Superoxygenation: Facts and Myths

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Introduction

Until recently the difficulties encountered in dissolving pure O_2 into wastewater at high concentrations have hindered attempts to maximize its amazing usefulness in preventing odor formation and in causing the rapid metabolism of dissolved sulfides by resident bacteria possible only under oxic conditions. However, a new process, Superoxygenation, as used in this discussion, utilizes pure oxygen under pressure in a unique gas transfer reactor to raise the dissolved oxygen (D.O.) in the discharged water to 10 to 300 mg/L, depending on the application. These high concentrations of D.O. enable *many extra years of infrastructure usefulness by the resulting corrosion control.* Furthermore, by the *prevention of H_2S formation* in head works, primary clarifiers, gravity interceptors and force main sewers, *odors can be eliminated without costly and troublesome capturing and scrubbing* of foul gases. *Avoidance of tertiary treatment often needed* to compensate for low reaeration rates in receiving waters is often possible by superoxygenating effluents to D.O. levels = BOD_{ult}; D.O. standards for rivers, canals, lakes and bays thereby may be attained consistently. *Odor and corrosion prevention in sludge holding tanks* prior to dewatering are also potentially achievable by superoxygenation technology.

It is well known that oxic conditions support the rapid chemical and microbial oxidation of H_2S and other reduced sulfur compounds present in raw wastewaters. As long as oxic conditions are maintained, additional H_2S formation is prevented. But aeration technology is limited economically in raising D.O. concentrations above 4 - 5 mg/L, due to the limited solubility of O_2 in water (air:21% O_2) of 7 – 14 mg/L at 35 and 0 ^{o}C respectively. Aeration techniques produce only D. O. <10 mg/L. Therefore the limitations of engineered aeration techniques in remediating wastewater problems are well known, as evidenced by the serious odor and infrastructure corrosion issues which trouble cities and industries worldwide.

All of the D.O. required for oxic microbial metabolism (i.e. 300 mg/L), can be added to the primary effluent and then the superoxygenated wastewater subsequently introduced to the activated sludge reactor when utilizing this pure oxygen technology. Depressurization under increased hydrostatic head at the bottom of a deep shaft and/or immediate dilution by low D.O. mixed liquor, may be incorporated to retain the very high D.O. concentrations in solution, facilitating use of open-topped microbial reactors for escape of CO_2 and negating the adverse impact of reduced oxygen transfer rates (alpha factor) caused by high mixed liquor suspended solids (MLSS) in membrane reactors. .

Pure O_2 costs approximately one tenth as much as alternative odor prevention chemicals (iron salts, nitrates, peroxide and MgO), but when used in this proprietary system, superoxygenation results in H_2S concentrations even lower than alternative chemicals can achieve, without a high financial burden and environmentally negative impact. In addition D.O. concentrations of <60 mg/L can be retained in solution for hours at ambient pressure, while D.O. concentrations of >100 mg/l can be diluted in seconds to retain the D.O. in solution. These critically important benefits make possible treatment applications heretofore very difficult to consider.[1]

Past and planned municipal, industrial and lake superoxygenation installations point to successful results in the future for new applications. Corroborating data available from several ongoing installations will be included. Since some water quality professionals may be unfamiliar with the superoxygenation approach to wastewater treatment, the author will also discuss 15 frequently mentioned misconceptions about superoxygenation technology and offer the scientific basis which refutes each perceived 'myth.'

Oxygen Transfer Requirements and Devices

Efforts to dissolve *pure oxygen* by using *aeration equipment* have long been ineffective due to the *differing* design objectives involved. Therefore a paradigm shift in gas transfer concepts is required to dissolve pure O_2 optimally in wastewaters.

Two imperatives must be kept in mind when evaluating superoxygenation advantages:

* *conventional aeration technology features are not easily adapted for superoxygenation purposes*

* *superoxygenation technology must be properly configured and carefully implemented to be used effectively*

A   Differing Design Objectives: Superoxygenation vs. Aeration Technologies

Several critical differences between superoxygenation using pure O_2 under pressure and aeration using air must be clarified, incorporating the two crucial warnings listed above, before evaluating the relative advantages of relying on aeration techniques or choosing the newer superoxygenation possibilities.

For instance economical and practical oxygen transfer requirements are not met equally well by both technologies, but must be successfully addressed before selecting the best treatment for a given water quality problem, These considerations should be based upon serious study to distinguish between the two different designs.

It also must be borne in mind that aeration technology is ineffective in transferring high concentrations of D.O. into wastewater *without stripping foul gases* contained therein. Superoxygenation, however, by achieving immediate and sustainable oxygen transfer in the earliest stages at high absorbency efficiency, does not strip foul volatile gases from the wastewater.

a.   economical considerations.

Since energy consumption is the controlling restraint in aeration technolog*y aeration designs typically are low O_2 absorption efficiency mechanisms* and thus not candidates for highly efficient oxygen transfer uses.

O_2, unlike air, is a commodity which has monetary value, making it mandatory that pure O_2 be dissolved with high absorption efficiency for the process to be economical. More than 90-95% absorption rates, concomitant with raising the D.O. to very high concentrations of >300 mg/L with low unit energy consumption, must be achieved for the use of pure O_2 to be economically feasible in many situations.

b.   practical considerations.

Over the years many attempts have been made to utilize pure O_2 in water quality management. An early choice was the application to activated sludge, using a cumbersome and costly gas-tight O_2-enriched head space constructed of concrete and fitted with mechanical mixers/splashers to provide O_2 transfer. Due to the closed head space, CO_2 from the microbial activity accumulated in the system and resulted in a depressed pH which hindered nitrification. O_2 transfer was also reduced because of lower O_2 composition,which in turn was due to dissolved N_2 stripping. The covered tank impeded maintenance and when foaming occurred in the closed head space, O_2 transfer was even further reduced.

