Innovative Deoxygenation of Ozonated Water

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Innovative Deoxygenation of Ozonated Water

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ABSTRACT

Dissolved oxygen levels exceeding normal saturation levels at ambient atmospheric conditions are typical in ozone treatment applications employing oxygen fed ozone generators. These oxygen supersaturated waters can cause operational problems for downstream treatment processes, corrosion in distribution and process piping and aesthetic problems in treated water.

The Vac-GDT™ process can efficiently reduce dissolved oxygen levels from 25 mg/L to less than 8 mg/L in a small packaged system. Ambient air is introduced through a Mazzei® injector for dissolved gas partitioning and rapid equilibrium attainment under vacuum conditions. Partitioned gases are removed from the two phase flow by a GDT™ centrifugal separator also operated under a vacuum.

Applications include deoxygenation of ozone treated water for use in ozone generator cooling water, potable water, industrial, swimming pools, etc.

Introduction

The development of ozone generators capable of high concentration (6-15% wt.) ozone production has helped position ozone as an affordable technology for oxidation, disinfection and microflocculation in water, wastewater and chemical process applications. The production efficiencies of these high tech ozone generators, operating on concentrated oxygen feed gas have dramatically lowered the cost to use ozone**.** **Figure 1** shows the impact of ozone gas concentration on the unit cost ($ per pound) of ozone produced.[1]

While these are data for the specific ozone generator tested, it is representative of the direction the industry is moving for development of high performance systems. In fact, the envelope for generator performance has been pushed even further since these performance data were developed. A reasonable assumption would be that the curve would shift further to the right as ozone generator technology continues to improve.

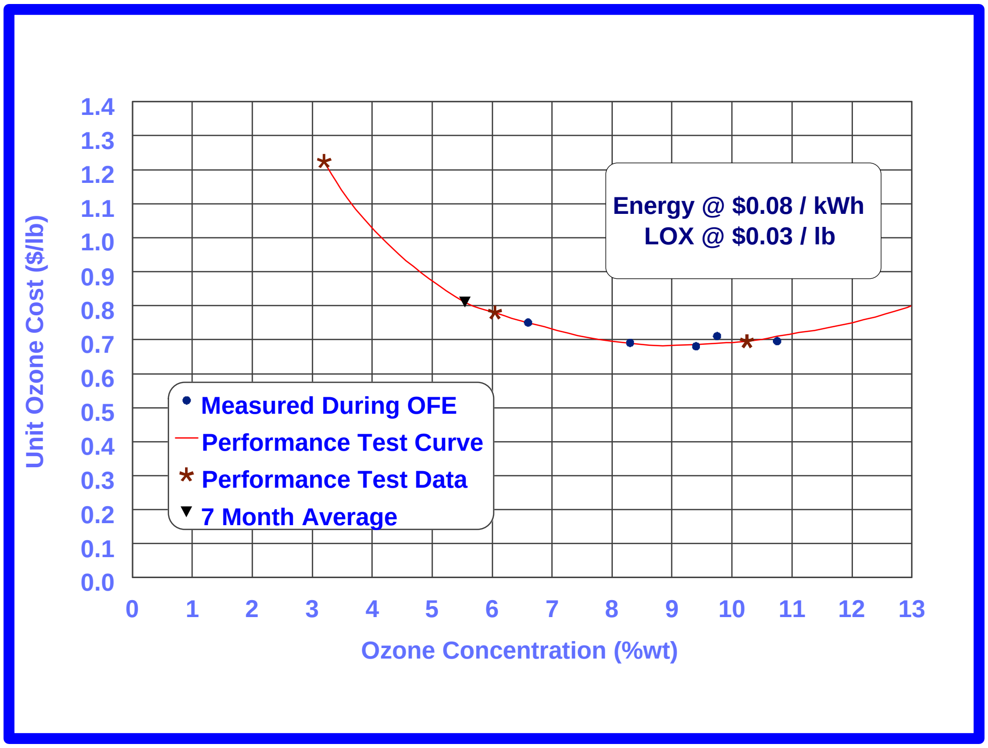

Figure 1 Unit Ozone Cost per Ozone gas Phase Concentration[1]

It has also been noted by many utilities and commercial and industrial operations that the benefits associated with oxygen fed ozone generation also bring the negatives associated with high dissolved oxygen (DO) levels. These included unwanted down stream process effects and increased corrosion potential to process equipment and piping, potential hydraulic water hammer and aesthetic effects such as milky water at customer water taps or in swimming pools, aquatic parks and aquascapes [2].

Microelectronic plants operating on ozone treated municipal water have experienced pump cavitation, inaccurate instrument readings and pressure filter binding or bypass, due to entrained gas formation following water temperature elevation to improve reverse osmosis system flux. Swimming pools receive bather complaints for cloudy waters in the pool and homeowners call utilities about health concerns when the tap water effervesces in the glass or spits when the tap is opened.

Ozonation plant designers may even decide to add recirculating chillers for generator cooling water rather than used otherwise acceptable treated water for fear that the high DO levels would lead to corrosion of the generator cooling jacket and tubes.

Gas Liquid Mass Transfer

The problems associated with high dissolved oxygen levels and the benefits of high ozone mass transfer efficiency are both direct functions of the gas phase concentration of oxygen and ozone. When a high concentration gas is applied to the stream to be treated the potential for supersaturation exists. The dissolved gas level in the finished water will be a function of the gas phase concentration applied and the specific mass transfer capability of the contacting system.

