

Superoxygenation Applications in Wastewater Collection and Treatment Systems

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Introduction

Odor problems and associated corrosion-caused infrastructure deterioration frequently have plagued wastewater collection and treatment systems worldwide due to the reaeration rate of gravity sewers being only $\sim 1/10^{\text{th}}$ of the oxygen demand in warm ripe wastewaters. Force mains are even more problematic because there is no reaeration. Resulting oxygen-deficient conditions cause the sulfate to be microbially reduced to H_2S , which then volatilizes to the head space. The oxic conditions usually found in the head space support the microbial oxidation of H_2S to H_2SO_4 , which can seriously corrode concrete. Treatment protocols capable of sustaining oxygen-rich environments throughout collection and treatment systems, therefore, would prevent odor and corrosion. Until recently, however, technology capable of providing such oxic conditions in all phases has not been exploited.

Superoxygenation, a high concentration dissolved oxygen (D.O.) treatment, will be discussed in this paper. The process dissolves pure O_2 at $>90\%$ efficiency under pressure to achieve D.O. concentrations of 50 to >300 mg/L. These high concentrations can be retained in solution with proper handling of the depressurized superoxygenated water. By contrast conventional aeration, which absorbs O_2 from air, can economically achieve D.O. concentrations of only < 5 mg/L.

Superoxygenation can successfully eliminate odor and corrosion even in *force mains* and *gravity interceptors*, minimizing negative public complaints as well as traffic disruptions caused by infrastructure replacement. *Sulfide odor-free head works* may also be achieved by appropriate application of superoxygenation to the influent interceptor sewer approximately one-half mile upstream of the wastewater treatment plant. Even in *sludge storage tanks* odor and corrosion may be prevented by proper application of superoxygenation.

Chemical/microbial oxidation of sulfides under oxic conditions proceeds approximately 3 to 6 times faster than the rate for nitrate respiration.¹ Oxic conditions also facilitate removal of dissolved H_2S to non-detectable concentrations. Nitrates and iron salts can economically reduce dissolved H_2S to only >0.5 mg/L which still causes odor and corrosion^{2,3}. The H_2S concentration in the gas phase in equilibrium with 0.5 mg/L H_2S in the liquid phase is still rather high at 75 ppm. Oxic conditions in warm ripe wastewater also support the complete removal of dissolved H_2S in 15 to 20 minutes vs partial removal in 2 hours for nitrate respiration.⁴ In addition the cost for pure O_2 (\$0.05 to 0.08 /lb O_2) is approximately $1/10^{\text{th}}$ of that for alternative chemicals such as hydrogen peroxide and nitrates (\$0.70/lb of O_2 equivalent).

Superoxygenation technology allows three additional applications in wastewater treatment:

- 1) *Primary clarifier* effluents may become sulfide-free since the long detention time enables the chemical/microbial oxidation of dissolved H_2S to be completed.
- 2) The *entire D.O. requirement* (200 to >300 mg/L) may be added to the *primary effluent*, thus requiring no additional oxygen transfer within the *activated sludge reactor* (especially advantageous in high mixed liquor suspended solids membrane reactors characterized by much reduced oxygen transfer characteristics).
- 3) Discharge of a *D.O./BOD_L-neutral final effluent* ensures that no net D.O. resources are consumed in *receiving waters*. This possibility is especially advantageous for receiving waters with low reaeration rates such as canals, pooled rivers and bays.

Superoxygenation principles, some of which contradict past conventional aeration practices, will be described in this paper to familiarize the reader with the unique advantages of superoxygenation. Field installations and laboratory studies will also be cited.

Oxygen Transfer Criteria

Many aeration, pure O₂ and chemical oxidation/precipitation treatments which have been devised in the past to address water quality issues usually have been limited by various environmental, financial or practical problems for odor/corrosion prevention.

A. Disadvantages of Past Treatment Systems

Traditional aeration technology cannot economically raise D.O. concentrations above 5 mg/L because of excessive electricity consumption. Since some water quality applications in wastewater collection and treatment are plug flow in nature, very high D.O. concentrations must be supplemented, making conventional aeration technology inappropriate. The high cost and negative environmental impact of chemical treatment are significant disadvantages. Past attempts to utilize pure O₂ in wastewater treatment have only maintained D.O. concentrations of <10 mg/L.