With the advent of superoxygenation technology, even activated sludge can now be more advantageously processed accommodating

open topped tanks,
CO_2 stripping from the open topped tanks,
higher pH - enhancing nitrification in the tanks,
greatly reduced VOC emissions and
increased VOC metabolism rates.

B   Pure O_2 Gas Transfer Devices

The following schemes have been utilized to dissolve pure O_2 into water with varying degrees of success:
* confined enriched O_2 head space with surface splashing (UNOX)
* Venturi jets
* pressurized loop reactors
* fine bubble diffusers
* down pumpers with bubble capture and recycle
* porous or bubbleless membranes
* spinning fine bubble diffusers
* injection of gaseous O_2 into force mains
* superoxygenation

Many of these devices operate with low O_2 absorption efficiencies of 30 to 75% and/or are unable to achieve high D.O. concentrations with low unit energy consumption. *Inefficient O_2 absorption can greatly increase life cycle costs of treatment.*

C   Optimization Criteria for O_2 Transfer

The past use of sub-optimal oxygen transfer processes should not prejudice professionals against investigating the superior advantages of superoxygenation in solving a significant variety of water quality management problems.

Many oxygenation systems in the past were partially ineffective and achieved only some of the following criteria. None, except for superoxygenation, can simultaneously incorporate all these criteria to achieve excellent performance.

Optimization criteria for O_2 transfer technology are as follows:
* high D.O. >100 mg/L
* high gas surface /liquid volume interfacial ratio
* prolonged retention of gaseous O_2 in the gas transfer reactor to achieve highly efficient (90 – 95%) absorption
* low unit energy consumption (300 - 1000 kwhr/ton D.O.)
* accommodation of raw unscreened wastewater containing rags and strings
* negligible stripping of volatile odorous sulfides and hazardous air pollutants

Conventional aeration and other techniques used at present are not able to achieve all of these criteria together as superoxygenation does, making the new technology worthy of serious consideration for a variety of water quality management objectives in the future.

Common Superoxygenation Misconceptions

Longtime familiarity with inefficient, low D.O. aeration technology results understandably may cause skepticism when new designs are introduced. However, as will be explained later, since aeration and superoxygenation techniques involve different design objectives, achievements previously not attainable by aeration are now possible.

Commonly mentioned objections to new superoxygenation concepts will make up the remainder of this paper. It will become evident, the author believes, that all the perceived 'myths' sometimes cited are invalidated both by science and practical field applications.

1.   *D.O. concentrations of >40 mg/L are highly supersaturated even using pure O_2.* Untrue.

Superoxygenation is capable of achieving much higher D.O. concentrations without effervescence occurring than aeration. At 20°C and sea level, 100% saturation using pure O_2 occurs at 44 mg/L D.O

without resulting in any effervescent loss of D.O. and will only lose D.O. in proportion to the gas surface exchange rate of the system. *Water may be supersaturated to >200% without spontaneous effervescence*.

2.   *Pure O_2 is readily and efficiently dissolved using many different gas transfer devices.*   Untrue

       As mentioned previously, the literature contains references to many gas transfer devices which use pure O_2 (see summary above). Nevertheless few of these devices have been able to achieve high O_2 absorption levels (90-95%) while maintaining highly elevated D.O. levels of >100 mg/L.
       For example, many municipalities inject pure O_2 into rising force mains to control odor. In using the force main as the oxygen transfer reactor, *gaseous pure O_2* is injected with the erroneous expectation that it will be efficiently dissolved as it moves through the force main. However much of the oxygen remains in the gaseous form and accumulates in the high points in the force main preceding reverse grades. The flow in the force main is thus reduced, due to the added head on the pumps when gas vent valves malfunction. Due to low velocities in most force mains, instead of dissolving efficiently, the gaseous O_2 bubbles rise to the crown of the pipe within about 50 ft of the point of injection, drastically reducing the gas/water interfacial area. Then the bubbles travel along the crown, causing undissolved O_2 to be wasted at the end. For this reason *gas phase separation in low velocity force mains is not conducive to efficient O_2 absorption*.

3.   *At high pressures pure O_2 will be quickly dissolved efficiently.*   Untrue.

       It is axiomatic that *bubble swarms require about 100 seconds of contact time with the water* to achieve efficient absorption. While high pressure in the O_2 transfer reactor does increase both the rate of O_2 transfer as well as the achievable D.O. concentration in the discharge, yet the O_2 under pressure alone still cannot be absorbed more efficiently because the mass of O_2 in the bubbles is proportionate to the pressure. Consequently no matter what the pressure may be in the oxygen transfer reactor, *pressure alone cannot cause more efficient absorption.*
       Since most bubbles rise at a velocity of nominally 1 ft/sec, it would require a 100 ft deep tank or other special technique to satisfy the required prolonged bubble swarm contact time. For example, injections of pure gaseous O_2 into a 2 mile long rising force main in San Diego with 440 ft of head at the beginning, resulted in only 50 to 70% O_2 absorption efficiency after 2 miles (~2 hours flow time). Studies conducted with gaseous O_2 injected into a 300 ft deep U-Tube also showed that even under such high pressure, low O_2 absorption efficiency resulted due to insufficient contact time with the bubbles.
       Failure to satisfy *the critical requirement for prolonged O_2 bubble contact* with the wastewater *adds significantly to operating costs* because of the wastage of undissolved O_2.

4.   *It is not practical to produce > 100 mg/L D.O. and retain it in solution*   Untrue.

