Purpose of Ozone and Oxygen to Decrease Chemical Oxygen Demand and Hydrogen Sulfide from an Improved Paper Dispensation Plant

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Abstract

A pilot learning was performed at the Fox River Fiber improved paper dispensation company in DePere, Wisconsin, to establish the amount to which inoculation of oxygen and ozone could decrease the high chemical oxygen command, COD, in the sewage and the efficiency of the ozone/oxygen stream in suppressing construction of hydrogen sulfide gas in downstream sewage appearance. Adaptive Ozone Solutions, LLC, complete the oxygen/ozone making and injection scheme. Samples were analyzed both before and after oxygen/ozone insertion. Hydrogen sulfide gas was incessantly monitored at sewer stations downstream of Fox River filament. Consequences showed that with an extremely short contact time, effluent COD was concentrated by over 20%. A straightforward kinetic model predicts that a contact time of fewer than 40 minutes possibly will decrease COD by as much as 65%. In calculation, downstream hydrogen sulfide gas manufacture in the sewage mains was also improved proscribed, such that expensive Bioxide applications could be concentrated. Hydrogen sulfide gas, fashioned as an effect of these conditions, is the most common odorous gas found in municipal wastewater compilation and management systems.

I. INTRODUCTION

In an increasing world, it is progressively more compulsory to treat municipal and manufacturing wastewaters using environmentally green technologies. In progress technologies often employ artificial chemicals as the most important management manager, but there are mounting concerns and problems connected with the remaining effects of putting more chemicals in wastewater. Displacing these chemicals with profitable, environmentally responsive processes offers an important market occasion.

Surrounded by primary manufacturing industries, paper industrialized is the fourth principal user of power and the largest originator of wastes, calculated by weight. Water is the basic intermediate of pulp and paper mechanized; it carries fibers throughout each treatment step and separates spent pulping chemicals and the absolute mixture of untreated residues from the pulp. The development of pulp and paper dispensation involves construction of effluent water streams with high chemical oxygen insist, COD, loads. COD is a determined of the oxygen condition of the organic matter vulnerable to oxidation by a muscular chemical oxidant.

In calculation, one of the challenges faced by wastewater behavior conveniences is hydrogen sulfide, H_2S, gas making in sewer lines, particularly in warmer weather. High natural and chemical oxygen insist loads collective with small dissolved oxygen content of sewage water and effluents from paper allowance facilities generate anaerobic infected conditions in sewage lines. Hydrogen sulfide gas, fashioned as an effect of these conditions, is the most common odorous gas found in municipal wastewater compilation and management systems. It emits a distinguishing smell of rotten eggs and is both toxic to humans and corrosive to strengthen and tangible. Concentration moisture on the side walls and crowns of sewer pipes absorbs H_2S and oxygen from the impression in the sewer and sulfur-oxidizing bacteria, *Thiobacillus*, then forms H_2SO_4. The sulfuric acid reacts with lime in tangible sewers causing crown deterioration and compromising the structural truthfulness of sewer lines.

The best defense for sanitary sewers is to use corrosion opposed to pipe, such as vitrified clay or plastic, but this may be inexpensively unreasonable in large systems. In these systems crown decomposition can be retarded by freshening to control build-up of H_2S gas. An additional treatment alternative is Bioxide,

an aqueous resolution of calcium nitrate, fashioned by Siemens Water Technologies, Inc. Bioxide creates a biological procedure that both removes dissolved H_2S and prevents its arrangement through the adding together of nitrate oxygen. It reduces manure behavior biological oxygen demand (BOD) loads while preventing decomposition of concrete or metal compilation systems. The biggest drawbacks to Bioxide are that it adds an innovative chemical, calcium nitrate, to a procedure. Fox River Fiber Company, FRF, is a small improved fiber paper manufacturing capability positioned in DePere, Wisconsin. The procedure of improving recycled paper involves deinking by either chemical or automatic means and creating market pulp ready for adaptation to manuscript products. The papermaking development uses on standard connecting 12 to 21 liters of water per kilogram of invention, which includes deinking and pulping chemicals, inks, coatings, adhesives, and cellulosic and lignin paper fibers.