B. Superoxygenation Technology

Superoxygenation utilizes pure O₂ under pressure in a unique conical downflow reactor to raise the D.O. in the discharged water to 50 to >300 mg/L, depending on the application. This system, the Downflow Bubble Contact Oxygenator, also referred to as the Speece Cone (see Fig. 1), incorporates the desirable conditions for >90% O₂ absorption while producing very high D.O. concentrations in the effluent. The conical reactor has no internals and thus uniquely accommodates raw unscreened wastewater with its rags and strings.

A finite amount of time is required for effervescent bubble formation and growth to occur after depressurization. Therefore to preclude effervescence after depressurization of the highly oxygenated discharge, the superoxygenated water is quickly diluted with water containing D.O. of 2 - 10 mg/L.

Excessive turbulence can also be avoided if the gas transfer reactor is placed in a caisson to achieve pressurization by the hydrostatic head without energy consumption or release. Thus there is a 'soft' type of depressurization as the water flows back to the surface which negates the intense turbulence/cavitation caused by a throttling valve. Depressurization with dilution under increased hydrostatic head at the bottom of a shaft is also advantageous to efficiently retain these high D.O. concentrations in solution without significant effervescent loss.

C Oxygen transfer optimization requirements and benefits

The downflow conical superoxygenation reactor shown in Fig. 1 traps O₂ bubbles indefinitely due to high inlet and low outlet velocities accordingly. This type of configuration provides >100 seconds bubble retention time necessary for efficient oxygen transfer. In addition, the high inlet energy prevents collapse of the bubble swarm, maintaining high gas bubble surface/water volume (A/V) ratio. Hydrostatic pressurization of this reactor increases both the rate of O₂ transfer and the potential discharge D.O. The configuration also provides reasonable energy costs with nil stripping potential for volatile components in the wastewater.



Fig. 1 Speece Cone Superoxygenation Installation

Principles of Superoxygenation

Superoxygenation technology design and operation principles differ significantly from traditional wastewater treatment practices and in some cases may contradict conventional aeration protocols. Such contradictions, however, make possible new applications to a wider variety of water quality problems than can be addressed by aeration. Therefore careful consideration of superoxygenation is recommended.

1. Gas phase separation in low velocity force mains is not conducive to efficient O₂ absorption

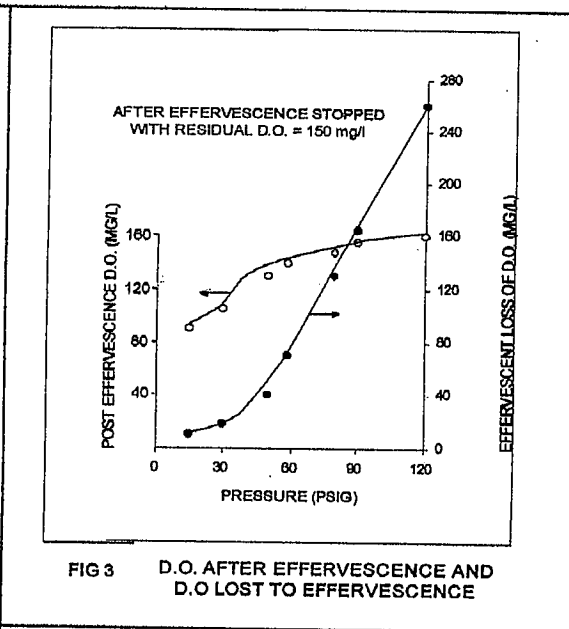
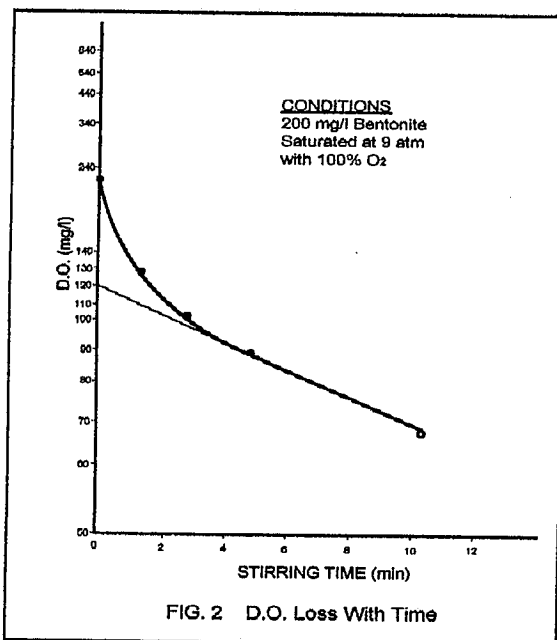
It is impractical to inject gaseous O₂ into force mains with reverse grades because the undissolved O₂ collects at the high points. It is noteworthy, therefore, that superoxygenation completely dissolves the gaseous O₂ before injection into the force main.⁶