       High levels of > 100 mg/L D.O. in the superoxygenation discharge are readily achieved with consistently high O_2 absorption efficiency by using an O_2 transfer reactor which retains the pure O_2 bubbles indefinitely in contact with a high gas surface/water volume (A/V) ratio. Utilizing existing pressure from a force main or excavated caisson is an energy efficient means of achieving superoxygenation.
       Absorption of pure O_2 is controlled by Henry's Law:
       $C_{sat} = (44$ mg/L-atmos$)(O_2$ partial pressure – atmos)   @ 20^oC and sea level.
                Oxygen transfer is then related to C_{sat}.
                $dc = k_L(A/V)(C_{sat}-C_{act})dt$.
However using pure O_2 transfer in a reactor under 68 ft of hydrostatic pressure results in a C_{sat} of 132 vs 9.2 mg/L for air at ambient pressure.
       A superoxygenation system located in a force main in Kentucky, which has a pressure of 200 ft at the beginning, raises the D.O. to >100 mg/L *to maintain oxic conditions in the discharge even after a 9 hour residence time in this long force main* .[2]

5.   *Effervescence at >100% saturation is spontaneous.*   Untrue.

Supersaturation is a necessary but insufficient condition to cause spontaneous effervescence. Several factors must be present for effervescence to occur.

A   Criteria for Predicting When Spontaneous Effervescence Will Occur

The combination of factors required for spontaneous effervescence are:
* elevated minimum threshold total dissolved gas supersaturation level
* elevated minimum threshold turbulence regime
* ambient pressure at discharge
* time/dilution characteristics
* nucleation sites in the water.

There is an *elevated minimum threshold D.O. supersaturation concentration* below which spontaneous effervescence will not occur. For instance the Columbia River flows for 80 miles at 130% supersaturation of total dissolved gas (TDG) without significant loss to the atmosphere because supersaturation is too low for effervescence to occur and the reaeration rate/turbulence regime of the river is very low. Farm ponds which are highly eutrophic also manifest D.O. concentrations of 20 to 30 mg/L during the peak sunlight hours without spontaneous effervescence.

An *elevated minimum threshold turbulence level* is also required to cause spontaneous effervescence for a given supersaturation concentration. Laboratory studies show that gentle mixing of water containing 100 mg/L D.O. does not result in spontaneous effervescence.

A 300 ml can of Coke contains about 1500 mL of dissolved CO_2 and is nominally at 500% saturation and 55 psig pressure. If the Coke can is vigorously shaken just before opening, there will be a very large gas interfacial area due to the high concentration of tiny bubbles in the Coke. Therefore opening/depressurizing the Coke can containing such a multitude of tiny bubbles with their large surface area results in violent loss of dissolved gas. However if the Coke can is left stationary with sufficient time for all the bubbles to rise to the surface and escape, so that the only gas interface is the surface, just a slight puff of 20-40 ml of gas is lost in the first few seconds after depressurization. The remainder of supersaturated gas takes hours to come out if left quiescently in the container.

B.   Differing Design Principles: High D.O. Retention vs Dissolved Air Flotation.

1.   *High D.O. retention achieved by low turbulence*

A principle of low turbulence is incorporated in effective superoxygenation.   Since water is non-compressible it can be depressurized in an excavated caisson or in a valved chamber *without energy release or associated turbulence/cavitation*. Valved chamber depressurization, such as gear and lobe type pumps or progressive cavity pumps on the discharge end of the pressurized oxygen transfer reactor, can achieve pressure reduction without the extreme turbulence caused by throttling valves.

The important principle of low turbulence and minimum threshold TDG supersaturation levels cannot be over-emphasized because under *marginal supersaturation* and/or *marginal turbulenc*e regimes*, spontaneous effervescence *either does not occur or ceases before it reduces TDG down to 100% saturation*.

Another principle which deserves attention is that superoxygenation does *not* utilize dissolved air flotation (DAF) features, thus controlling spontaneous effervescence. Thus by using an O_2 transfer reactor which maintains a high A/V ratio, with pure O_2 as the oxygen source, and utilizing either induced or existing pressure (force main or excavated caisson), *it is possible to add high D.O. concentrations to wastewater and retain them in solution*.

The throttling valve on a pressurized O_2 transfer reactor may also be placed at the bottom of a deep column of water, resulting in the depressurization taking place at elevated hydrostatic pressure rather than at ambient pressure. As will be described later, dilution water may also be pumped down to the bottom of the column of water so that the D.O. is also immediately diluted to further preclude spontaneous effervescence of the superoxygenated water as it rises to the surface ambient pressure.

2. Dissolved air flotation

There are multiple ways to depressurize water depending on whether it is desirable to precipitate the dissolved gas out of solution, as in DAF, or retain it in the dissolved state, as in superoxygenation. Pressure throttling valves, which generate intense turbulence/cavitation, are essential to achieve effective DAF. However to produce and maintain high D.O. in the water, equipment which specializes in producing the phenomenon of DAF *cannot* be adapted for superoxygenation use because the underlying design objectives of the two processes are categorically opposed.

All design variables for DAF are optimized to promote effervescence of the right size and number of micro-bubbles. As a result it must be understood that *TDG –retention measures* are not consistent with *DAF-optimizing goals*.

Spontaneous effervescence is enhanced by the combination of conditions which are incorporated in DAF. For DAF to be most effective, the saturator pressure must be over 40 psig. The pressure is commonly operated at 70 to 80 psig, capable of raising the dissolved gas concentration in the wastewater to 500% of ambient pressure saturation. Under optimal DAF operation, with the saturator operated at 75 psig (600% saturation) and 10% recycle, there are approximately 80,000,000 bubbles per liter with bubble diameters of 60 microns, with 200 microns between bubbles and 9000 ppm bubble volume concentration.[9]

The supersaturated liquid is passed through a nozzle (or throttling valve) which impinges on a plate to enhance the rapid formation of the bubbles. [3] The pressure drop across the nozzle is equal to the operating pressure of the saturator or about 75 psig, which generates extreme turbulence/cavitation. When depressurization is at ambient pressure and under such high pressure differential and intense turbulence/cavitation, the dissolved gas quickly and completely precipitates out of solution, resulting in a reduction of TDG down to almost 100% saturation.

