could be made regarding total mass balance of total sulfides.

Table 1. Wastewater Total Sulfide Results for Raw and Treated Influent

Date	Time	Sulfides (ppm)		Flow (MGD)	lbs/day Sulfide Raw (ppm)	lbs/day Sulfide Post-trt (ppm)	% Reduction	Scrubber Sulfide (ppm)	lbs/day Sulfide to Scrubber Post-trt	Est. Sulfide Treated Total lbs/day
		Raw	Treated							
9/14/04	0700	15.85	2.50	14.11	1865	294	84.2	65	252	1319
“ “	1000	26.50	1.38	13.63	2807	157	94.4	30	116	2534
“ “	1400	22.15	1.48	11.69	2159	144	93.3	5	19	1996
9/16/04	0700	26.10	3.03	14.57	3178	369	88.4	50	194	2615
“ “	0900	19.80	2.05	16.51	2725	282	89.6	75	291	2152
“ “	1000	25.75	3.38	14.40	3092	406	86.8	40	155	2531
“ “	1200		1.05	14.33		125				
“ “	1400	24.90	2.10	13.75	2855	240	91.6	25	97	2518
“ “	1600		0.90	16.61		125				

Scrubber data for incoming airborne hydrogen sulfides were also taken using the existing plant meter prior to the scrubbers. Table 2 depicts that information during the treatment period. Note that the hydrogen sulfide levels were taken to zero during the study on the 14th when flows and sulfide levels were within a reasonable range of dosage capability. Levels of hydrogen sulfide entering the scrubber during treatment on the 16th were also quite low but did not reach zero. The VTX dosage during this period was very close to the desired dosage but did not quite get to optimum.

Table 2. Influent Scrubber Data for Hydrogen Sulfide During Studies

Date	Time	Intake Sulfides (ppm)
9/14/04	0700	92 (Treatment started 0617)
“ “	0900	43
“ “	1100	5
“ “	1300	0
“ “	1500	0 (Treatment ended 1420)
“ “	1700	108
9/16/04	0500	123 (Treatment started 0520)
“ “	0700	11
“ “	0900	67
“ “	1100	24
“ “	1300	17
“ “	1500	14
“ “	1700	15 (Treatment ended 1730)
“ “	1900	16
“ “	2100	120

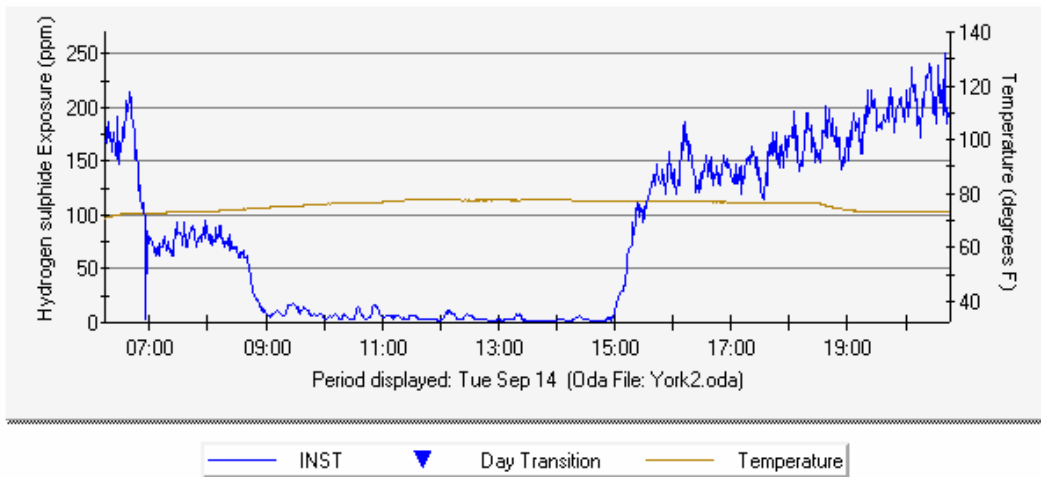
The Odallogger indicated that airborne hydrogen sulfide entering the scrubbers without treatment ranged from 125 ppm to 225 ppm during the study period. The total mass of sulfide removed to the scrubbers for these concentration ranges were calculated to be from 484.5 lbs/day to 872.1 lbs/day. This represents about 4.1 to 7.5 ppm of total sulfide within the raw wastewater removed to the scrubbers from the influent under normal circumstances (i.e. ~14 MGD of flow).