Many municipalities inject gaseous O₂ into rising force mains to control odor. In using the force main as the oxygen transfer reactor, gaseous pure O₂ is injected with the erroneous expectation that it will be dissolved efficiently as it moves through the force main. Due to low velocities in most force mains, though, instead of dissolving efficiently, the gaseous O₂ bubbles rise to the crown of the pipe within about 50 ft of the point of injection, drastically reducing the gas/water interfacial area. Subsequently the O₂ gas travels along the crown. For example, injection of pure gaseous O₂ into a 2 mile rising force main in San Diego with 440 ft of head at the beginning, resulted in only 50 to 70% O₂ absorption efficiency after 2 miles (~2 hours flow time).⁵

2. Effervescence of highly elevated D.O is not spontaneous at >100% saturation

It is crucial to avoid effervescent loss of D.O. The important principles of minimum threshold turbulence and minimum threshold total dissolved gas supersaturation levels cannot be over-emphasized because under marginal supersaturation and/or marginal turbulence regimes, spontaneous effervescence either does not occur or ceases before it reduces total dissolved gas to 100% saturation.

There are multiple ways to depressurize water, depending on whether it is desirable to precipitate the dissolved gas out of solution, as in dissolved air flotation (DAF), or retain it in the dissolved state, as in superoxygenation.



A. Minimum D.O supersaturation threshold

Supersaturation is a necessary but insufficient condition to cause spontaneous effervescence. Due to an elevated minimum threshold D.O. supersaturation concentration level below which spontaneous effervescence will not occur, water may be supersaturated to >200% of O₂ saturation without spontaneous effervescence.

Fig. 2 shows the results of a laboratory study by the author in which a gently stirred vessel containing water was pressurized using pure O₂ to 120 psig (9 atmos.) for an extended period to approach saturation D.O. The vessel was depressurized while being gently stirred and the D.O. was measured in the un-pressurized reactor vs time. Immediately after depressurization the D.O. dropped from ~ 400 mg/L to 235 mg/L due to spontaneous effervescence and within 2 minutes had decreased to 105 mg/L. Thereafter the D.O. decreased according to first order kinetics to 70 mg/L in 10 minutes. The D.O. had to be raised to >120 mg/L before spontaneous effervescence occurred.

B. Low turbulence threshold and immediate dilution

Effervescence can be avoided if dilution by low D.O. water is practiced within a few seconds after depressurization of the superoxygenated water. In dissolved air flotation (DAF), spontaneous effervescence is maximized by the combination of conditions which are incorporated. For DAF to be most effective, the saturator pressure is commonly operated at 70 to 80 psig, capable of raising the dissolved gas concentration in the wastewater to 600% of ambient pressure saturation. Pressure throttling nozzles directed at flat plates maximize intense turbulence and cavitation and are essential to achieve effective DAF.^{7,8} In contrast, measures taken in superoxygenation maximize D.O. retention upon depressurization by managing the turbulence/dilution regime.

In a series of experiments designed by the author to characterize effervescence and residual supersaturation, a stirred laboratory reactor was pressurized with pure O₂ for prolonged periods of pressure and mixing to achieve supersaturation of up to 600% (270 mg/L D.O.). After reaching the various levels of supersaturation indicated, the reactor was depressurized (without turbulence in the liquid phase) and the residual D.O. measured after all effervescence had ceased. The residual D.O. was nominally 120 to 160 mg/L over a wide supersaturation range (see Fig. 3).