C. Differing Regime Results: Gas Surface Exchange vs. Spontaneous Effervescence

Minimal supersaturation in combination with quiescent regimes result in inefficient effervescence of supersaturated TDG, or >100% residual saturation (see examples included below which will define the parameters for marginal supersaturation and marginal turbulence regimes).

The process of *gas surface exchange* is orders of magnitude slower when contrasted to spontaneous bubble effervescence. Gas surface exchange is hours to days slower than spontaneous effervescence (within seconds) and is in proportion to the D.O. excess and the reaeration rate.

For example in a 1 m by 1 m by 3 m deep *open topped tank* at the University of British Columbia, the D.O. was raised to 55 mg/L using pure O_2. Even under continuous stirring, the D.O. remaining after 16 hours was still measured at above 50 mg/L.[4]

Fig. 1 shows the results of a laboratory study in which water was raised to saturation level in a gas transfer reactor using pure O_2 at a given pressure (indicated on the x axis) and discharged through a pressure reducing valve into water maintained at zero D.O. using cobalt catalyzed excess sulfite. Subsequently the D.O., which effervesced upon depressurization was measured and the D.O. retained in solution calculated. Only about 10% of the D.O. in water superoxygenated to 270 mg/L at 90 psig was lost from solution upon depressurization/dilution.

Fig. 2 shows the results of a laboratory study in which a gently stirred vessel containing water was pressurized to 120 psig (10 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 unpressurized reactor vs time. Immediately after depressurization the D.O. dropped from about 400 mg/L to 235 mg/L 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.

CONDITIONS
200 mg/l Bentonite
Saturated at 9 atm

FIG. 2   D.O. Loss With Time

Fig. 1 D.O. Consumed and Effervesced
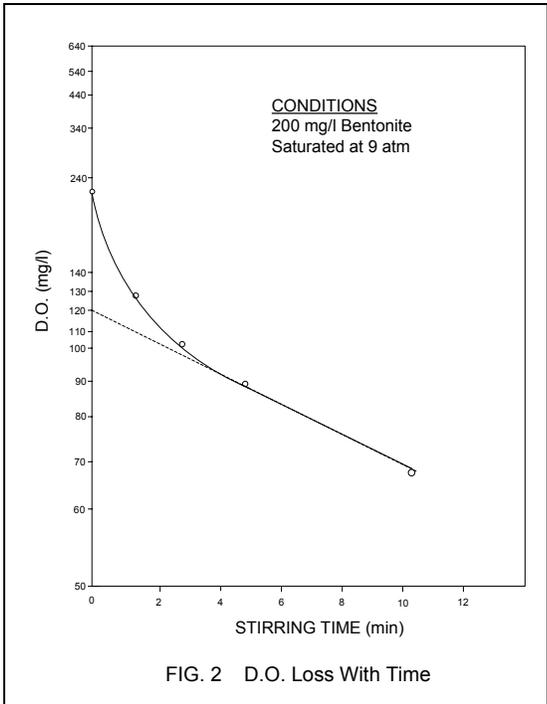
D. Prevention of Effervescence

A finite amount of time is required for effervescent bubble formation and growth to occur after depressurization. Therefore if depressurization of the highly oxygenated flow is quickly diluted with water containing low D.O. (2 – 10 mg/L), effervescence is precluded.

In laboratory experiments in which water was placed in a stirred pressure vessel with a head space of pressurized pure O_2, the D.O. had to be raised to over 100 mg/L before spontaneous effervescence would occur upon depressurization. The initial water was already saturated with the N_2 in air at 0.79 atmospheres partial pressure before being placed in the pressure vessel for the experiments. Since 100 mg/L of D.O. corresponds to 2.3 atmospheres partial pressure, the TDG pressure was (2.3 + 0.79) 309% saturation before spontaneous effervescence was observed.

1.   Soft Depressurization

Excessive turbulence can 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 which negates the energy dissipation which creates intense turbulence/cavitation.

In a series of experiments designed to characterize effervescence and residual supersaturation, a stirred laboratory reactor was pressurized with pure O_2 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).

AFTER EFFERVESCENCE STOPPED
WITH RESIDUAL D.O. = 150 mg/l

FIG 3   D.O. AFTER EFFERVESCENCE AND
D.O LOST TO EFFERVESCENCE
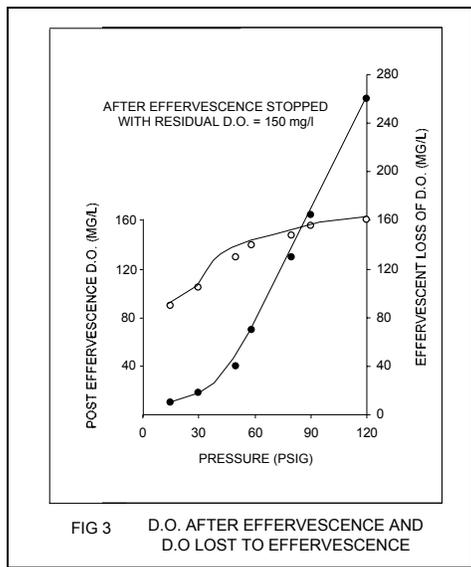
2.   Speece Cone Superoxygenator

One system which incorporates the desirable conditions for efficient O_2 absorption while producing very high D.O. concentrations in the effluent is the Downflow Bubble Contact Oxygenator, dubbed the Speece Cone (see Fig. 4 photo), by Prof. Alex Horne of U.C. Berkeley.