The average mass reduction of sulfides attributable to the VTX treatment averaged 2238 ppm for all times reported in Table 1. A calculation of the ratio of lbs of hydrogen peroxide to sulfide treated using this figure indicates that treatment was accomplished at less than the projected destruction ratio of 1.5:1 of peroxide to total sulfide on a mass:mass ratio.

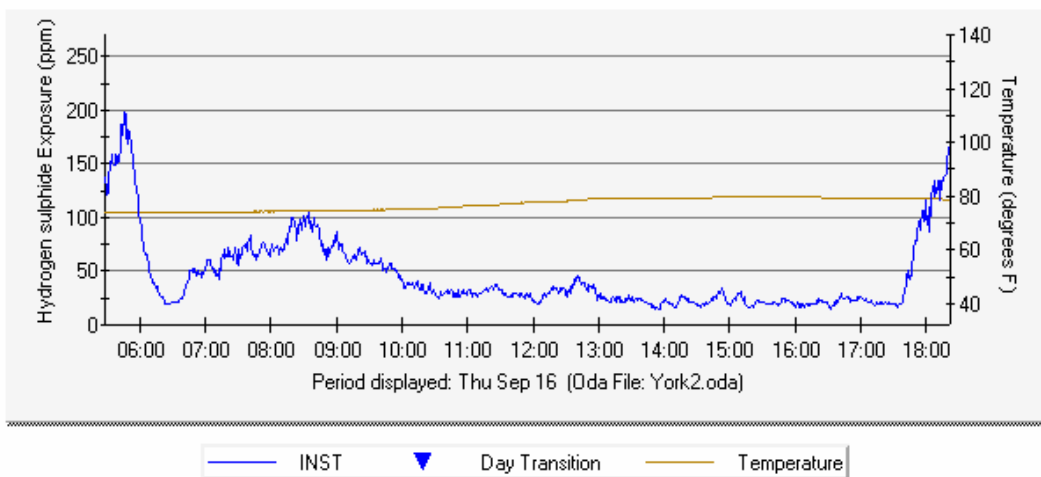
Odalloggers were hung in two locations within the plant. The primary location for hydrogen sulfide monitoring was above the wastewater traveling through the aerated grit chamber in the headworks building. A second Odallogger was hung above the wastewater at the distribution splitter box just past the grit chamber prior to the primary clarifiers.

The following are the Odalog graphs for periods before, during and after treatment within the aerated grit chamber for the 14th and 16th of September.

- Session: 2 (OdaLog: OL45031346)



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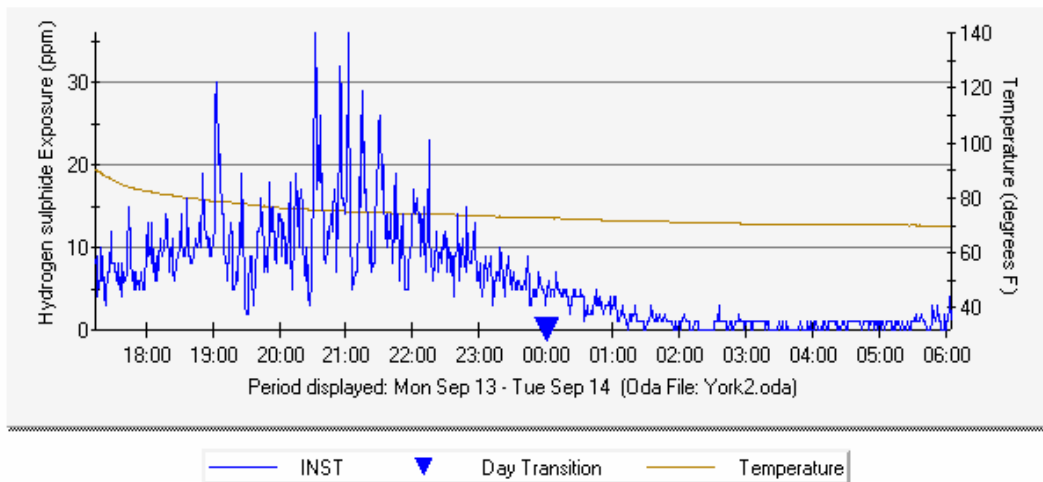
As mentioned earlier, treatments were initiated at 6:17 AM and 5:20 AM for the 14th and 16th, respectively. Treatments were stopped at 2:10 PM and 5:30 PM, respectively for those dates. One can note that hydrogen sulfide levels begin to drop shortly after the initiation of treatment and begin to rise again shortly after the treatment process is turned off. Treatment on the 14th resulted in very low levels of hydrogen sulfide within the grit chamber as flows subsided from the morning surge. OdaLogger levels often approached zero and the influent scrubber meter was zero for several hours.