Fig. 4 shows the results of a laboratory study in the author's laboratory in which water was raised to saturation level in a gas transfer reactor using pure O₂ at a given pressure and discharged through a pressure-reducing valve into water maintained at zero D.O. using cobalt catalyzed excess sulfite. Subsequent determination of D.O. retained in solution after depressurization caused effervescence revealed that approximately 10% of the D.O. in water superoxygenated to 270 mg/L was lost from solution upon depressurization/dilution. Proper diffuser/depressurization design and immediate dilution of superoxygenated water into low D.O. water effectively retains the D.O. in solution.

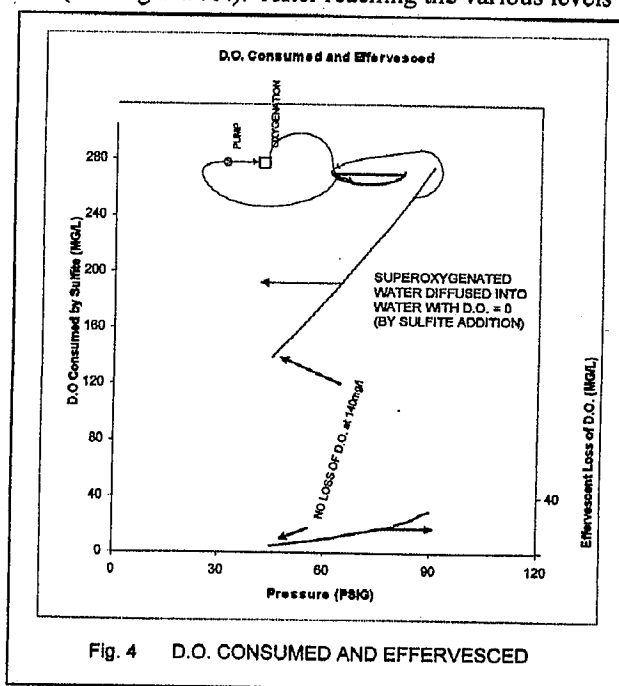


Fig. 4 D.O. CONSUMED AND EFFERVESCED

3. Superoxygenation can reduce H₂S, mercaptans and disulfides to non-detectable concentrations in wastewater

Gaseous O₂ injection into a 2 mile 25 MGD rising main in San Diego demonstrated that all dissolved H₂S, mercaptans and disulfides were chemically/microbially oxidized to non-detectable concentrations when sufficient D.O. was provided to ensure oxidic conditions throughout the entire force main to its discharge.⁵ With D.O. present, the H₂S in the discharge manhole head space is readily reduced

to non-detectable (< 1 ppm), as confirmed in a Los Angeles installation using superoxygenation in a 3-mile force main⁶ (see Fig. 5).

High concentrations of H₂S in the gas may be found at force main discharges before significant polysulfide formation occurs. Since 2 to 55 ppm concentration of H₂S in the gas phase enables crown corrosion to proceed at 50% of the maximum rate, a significant improvement in odor perception may be achieved with little reduction in the rate of concrete corrosion when using nitrate or iron salts since >0.5 mg/L dissolved H₂S is still present in the wastewater.^{9,10} Successful dissolved H₂S reduction is possible because D.O. is a much preferred electron acceptor compared to nitrate for microbial metabolism of H₂S.

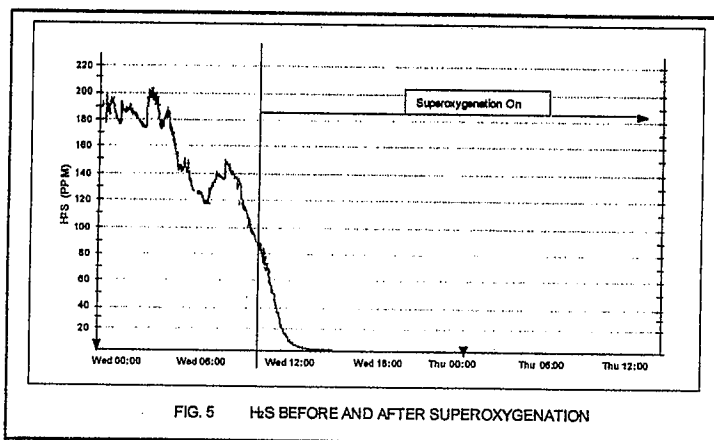


FIG. 5 H₂S BEFORE AND AFTER SUPEROXYGENATION

4. Superoxygenation of raw wastewater will not strip out H₂S

In principle pure O₂ absorption into D.O. deficient wastewater simultaneously would result in stripping out non-D.O. volatile compounds such as dissolved N₂, H₂S, mercaptans, etc. However the efficient O₂ absorber used in superoxygenation is a very inefficient H₂S stripper.