Key advantages of this type of configuration are:
- a.   the *extended bubble retention time* which achieves *high O_2 absorption efficiency*
- b.   the ease with which it can be *pressurized to produce D.O. >100 mg/L*
- c.   the ability to handle *even unscreened raw wastewater*

As would be expected it performs poorly with air as the O_2 source.

6.   *Superoxygenation cannot reduce H_2S, mercaptans, disulfides, etc. to non-detectable concentrations in wastewater.*   Untrue.

It is not economical to use nitrates or iron salts to reduce the H_2S concentrations below 0.5 mg/L. At pH 7.0 about 50% of the H_2S is in the un-ionized volatile form. With the equilibrium of H_2S being nominally 300 ppm in the gas phase per 1 mg/L H_2S in the liquid phase, 75 ppm H_2S in the gas phase would be in equilibrium with 0.5 mg/L total H_2S in the water. Thus even at this low level of dissolved H_2S in the wastewater, rather high H_2S concentrations can be formed in the pipe crown head space and manholes above the wastewater. These concentrations may be found at force main discharges before significant polysulfide formation occurs. Since 2 to 55 ppm is the concentration of H_2S in the gas phase reported to enable crown corrosion to proceed at 50% of the maximum rate, a significant improvement in odor perception may be achieved but with little reduction in the rate of concrete corrosion with 0.5 mg/L H_2S present in the wastewater.

Fig. 4 Speece Cone Installation – Orange County, CA

D.O. is a much preferred electron acceptor compared to nitrate for microbial metabolism of H_2S. With D.O. present, the H_2S in the head space is readily reduced to non-detectable (< 1 ppm) as confirmed in multiple field installations using superoxygenation of force mains (see Fig. 5). This advantage of superoxygenation can also be applied for primary clarifier odor control.

Biofilter technology, having gas contact residence times of 5 to 50 seconds, *has proven to be a very effective odor control system at municipal wastewater treatment plants*. Malodorous volatile gases (reduced sulfur compounds, mercaptans, indoles, skatoles, etc) produced under anaerobic conditions in domestic wastewater, *are*
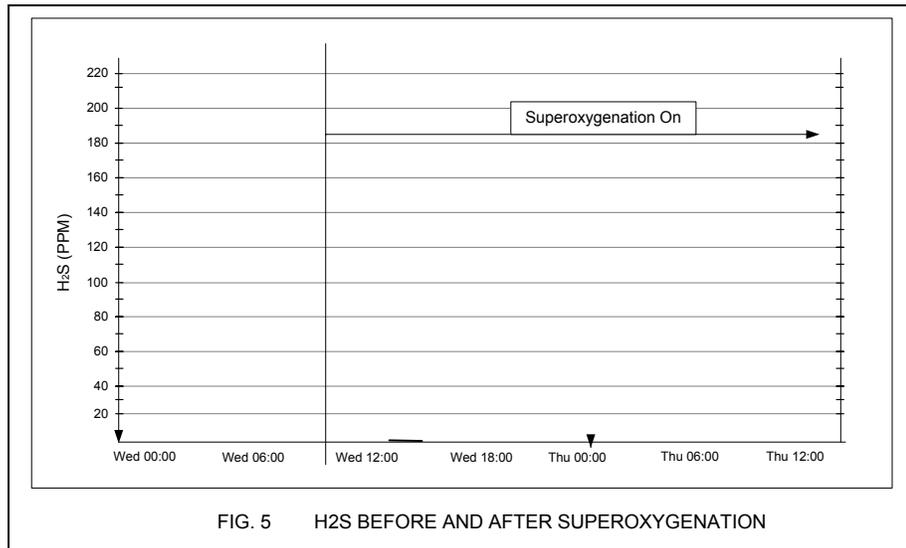

FIG. 5   H2S BEFORE AND AFTER SUPEROXYGENATION

readily biodegraded under oxic conditions by resident bacteria in the biofilter at their own individual kinetic rates. The malodorous volatile gases biodegraded in a biofilter would also be reduced by the resident bacterial population in raw wastewater *if given sufficient reaction time under oxic conditions,* as is now possible by using superoxygenation.

   In field studies on a 25 MGD rising main in San Diego, all H_2S, mercaptans and disulfides were microbially reduced to non-detectable concentrations when sufficient D.O. was provided to ensure that oxic conditions prevailed throughout the entire force main to its discharge.

7.   *Superoxygenation of raw wastewater will strip out H_2S.*   Untrue

   Theoretically pure O_2 absorption into D.O. deficient wastewater simultaneously would result in stripping out non-D.O. volatile compounds such as dissolved N_2, H_2S, mercaptans, etc. However the efficient O_2 absorber used in superoxygenation is an inefficient H_2S stripper.

   Stripping is a measure of the off-gas ratio from the O_2 transfer reactor. Therefore while aerators with low O_2 absorption efficiencies 5 – 15%, are very efficient strippers of H_2S from the wastewater, on the other hand efficient O_2 absorption results in nil stripping of H_2S and other malodorous volatile compounds from the wastewater.

   An aerator with 5% O_2 absorption has 99 ft^3 of stripping off-gas for each 1 ft^3 of O_2 absorbed, while pure O_2 absorbed at 90% efficiency has 0.1 ft^3 stripping off-gas per 1 ft^3 of O_2 absorbed. There is a 1000 fold decrease in stripping off-gas from an efficient pure O_2 absorber vs conventional diffused air or surface aerators.