In categorize to control the opening of pollutants into the sewerage organization and, eventually, its capability, GBMSD has implemented an industrial pretreatment curriculum to normalize certain industries called Significant Industrial Users (SIUs). SIUs must conform to federal, state, and local requirements throughout a permit scheme that includes self monitoring and observance. GBMSD also inspects SIUs annually to assessment operations and encourage pollution anticipation. FRF for the reason that of its high effluent COD levels has been selected as an SIU. In calculation to high COD loads, to suppress construction of hydrogen sulfide gas in sewage mains, Fox River Fiber applies as much as 1790 liters per day of Bioxide to their effluent throughout warm summer months when H_2S manufacture is at its nastiest. Lower quantities are functional during colder months. GBMSD requires that effluent from Fox River Fiber does not lead to H_2S gas levels in the air freedom of the downstream sewage scheme that surpass a greatest peak of 40 ppm and an average of 20 ppm over a twenty-four hour epoch. The plant's normal operating temperature is about 40° Celcius, which contributes to H_2S gas manufacture and makes COD, decrease more tricky.

II. LITERATURE REVIEW

Preceding studies have measured applications of ozone to water management, but principally as a antiseptic, where ozone's efficiency is well recognized. Ozone is shown to decrease cryptosporidium and manage taste and odor problems in outside water treatment systems. Current studies investigated ozonation to augment the biodegradation of challenging textile wastewaters containing dyes and detergents.

Many profitable laundering systems have used ozone productively and its microbiological settlement has been experimental. An additional recent study summarized potential options for development of wastewater management plant effluents by means of ozone and incorporation of ozone knowledge to obtainable and conservative plants. Preozonation has also been measured to improve the biodegradability of unmanageable compounds prior to biological behavior of wastewater. In adding together, the applicability of ozone to treatment and mass decrease of wastewater sludge has been calculated.

A direct study was performed on the Fox River Fiber effluent to conclude to what extent COD decrease could be achieved through calculation of high heaviness oxygen and ozone. In adding up, containment of H2S gas construction in sewage lines was monitored. The study incorporated diminution of Bioxide submission throughout oxygen/ozone vaccination. To conclude the project's achievement, COD was monitored in the FRF's effluent earlier than and after oxygen/ozone addition as well as dissolved oxygen (DO), pH, and warmth. Experiments were performed to representation the kinetics of the oxygen COD deprivation response and estimate the overall possible of the process for a longer contact time that would be integrated in an enduring scheme.

A third oxygen/ozone experiment was conducted to calculate the consequence of escalating ozone levels on COD elimination. In totaling, H_2S gas was monitored at several significance sewage mains downstream of Fox River Fiber. Although other effluent streams join the water flow to GBMSD, the warmth and COD load connected with Fox River Fiber's effluent make it the greatest provider to low DO levels and H_2S gas construction in sewage lines.

A number of factors must be present before ozone degradation of synthetic rubbers forms cracks that grow and lead to material failure. First, elongation must be present for crack formation. Unscratched rubber reacts with ozone until the entire surface twice bonds are inspired, and then the response ceases. In the procedure, a gray film, or frosting, appears on the surface of the rubber, but no cracks form. Ozone will continue to react with rubber only if the surface of ozonized products is moved aside to expose underlying Unscratched. Consequently, cracks only form and grow if the rubber is stretched to expose underlying Unscratched.

The gray film, or frosting, connected with surface assault should materialize, but the compressive forces investment the gasket in place should avoid the

critical elongation necessary to representation underlying dispersion. Assortment of an EPDM, neoprene or Viton gasket substance will also protect alongside loss of service due to gasket disappointment.

III. EXPERIMENTAL METHODS AND RESULTS

Adaptive Ozone Solutions, AO_3, LLC, designed and installed the ozone organization used in all pilot studies and experiments. The corporation positioned in Lenexa, Kansas, manufactures and sells oxygen and ozone systems for municipal and manufacturing applications. Their patented knowledge uses electrochemical cells to produce ozone and supplies determined oxygen and ozone feed streams to wastewaters using aerosol diffusers.

Dissolved oxygen, pH, and temperature were measured using a Hach HQ40d Intellical TM portable field kit. COD was measured using Hach standard method 8000 photometric analysis with a Hach DRD200 reactor, Hach DR890 colorimeter, and Hach high range (0 to 17,000 ppm) plus reagent tubes. The entire tests were performed in triplicate with averages accessible. Dissolved ozone concentration was calculated with a model Q45H portable dissolved ozone analyzer from Analytical knowledge, Inc. The analyzer has competence to measure dissolved ozone in the low range of 0–250 ppb and also the assortment of 0–2 ppm, typical of water bottling or community water behavior applications.