Stripping is a measure of the off-gas ratio from the O₂ transfer reactor. A bubble aerator with 5% O₂ absorption has 99 ft³ of stripping off-gas for each 1 ft³ of O₂ absorbed, while pure O₂ absorbed at 90% efficiency has 0.1 ft³ stripping off-gas per 1 ft³ of O₂ absorbed. This is a 1000 fold decrease in off-gas stripping routinely produced by conventional diffused air or surface aerators. Thus even though very high D.O. concentrations are achieved, there is nil H₂S and other volatile compound stripping.

5. It is possible to add >100 mg/L D.O. to a force main and retain it in the dissolved state in raw wastewater for long hydraulic retention times

If a force main has >100 ft. of head at the pump discharge it is possible using superoxygenation technology to raise the D.O. to >100 mg/L. Since the force main is full, there is no gas/water interface for gas transfer to occur. D.O. is consumed as the force main rises and the hydrostatic head decreases. These factors therefore tend to compensate and keep the saturation concentration at <100% for the respective pressurized conditions throughout the force main all the way to the ambient pressure discharge.

A superoxygenation system located in a force main in Kentucky, which has a pressure of 200 ft at the beginning, allows the D.O. to be potentially raised to as high as 200 mg/L. The saturation concentration at this pressure is 275 mg/L, so the D.O. in the wastewater is actually under-saturated at this pressure with no potential for effervescence. Thus it is possible to maintain oxidic conditions at the discharge even after a 9 hour residence time in this 9 mile force main.⁶

6. 20 mg/L D.O. supplemented to a gravity sewer will not increase the head space O₂ composition to > 23.5%, posing no potential explosion hazard should hydrocarbons be present

D.O. excess above air saturation combined with the reaeration rate in a partially full sewer causes stripping of D.O. to the head gas. However, this increase in the O₂ composition is insignificant for D.O. <20 mg/L, as the following example shows.

The O₂ composition in the head gas of a 4 ft diameter sewer, flowing 50% full and containing 20 mg/L D.O., will peak at 21.0 % O₂ (an increase of 0.1% O₂ composition) after flowing 2 miles if the ratio

of air velocity to wastewater velocity is 1.0 (see computer model projection in Fig. 6). Also the O₂ composition of the air over the wastewater will increase by 0.25% to 21.15% if the sewer is flowing 90% full. This increase will be 3 times greater if the relative air to wastewater flow is 0.3 vs 1.0. Under typical conditions superoxygenation of wastewater to 20 mg/L D.O. in gravity sewers is possible without approaching the lower explosive limit in the gas phase.

7. Supplementation of 20 mg/L D.O. can be effectively retained in gravity interceptors for 2 miles, supporting the aerobic microbiota for H₂S metabolism and corrosion prevention at the head works

Superoxygenation applied to warm ripe wastewater >15 to 20 minutes' travel time upstream of the headworks maintains oxic conditions, enabling the

microbiota to metabolize any dissolved H₂S completely. This will prevent odor/corrosion and negate the need to cover, collect and scrub foul gases at the head works. A study at a large municipality in the southern U.S.A. has estimated that odor prevention by superoxygenation upstream of the head works would cost only 10% of the expense incurred for covering the headworks and scrubbing the foul gases.