8.   *Superoxygenation of primary influents will result in spontaneous effervescence and*
    suspended solids will float to the surface   Untrue

   The possibility of achieving >20 mg/L D.O. successfully dissolved in the influent to a primary clarifier provides a significant advance in odor control technology. H_2S in the influent will be fully oxidized during passage through the primary clarifier and continuous oxic conditions maintained throughout the primary clarifier, will preclude additional H_2S generation. *Lower levels of supersaturation, coupled with the quiescent conditions in the primary clarifier will preclude spontaneous effervescence and thus also preclude flotation of suspended solids.*

   The D.O. uptake of warm ripe wastewater is nominally 10 mg/L-hr and the detention time in the primary clarifier is about 2 hours. At 30^oC the D.O. saturation with pure oxygen is 36 mg/L. Therefore 20 mg/L of D.O. is 0.56 atmospheres partial pressure.   At 11 ft below the water surface, this relative concentration would correspond to only 100% TDG saturation, due to hydrostatic pressure. In both cases the result would be far below the spontaneous effervescence threshold of >200% required to effervesce and float suspended solids.

9.   *It is not possible to add 100 mg/L D.O. to a force main and retain it in the dissolved*
    form in the bulk flow for long hydraulic retention times.   Untrue

   If a force main has 100 ft. of head at the beginning it is possible with superoxygenation technology to raise the D.O. to 100 mg/L. For this hydrostatic head, 100 mg/L D.O. is at less than 100% saturation, preventing effervescence from occurring. Additionally since the force main is full there is no gas/water interface for O_2 transfer to occur.   As the force main rises and the hydrostatic head decreases, D.O. is consumed. 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.

10.   *If >10 mg/L D.O. is added to a gravity sewer, the D.O will be lost quickly and*
    therefore is of no value to the microbiota for odor prevention.   Untrue

A detention time of 15 to 30 minutes must be provided after highly oxic conditions (>5 mg/L D.O.) are established in warm ripe wastewaters to allow the chemical and microbial oxidation of H_2S to reach non-detectable levels. *Therefore if injected at a point over 30 minutes of travel time before a wastewater reaches the head works, superoxygenation maintains oxic conditions to enable the microbiota to prevent odor at the head works.*

In the absence of extreme turbulence/cavitation, as wastewater flows in a gravity sewer, 20 mg/L D.O. (135% TDG) would be well below the threshold effervescence level. The only gas transfer would be at the gas/water interface and would be stripped in proportion to the reaeration rate.

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). Thus odor prevention is possible at the head works by superoxygenation of raw wastewater 15 to 30 minutes upstream from the wastewater treatment plant head works.

11. *If D.O. in a gravity sewer is >10 mg/L, it will increase the head space O_2 to > 23.5% and therefore pose a potential explosion hazard if hydrocarbons are present.*   Untrue

The Lower Explosive Limit (LEL) for O_2 is 23.5%. Generally the O_2 composition in sewer head gas is <20.9%, due to consumption of O_2 by the wastewater microbiota. However there will be no enrichment of O_2 in the head gas even if D.O levels in the wastewater are 8-10 mg/L. If the D.O. is raised to >10 mg/L there will be some D.O. stripped from the wastewater to the head gas in proportion to the D.O. excess above 8-10 mg/L, combined with the reaeration rate (k_2) in the sewer.

A.   Factors controlling increase in O_2 composition of the head space

Several factors contribute to a potentially explosive environment in the head space:
*   relative flow rate of air above the water surface to that of the wastewater flow rate (nominally about 0.3)
*   D.O. supersaturation level
*   reaeration rate (k_2)
*   % fullness of wastewater flow in the pipe
*   temperature

These factors combine to determine the O_2 concentration in the headspace above the wastewater.

B   Validated equations to predict the reaeration rate

Sewer systems may be modeled for reaeration and stripping as accurately as rivers. Tracer studies may also be used to determine the reaeration rate in a given section of sewer just as with rivers.

Reaeration (gas exchange) in a gravity sewer is characterized by the following:[5]

$$K_2 (20°C) = 0.86 (1+0.20 F^2)(s\ u)^{3/8}\ d_m^{-1}$$

F = Froude number $F = u/(gd_m)^{0.5}$
u = mean velocity m/sec
s = slope m/m
d_m = hydraulic mean depth, water cross section / width of water surface, m

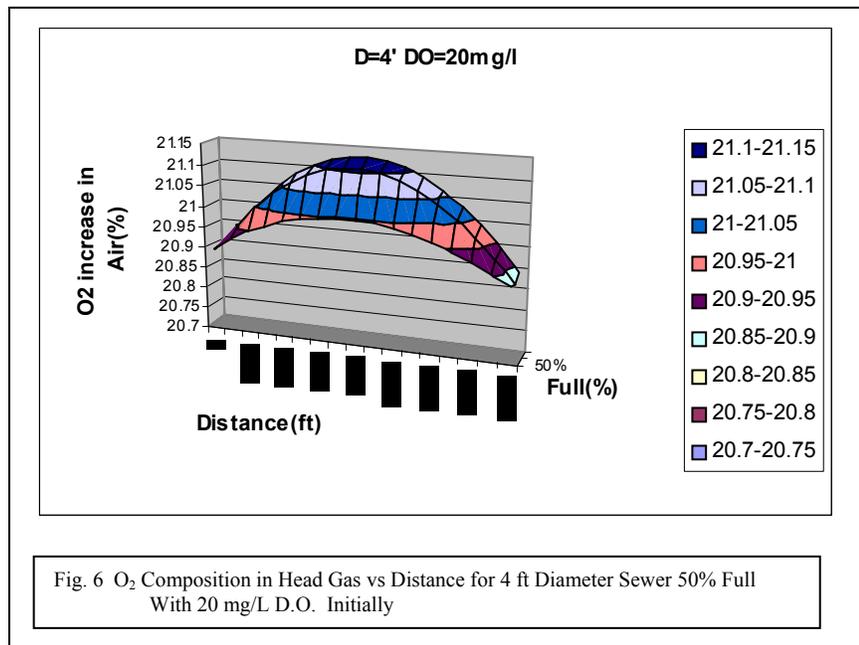Air velocities above the water interface can be determined relative to the wastewater velocity. There are also validated equations to predict air velocity, which is mainly driven by the shear from the wastewater velocity.