A. Ozone Corrosively

Because of the potentially corrosive nature of ozone to synthetic rubber gasket materials, tests were performed to determine how long after injection into a pipe system ozone maintains a residual. Each material has a limited life-span. The length of the life-span depends on the nature of the material and on environmental conditions. The first technique of corrosion avoidance is the choice for the most importunate material and a solid manufacture of the cooling system. Once the cooling water system is in use, corrosion can be prohibited by alteration of the water superiority.

The arrangement consisted of an ozone producer, ozone diffuser, and four inch PVC piping scheme designed by Adaptive Ozone Solutions, LLC. The originator fed ozone in an oxygen stream into the method at a rate of 18 grams/hour ozone. To calculate ozone residual, nine test ports were installed into the piping system. Each of these was associated to a dissolved ozone monitor and cell. The sample ports were positioned at 1.5, 4.5, 10.7, 16.8, 22.9, 29.0, 50.3, 53.3, and 59.4 meters, correspondingly, from the diffuser.

Wastewater flow during the system was 76 liters/minute. Ozone capability in use at the first illustration port, 2 meters from inoculation, showed no remaining ozone. Tests were performed numerous times to verify the zero understanding. The same was the case for all downstream sample ports. For 11-centimeter outer diameter PVC pipe, a 79 liter/minute flow gives a water velocity of about 21.7 cm/second and a residence time of 9.6 seconds to reach the 2 meter sample port. Therefore, the ozone residual in the water was less than 9.6 seconds.

B. Effect of Ozone and Oxygen on COD Effluent from Fox River Fiber:

An AO_3 installed ozone generator injected 4 grams/minute of ozone, in addition to high pressure oxygen, into the approximately 79 liters/min effluent water stream of Fox River Fiber Paper Company. The ozone loading rate was 0.073 grams/min/liter water and that for oxygen was 0.73 grams/min/liter water. During this time, Bioxide addition was reduced incrementally from its peak application rate of 1590 liters per day to 1360 liters per day, 990 liters per day, and finally 610 liters per day. Dissolved oxygen, pH, temperature, and COD were measured both at a sample point upstream of the injection point and one downstream of the injection point, but prior to entering the GBMSD sewage lines. Process boundaries required that the post ozone injection example point be positioned within the plant, such that the contact time of the oxygen/ozone stream in the system prior to the second sample point was limited to something like two minutes. Table 1 show the pre- and post injection point averages for triplicate samples collected bi-weekly during the nine week pilot run.

Table 1: Pre- and post-O_2/O_3 Injection Measurements (O_3 Loading rate of 0.053 g/min/liter water and O_2 Loading rate of 0.53 g/min/liter water).

	Temperature (^oC)	pH	DO (mg/L)	COD (mg/L)	Standard deviation
Pre injection	50.4	9.47	1.12	6244	362
Post injection	50.6	9.31	21.56	4422	266

C. Kinetic Study

Since of the limitations connected with the accessible piping system at Fox River Fiber, the preceding COD and DO measurements were taken after a contact time of only something like two minutes. Specified an almost 16% decrease in COD for such a short response time, experiments were performed to approximation the kinetics of the response of oxygen with COD waste and, hence, approximation the effectiveness of oxygen and ozone to maintain to reduce COD in Fox River Fiber's sewage. First-order kinetics:

$$\ln\left(\frac{C}{C_o}\right) = -kt, \qquad (1)$$

With respect to oxygen degradation, were assumed for the reaction

$$O_2 + COD \Longleftrightarrow CO_2 + H_2O \qquad (2)$$

Where C_o is preliminary recorded DO at the post injection example point, C is DO outstanding in water after time t, t is response, or contact time of oxygen with COD waste, and k is answer rate invariable (min^{-1}).

The COD was reduced 18.7% based ahead this. Table 2 shows the percent of oxygen that would be inspired as a function of time, which would lead to subordinate COD levels if the example point was supplementary downstream of the inoculation point. While the exact decrease cannot be accurately quantified without more information about the personality of the COD waste, it is clear that actual decrease in COD sent to GBMSD would be significantly lower than that recorded from the post injection sample point at Fox River Fiber.