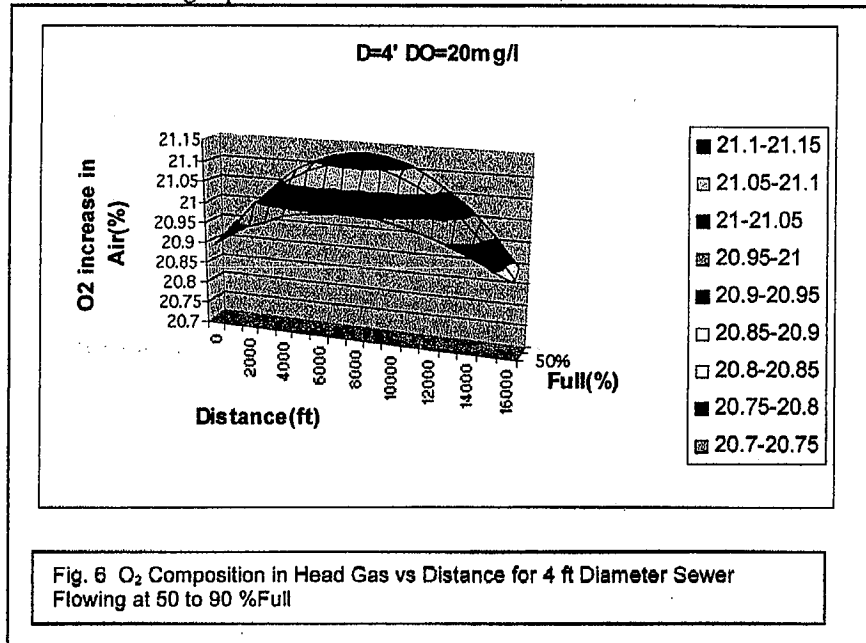
For typical wastewater flows in a gravity sewer, 20 mg/L D.O. (135% total dissolved gas) would be well below the threshold effervescence level. The only gas transfer would be at the gas-water interface. The reaeration rate for a 4 ft diameter sewer pipe, flowing 50% full at 1 ft/sec, is nominally 2/day. Therefore if the D.O. is raised to 20 mg/L, less than 1 mg/L of this D.O. would be stripped and lost from the wastewater to the headspace over a distance of 2 miles (~ 2 hours flow time).

8. Superoxygenation can be applied successfully to primary clarifier influents

The H₂S increase in wastewater passing through primary clarifiers causes major odor problems. The possibility of completely absorbing >20 mg/L D.O. in the influent to a primary clarifier provides a significant advance in odor control technology. H₂S in the influent can be fully oxidized during passage through the primary clarifier using superoxygenation.

Usually primary clarifier detention requires about 2 hours and the D.O. uptake in warm ripe wastewater is approximately 10 mg/L-hr. At 30°C the D.O. saturation with pure oxygen would be 36 mg/L. Therefore 20 mg/L of D.O. is equivalent to 0.55 atmospheres of O₂ partial pressure. Below the water surface, this relative saturation will be proportionately less due to the increased hydrostatic pressure. Thus this D.O. in the primary clarifier would be far below the spontaneous effervescence threshold required to cause suspended solids to float.

Full scale studies were conducted for odor/corrosion control by superoxygenation in the primary clarifiers at a large wastewater treatment plant in Dallas, Texas and a full-scale system is being installed but is not yet in operation. Fig 7 shows a schematic as well as a photograph of the installation.



9. It is possible to add the entire D.O. demand (200 to 300 mg/L) to a primary effluent and efficiently keep it in solution in the activated sludge reactor

Supplementing the total D.O. requirement to a primary clarifier effluent before discharge into the activated sludge reactor represents a radical new advancement in wastewater treatment.

Superoxygenation is well suited to using open topped biological reactors which positively impact cost and maintenance issues. The configuration also precludes the buildup of CO₂ and associated pH decrease which characterize closed reactor technology. It can be shown that unit energy consumed per unit weight of D.O. added is relatively constant (<1000 kwhr/ton D.O.) over the entire pressure range corresponding to superoxygenation concentrations up to 300 mg/L D.O.

Depressurization of superoxygenated primary effluent by a throttling valve at the bottom of a shaft and/or dilution with low D.O. mixed liquor from the biological reactor enable efficient retention of these high D.O. quantities in solution. Fig. 8 is a schematic of such a proprietary device. A 24 MGD superoxygenation system with the D.O. raised to 150 mg/L has been demonstrated to retain the D.O. in solution efficiently after immediate dilution by depressurization in a 30 ft deep basin where the D.O. was maintained at <4 mg/L.

By adding all of the required D.O. to the primary effluent, the greatly reduced resistance to O₂ transfer (low alpha factor) associated with high mixed liquor suspended solids (8000 to 18,000 mg/L) in membrane reactors or immobilized biofilm reactors, becomes irrelevant.¹² Much reduced volatile organic contaminant emissions from the activated sludge would also result because of the negligible stripping which occurs in superoxygenation. No additional D.O. transfer is required in the activated sludge reactor but adequate time must be provided for the microbial reaction.