The O_2 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 % O_2 (an increase of 0.1% O_2 composition) after flowing 2 miles if the ratio of air velocity to wastewater velocity is 1.0 (see computer model in Fig. 6). Also the O_2 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. Thus under typical conditions superoxygenation of wastewater in gravity sewers to 20 mg/L D.O. can be practiced without exceeding the LEL in the gas phase of 23.5% for O_2.

12. *It is not possible to add the entire D.O. demand to a primary effluent (100 to 300 mg/L) and keep it in solution*.   Untrue

Superoxygenation can also be used for oxygenation of activated sludge in an open-topped tank by either pulling off a side stream of mixed liquor, superoxygenating it and returning it to the activated sludge reactor or superoxygenating a side stream of secondary effluent, and then adding it back into the activated sludge reactor. This latter scheme would avoid potential floc damage, but would increase the hydraulic loading on the secondary clarifier**.** Superoxygenation of the primary effluent instead of the mixed liquor avoids adverse shearing of the floc structure which may result in increased suspended solids in the secondary clarifier discharge.

Because of the major disadvantage related to the 79% N_2 composition of air, it is not uncommon for oxygen transfer in activated sludge to limit the overall process, especially with the prospect of utilizing immobilized biomass carriers or membrane reactors to greatly increase the biomass which can be maintained in the biological reactor.   But although with aeration it is unthinkable that 300 mg/L D.O. could be dissolved into wastewater and kept in solution, *superoxygenation technology enables 100 to 300 mg/L D.O. to be readily dissolved into wastewater* because there is no N_2 present in pure oxygen and adequate pressure is provided to achieve these high levels of superoxygenation. Depressurization by a throttling valve at the bottom of a shaft and dilution with low D.O. mixed liquor from the secondary reactor can enable efficient retention of these high D.O. concentrations in solution**.**

Fig. 6 O_2 Composition in Head Gas vs Distance for 4 ft Diameter Sewer 50% Full With 20 mg/L D.O. Initially

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 of >300 mg/L D.O.   By adding all of the D.O. to the primary effluent, the greatly reduced alpha factor associated with fine bubble diffusers or with high Mixed Liquor Suspended Solids (8000 to 18,000 mg/L) in membrane reactors is rendered irrelevant. [6]   This would also result in much reduced VOC emissions from the activated sludge basin.

Size reduction of the oxygen transfer reactor can be accomplished without incurring an energy penalty. For instance doubling the pressure (and consequently the D.O. in the discharge) and halving the flow, and thus volume of the reactor, results in the same required pump HP for the same net tonnage of D.O. per day .
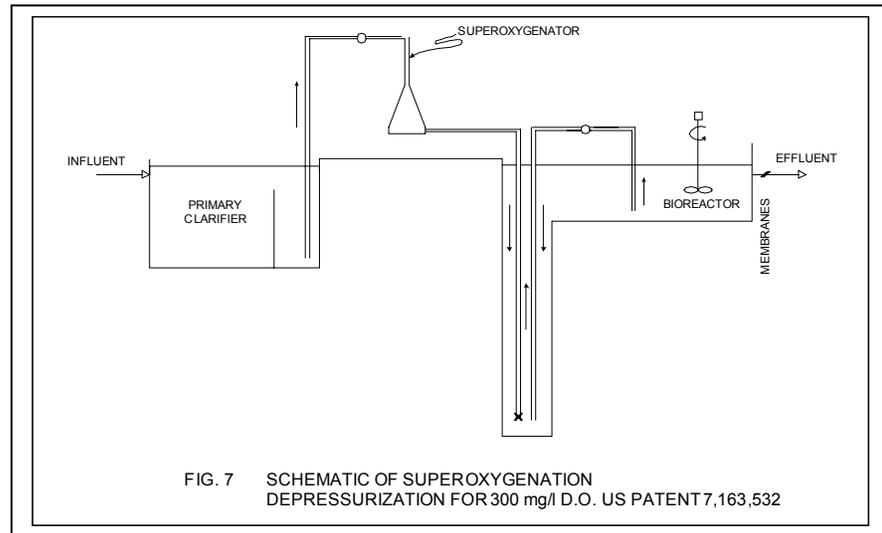
The practical limit of a smaller oxygen transfer reactor is determined by the maximum D.O. concentration which can be retained in solution upon depressurization at the bottom of a depressurizing/diluting shaft or by direct dilution with diffuser nozzles within the activated sludge reactor. Laboratory studies mentioned previously have demonstrated that D.O. concentrations as high as 270 mg/L can be depressurized into water at ambient pressure with a D.O. level of less than 2 mg/L, resulting in > 90% of the D.O. being retained in solution after depressurization.

No additional D.O. is required, therefore in the activated sludge reactor where 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. will be maintained at a low D.O. of < 10 mg/L. Therefore even though the feed wastewater may contain as much as 300 mg/L D.O., this continuous microbial D.O. uptake results in a low steady state D.O. in the open-topped activated sludge reactor. Low bulk D.O. also greatly facilitates depressurization/dilution of the superoxygenated feed without effervescent loss of the D.O.(see Fig. 7).

13.   *It is not possible to keep sludges in holding tanks oxic for prevention of odor/corrosion production.* Untrue.