Table 2: Kinetics of First-Order Reaction with k = 0.12/min

Time (min)	*C/Co*	% Un reacted O_2
1	0.89	89%
2	0.79	79%
5	0.55	55%
10	0.30	30%
20	0.09	9%

D. COD as a purpose of O_3

A concluding experiment was a final experiment was performed to measure the effect of increase the ozone injection rate on sewage COD. A 9.5 liter/min side stream of Fox River Fiber's effluent stream was abstracted and dosed with increasing quantities of ozone under the same water flow rapidity and contact time as tests performed on the total effluent torrent. Ozone was generated and injected with oxygen as aerosol bubbles with an AO_3 system as shown in Figures 1 and 2. Primarily just oxygen was added, after which both oxygen and ozone were additional with the oxygen amount something like constant at 0.53 grams/min/liter water. At each ozone level, samples were drained and analyzed for DO and COD. Table 3 summarizes the consequences.

Figure 1: O_3/O_2 aerosol bubble Injection Contact Chamber.

Figure 2: Close-up of Aerosol Bubble Mass Transfer.

E. Hydrogen Sulfide Suppression

In adding up to COD decrease, another apprehension of GBMSD with the high COD unconfined by Fox River Fiber is the production of H_2S gas in importance sewer lines among GBMSD and FRF. Both prior to and subsequent installation of the oxygen/ozone system, continuous capacity of H_2S gas at a number of illustration locations in the air space of the sewage lines were performed with Odalog gas loggers, uncovering Instruments business, in the 0 to 200 ppm range. Table 4 summarizes the results. Dissolved sulfides in the liquid segment were also calculated and varied connecting 0 and 0.5 ppm.

A relationship of peak H_2S data in Table 4 for the cases of just 1520 liters/day Bioxide and 1520 liters/day Bioxide with ozone/oxygen production shows that supplementary of ozone/oxygen to the FRF effluent did decrease the peak H_2S. Dropping the Bioxide adding up to 1330 liters/day and 950 liters/day did not result in augmented H_2S peak values, and average values were constantly below 20 ppm.

For all example sites, peak H_2S remained below the maximum satisfactory upper limit of 40 ppm. In adding together, average H_2S remained underneath the necessary 20 ppm for all but one quantity. Supplementary reducing Bioxide to 150 gal/day resulted in two H_2S peaks that exceeded the satisfactory upper limit and many averages exceeding 20 ppm.

Table 4: Peak Hydrogen Sulfide Gas as a Function of Bioxide Addition at Sample Sites Downstream of Fox River Fiber.

Sample site	Peak H_2S : no O_3 1520 L/day	Peak H_2S (ppm) for each Bioxide application rate with O_3			
		1520 L/day	1330 L/day	950 L/day	570 L/day
NSI035	3	3	2.5	4	4
NSI028	7	6	4	3	12
NSI013	6	1	0	9	22
ASC020	20	0	0	22	68
ASC013	17	1	2	11	25
ASC008	30	2	4	22	47
ASC005	9.5	1	1	9	25

IV. CONCLUSION

Accumulation of a high pressure oxygen/ozone torrent to the effluent discharged by Fox River Fiber Corporation to the GBMSD system concentrated COD sent to GBMSD by FRF by over 15% despite a very small contact time. There are some procedure is supposed to be held over here:

- kinetic model of the deprivation reaction among oxygen and COD predicts as great as a 60% COD lessening if the contact time was augmented via additional piping to as few as 30 minutes.
- Dissolved oxygen in the scheme was significantly augmented by the Adaptive Ozone Solutions development.
- A 60% diminution in effluent COD could save the plant as much as $730,000 per annum. While this analysis did not consist of the electrical cost of the ozone generator, this quantity would be small compared to the impending savings.
- Hydrogen sulfide gas monitoring throughout the study showed that the Adaptive Ozone Solutions, LLC, procedure could suppress H_2S gas construction in the air space of the sewage mains to beneath peaks of 40 ppm, the maximum acceptable value, under concentrated Bioxide applications.
- Supplementary experimentation would be mandatory to establish the exact point between 570 and 950 liters per day at which hydrogen sulfide peaks would develop into inappropriately high.

Hydrogen sulfide gas, fashioned as an effect of these conditions, is the most common odorous gas found in municipal wastewater compilation and management systems. The papermaking development uses on standard connecting 12 to 21 liters of water per kilogram of invention, which includes deinking and pulping chemicals, inks, coatings, adhesives, and cellulosic and lignin paper fibers.

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