Because of the continual D.O. uptake of the microbial reactor, the bulk liquid D.O. can be maintained at a low D.O. of < 10 mg/L. Therefore even though the feed wastewater may contain > 300 mg/L D.O., immediate dilution coupled with continuous microbial D.O. uptake results in a low steady state D.O. in the open-topped activated sludge reactor. Thus low bulk D.O. facilitates depressurization/dilution of the

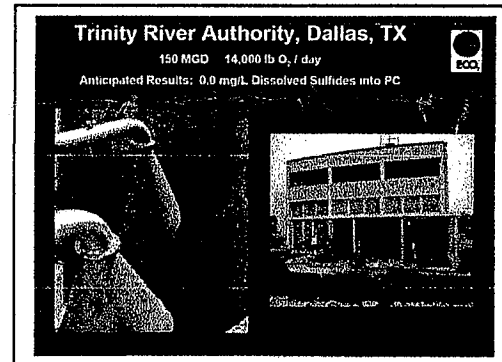
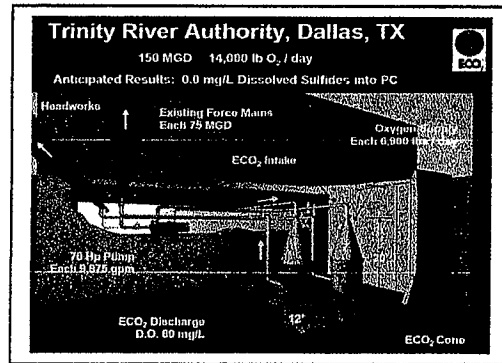
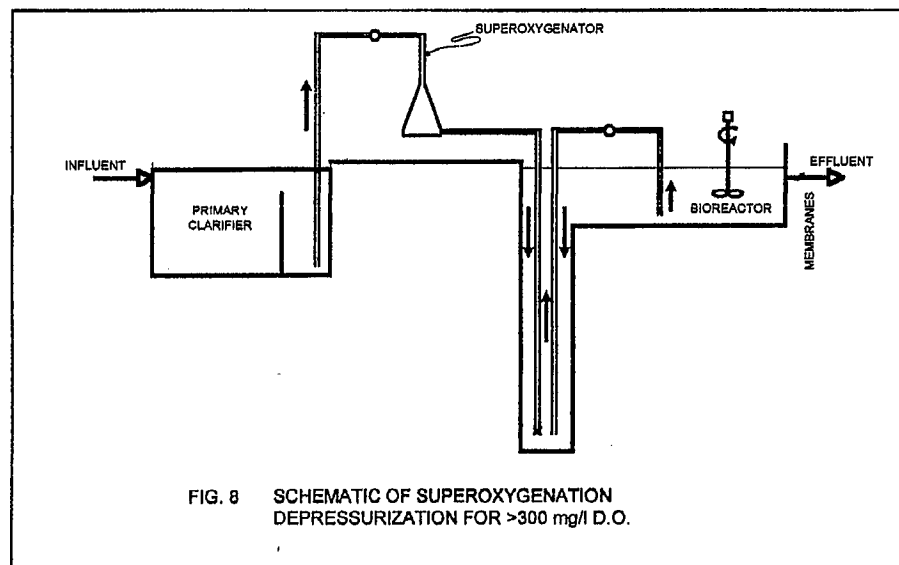


Fig. 7. Superoxygenation application of primary clarifier influent for odor-corrosion prevention



superoxygenated feed, preventing effervescent loss of the D.O.

10. It is possible to supplement D.O. = BOD_{ult} to a wastewater treatment plant effluent and keep it in solution to avoid consumption of D.O. resources in the receiving water

D.O. addition equal to the BOD_{ult} in a wastewater treatment plant discharge that comprises a fraction of the flow in the receiving stream, provides the possibility of negating the need for costly tertiary treatment. Such elimination of additional treatment is even possible when the wastewater treatment plant effluents represent the major portion of flow in the receiving stream.