A major odor/corrosion problem at municipal WWTP is associated with the sludges stored in holding tanks prior to dewatering. The prolonged holding times occasion odor/corrosion issues within the tanks above the low water line and under the covers. On-site experiments need to be conducted to determine the D.O. uptake rates of primary and thickened Waste Activated Sludge. A second piece of required data is to determine the time of suppression – or lag time – after the sludge is made oxic to various D.O. concentrations, before sulfide generation commences again and at what rate.

FIG. 7   SCHEMATIC OF SUPEROXYGENATION DEPRESSURIZATION FOR 300 mg/l D.O. US PATENT 7,163,532

It is not unreasonable to consider superoxygenating thickened sludges. Plant effluent reuse water can be raised to about 300 mg/L D.O.. Or if the piping arrangement is convenient, Waste Activated Sludge can be the superoxygenation side stream rather than plant effluent reuse water.   This superoxygenated, high pressure discharge would be injected into a line through which 10 parts of sludge would be recirculated for each 1 part of superoxygenated plant reuse water flow – or WAS. Such a protocol would immediately dilute the 300 mg/L within < 1 second down to 30 mg/L D.O. in the sludge flow line, precluding the effervescence typical of dissolved air flotation systems.   Thus rapid dilution within < 1 second can result in retention of 90-95% of the 300 mg/L D.O. in the dissolved state within the sludge mass. Dilution with a 10% superoxygenated side stream would result in the sludge concentration decreasing by 10% e.g. 5.5 down to 5.0%.

Since this oxygen transfer occurs without H_2S stripping, there are no offensive off-gases, as is the case with aerating the sludge tanks with coarse bubbles.

14.   *Total dissolved gas has the same effect on fish whether it results from supersaturation by air or pure O_2.* Untrue

Depending on whether N_2 or O_2 is causing the supersaturation of TDG, there is a significantly different response by the fish. Fish are subject to gas bubble disease similar to the 'bends' in humans if raised in water that contains excessive dissolved gas concentrations. TDG in surface waters will be comprised mainly of dissolved N_2 and dissolved O_2, with minor contributions of argon and CO_2. The adverse impact of dissolved N_2 in the blood of fish will be considerably more than that caused by D.O., since D.O. is consumed by metabolic processes. Fish hatcheries often use pure O_2 because it raises the D.O. substantially while reducing the dissolved N_2.

Studies to identify safe upper limits for D.O. levels in fish hatcheries using pure O_2 recommend that the D.O. not exceed 300 mm Hg or 21 mg/L at 12^oC[7].

15.   *It is not possible to add D.O. = BOD_{ult} in a wastewater treatment plant effluent and keep it in solution in order to avoid consuming any net D.O. resources from the receiving water.* Untrue.

Superoxygenation makes possible the very rational concept of raising the D.O. in a wastewater treatment plant effluent equal to its BOD_{ult}, thus rendering it a "D.O. neutral" effluent which does not consume any net D.O. resources from the receiving water for stabilization of the residual organic matter.

D.O. addition equal to the BOD_{ult} for a wastewater treatment plant having a discharge that comprises a fraction of the flow in the receiving stream, opens up 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 little dilution, 20 mg/L would be compatible with the fishery and 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 about 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 rivers in flat terrain which have low reaeration rates and do not meet D.O. standards even upstream of the wastewater treatment plant discharge. Superoxygenation offers a paradigm shift in meeting river regulatory policy and possibly the need for tertiary treatment in some cases.

Summary

To ensure the arrest of odor production and corrosion damage in wastewater treatment, *oxic conditions must be sustained continuously in the water throughout the collection and treatment systems.* However until recently oxygenation transfer technology was not sufficiently developed to guarantee the high O_2 absorption efficiency along with high D.O. concentrations necessary to accomplish this goal. Inappropriate gas transfer technology and the erroneous assumption that spontaneous effervescent loss would occur at D.O. concentrations above air saturation (10 mg/L), proved to be unfortunate obstacles to successful utilization of the inherent ability of oxic conditions to prevent sulfide production.

Accurate differentiation between the design objectives of aeration vs superoxygenation technologies is imperative to clarify the reasons for the superoxygenation potential applications now available to remediate common aeration failures. Serious shortcomings of conventional aeration techniques should not prejudice water quality professionals against objective research into this alternative approach to wastewater quality management.

Superoxygenation techniques provide exceptional odor control and infrastructure protection, both economically and practically. After the initial purchase of equipment, low operation and maintenance costs and recovery of capital expenditure in three to five years can be achieved, while at the same time protecting the environment and eliminating public outcry against malodorous emissions.

Superoxygenation technology employs standard gas transfer principles using pure O_2 and pressure in a unique gas transfer reactor. Exceptionally high concentrations of D.O. can be dissolved into wastewaters, and by incorporating novel depressurization and/or dilution techniques, the elevated D.O levels kept in solution. Volatile compounds, which are metabolized by aerobic bacteria, are not removed due to the low stripping potential implicit in efficient O_2 absorption. This green technology also accommodates rags and strings in raw unscreened wastewaters. Salinity problems and increased sludge production, which accompany iron salts treatment, are avoided as well as the need for capturing/scrubbing of foul gases. The technology can also enable the discharge of a D.O./BOD neutral WWTP effluent, thus avoiding depletion of D.O. resources in stabilizing residual organics in the receiving water and eliminating the necessity for tertiary treatment in some cases.

Head works, primary clarifiers, and gravity and force mains are all promising candidates for applying the new type of treatment.. Direct supplementation of D.O. to *rivers, lakes and bays* is also now readily feasible using superoxygenation techniques. Through mobile units which do not impede harbor traffic, D.O. deficiencies even in *ship channels* can now be addressed such as an installation in Savannah harbor.

Field tests and ongoing installations cited in the paper provide data for consideration of diverse future applications. By implementing superoxygenation techniques, many significant water quality problems which were not amenable to successful treatment by conventional aeration practices, may now be possible.

Acknowledgements

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