Higher flows and the concomitant increase in sulfide mass on the 16th resulted in hydrogen sulfide levels in the range of 25 to 30 ppm (OdaLog) as flows subsided in the afternoon. Hydrogen sulfide entering the scrubbers was about half of the OdaLog readings at 14 to 17 ppm (Table 2).

Hydrogen sulfide levels earlier in the day during the peak flows of 7 to 9 AM resulted in much higher levels of hydrogen sulfide going to the scrubbers. During periods of higher mass loading on the 16th the 23.6 GPH of VTX treatment chemistry was not sufficient to treat the mass of sulfide entering the plant. Calculations indicate that from 2 to 5 more gallons per hour of VTX treatment chemistry would have been necessary to adequately treat the excess sulfides during these hours. The metering pumps were not capable of pumping at the rate required.

The second Odalogger was hung in the distribution box after the grit chamber. The following Odalogger graph recorded the hydrogen sulfide levels without treatment. It is noteworthy that levels exceeded 10 ppm on numerous occasions.

- Session: 1 (OdaLog: OL45031346)



Corrosion Reduction

A “Corrator” corrosion rate monitor was put in place for the study. Unfortunately, the instrument did not work properly during testing. Documentation of the reduction in corrosion due to the VTX process is expected to show a significant reduction in corrosivity of the wastewater. It is notable that the wastewater prior to treatment was consistently dark, almost black in color. After initiation of treatment, the wastewater turned to a milky color from the bar screens through the primary clarifiers. It is suspected that the color change was primarily a result of a significant change in the oxidation-reduction potential of the wastewater. Certainly, documentation of a drastic reduction in corrosivity of the wastewater would be of great benefit. Significant reductions in corrosion will translate into significant savings in operation and maintenance costs.

A further effort is going to be made to document the change in corrosivity. An addendum to this report will be made at that time.

Conclusions

The results of this study confirmed that the VTX process was an effective method for control of sulfides into the York River WWTP. Specific conclusions are as follows:

1. The mass:mass ratio of hydrogen peroxide and VTX to total sulfides are no more than 1.5:1 which is roughly half of the expected ratio for hydrogen peroxide alone.
2. The VTX process is capable of controlling most, if not all, of the sulfide entering the York River WWTP and reducing airborne hydrogen sulfide entering the scrubber system to negligible or non detection levels.
3. Control of sulfides entering the York River WWTP can be accomplished within the existing grounds of the complex from existing infrastructure.
4. A color change within plant influent from black to milky indicates a probable reduction in corrosivity of wastewater. Further documentation is warranted to confirm the significance of the corrosivity reduction.

Total Sulfide Treatment Results for September 3, 2004

Date	Time	Dilution	Reading	Raw S ⁼ (ppm)	Treated S ⁼ (ppm)	Location	~Flow (MGD)
9/3/04	0820	50:1	0.320	16.00		Raw sink	15.55
	1015	25:1	0.050		1.25	PCI	16.20
	1215	“	0.052		1.30	PCI	15.07
	1300	“	0.069		1.73	PCI	16.80
	1340	“	0.056		1.40	PCI	17.40

System on at ~0730 AM and off at 1435. Rate was set at 23.6 GPH

Total Sulfide Treatment Results for September 15, 2004

Date	Time	Dilution	Reading	Raw S ⁼ (ppm)	Treated S ⁼ (ppm)	Location	~Flow (MGD)
9/15/04	0649	50:1	0.491	24.55		Fire Stn	14.11
	0655	25:1	0.315		7.88	PCI	14.11
	0815	25:1	0.028		0.7	PCI	18.26
	0910	25:1	0.036		0.9	PCI	17.04
	0956	50:1	0.460	23.0		Fire Stn	15.84
	1004	25:1	0.106		2.65	PCI	15.84
	1201	25:1	0.076		1.90	PCI	15.07
	1402	50:1	0.445	22.25		Fire Stn	14.98
	1407	25:1	0.088		2.20	PCI	14.98

System started at 0619 and turned off at 1410. Rate was set at 23.6 GPH

Odalog for September 1 through September 3 within Aerated Grit Chamber

- Session: 1 (OdaLog: OL45054054)