Even with no dilution, 20 mg/L D.O. is presently utilized in aquaculture and therefore is compatible with the receiving water fishery. This elevated D.O. would result in only a minor loss of D.O. being stripped from solution as long as the reaeration rate of the receiving stream is less than approximately 3/day. Should the receiving water have a series of pools connected by riffles, there would still be little loss of D.O. in the highly turbulent shallow riffles because of the relatively short transit time. This concept is especially attractive for treated wastewater being discharged into rivers in flat terrain which have low reaeration rates and do not meet D.O. standards even upstream of the wastewater treatment plant discharge.

11. It is possible to oxidize sulfide in concentrated sludge holding tanks by superoxygenation to prevent odor/corrosion production

A major odor/corrosion problem in municipal wastewater treatment plants is associated with the sludges stored in holding tanks prior to dewatering. Prolonged holding times promote odor/corrosion formation within the tanks above the water line and under the covers.

Sulfide is chemically/microbially oxidized at a much higher rate than volatile fatty acids in a microaerophilic environment. Therefore if D.O. is added to a sludge storage tank at the rate at which sulfide is generated, it will be utilized preferentially in sulfide oxidation even though little increase in oxidation-reduction potential is noted. These findings have been demonstrated in an anaerobic digester.¹³ Thus sulfide can be maintained at low concentrations without oxidizing significant levels of volatile fatty acids.

Plant effluent reuse water or waste activated sludge (WAS) can be raised to concentrations of >300 mg/L D.O. This superoxygenated, high pressure discharge can be injected into a line through which 20-100 volumes of sludge from the storage tank would be re-circulated for each 1 volume of superoxygenated plant reuse water or WAS. Such a procedure would immediately dilute the >300 mg/L within < 1 second in the sludge flow line, precluding the effervescence typical of dissolved air flotation systems.

Thus rapid dilution can result in retention of 90-95% of >300 mg/L D.O. in the dissolved state within the sludge mass. Dilution with a 1 to 5% superoxygenated side stream would result in little reduction of the sludge concentration. Since superoxygenation occurs without H_2S stripping, there are no offensive off-gases, as is the case with aeration of sludge holding tanks.

Summary

Water quality management technology capable of maintaining the oxic conditions necessary for preventing odor and corrosion production in wastewater collection and treatment systems has not been available.

Superoxygenation, a new green technology which combines standard gas transfer principles with pure O_2 and pressure in a unique gas transfer reactor, provides exceptionally high O_2 absorption efficiency as well as high rates of D.O. transfer. The oxygen transfer reactor also accommodates rags and strings inherent in raw unscreened wastewaters. By incorporating novel depressurization and/or dilution techniques, the elevated D.O. quantities can be kept in solution. Use of the technology can keep force mains oxic for miles by proper treatment of the inlet raw wastewater. Because of the low reaeration rate even gravity interceptors can be supplemented with high D.O. concentrations with little loss of D.O. from the wastewater and little increase in the O_2 composition of the head gas.

Due to the low stripping potential inherent in efficient O_2 absorption, volatile compounds, which can be metabolized by aerobic bacteria, are not stripped. Compared to nitrate use for sulfide prevention, superoxygenation supports a three to six fold increase in rate of sulfide removal at $1/10^{\text{th}}$ of the cost of alternative chemicals. In addition non-detectable dissolved H_2S concentrations can be achieved compared to >0.5 mg/L economically achievable with nitrate or iron salts, which still causes odors and corrosion.

Superoxygenation of the wastewater treatment plant influent line makes possible an economical and practical alternative to covering the headworks and scrubbing the foul gases for odor control. By providing oxic conditions at a sufficient distance upstream of the headworks, the inlet line becomes the reactor for H_2S oxidation. Superoxygenation of the influent to primary clarifiers for odor-corrosion control also avoids the need for costly covering of tanks. Superoxygenation also offers the potential to add the entire D.O. demand to the primary effluent as it is delivered to the secondary biological reactor, avoiding the need for additional transfer of oxygen into membrane reactors having very high mixed liquor characterized by low alpha factors. In addition uperoxygenation of a wastewater plant discharge to a D.O. equal to its BOD_L results in an effluent that avoids depletion of D.O. resources in the receiving waters while stabilizing residual organics. Tertiary treatment may thereby be unnecessary.

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