The driving force for mass transfer is the difference between the gas solubility and the already dissolved gas concentration. Henry's law can describe the solubility of a gas in water. Henry's law states that the solubility of a gas is almost directly proportional to its partial pressure in the gas phase [3,4.] Strictly speaking, this law applies only to gases that do not undergo chemical reaction with water during the mass transfer. Dalton's law states that the partial pressure of a gas is equivalent to its volumetric concentration in the gas phase multiplied by the absolute pressure of the system [3,4]. One form of Henry's law that expresses dissolved gas concentration in units of mg/l is as follows [4]:

$$\mathbf{C_S = B \times M \times P}$$

C_S = Dissolved Gas Concentration, mg/L **M** = Gas Phase Density, mg/L
B = Bunsen Absorption Coefficient **P** = Partial Pressure In Atmospheres

A number of parameters influence the solubility of certain gases in water. They include system pressure, temperature, pH, solution ionic strength, the decomposition of the gas if any and concentration in gas-liquid phases. Much research has been done to determine the Bunsen absorption coefficient for gases under various conditions [4].

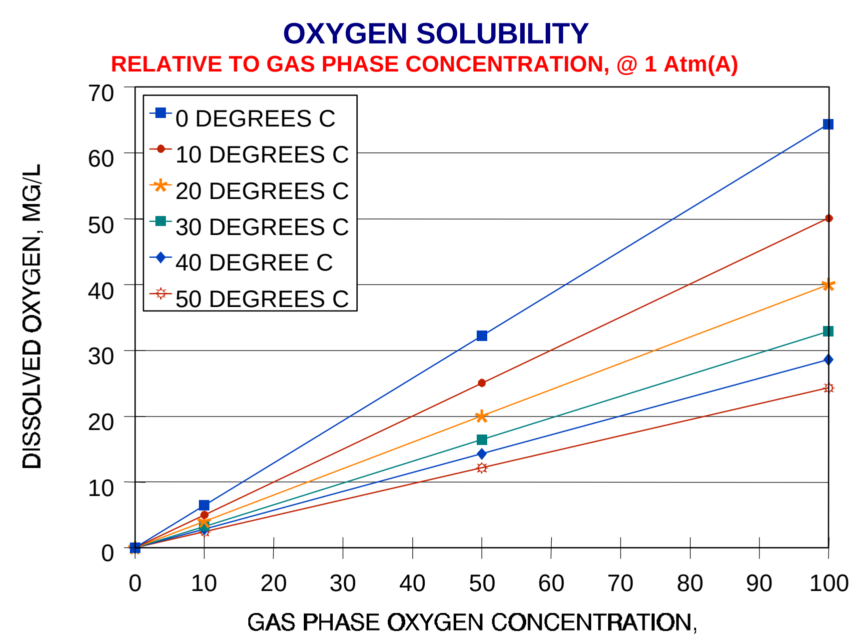

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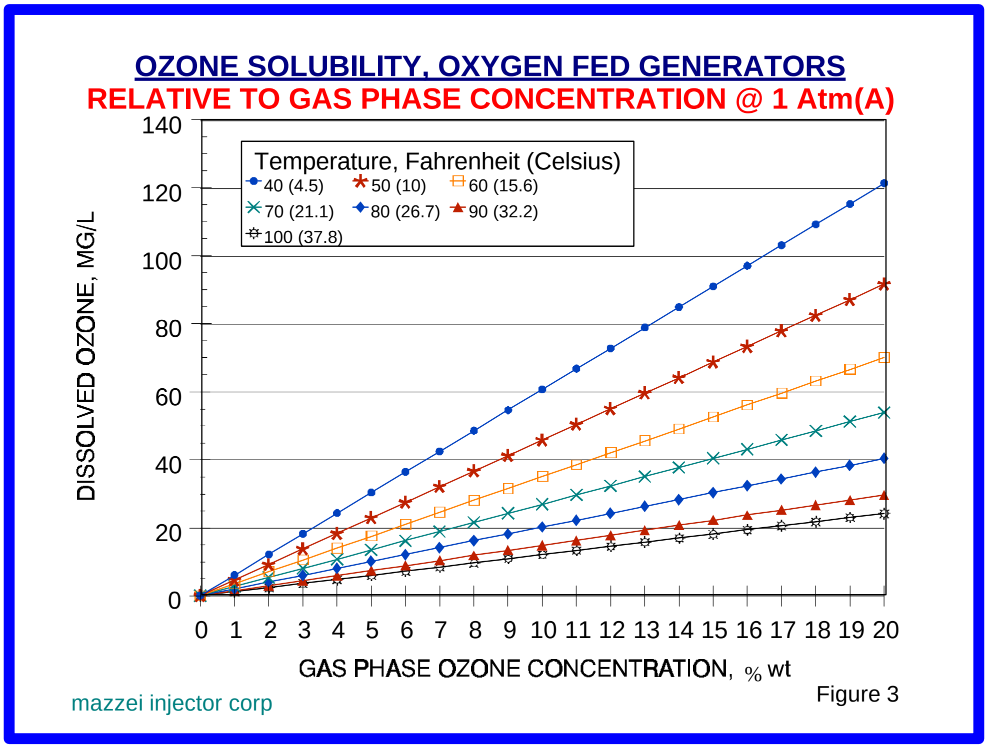
Figure 2



Figures 2 and 3 illustrate the effect of partial pressure (concentration) on calculated oxygen and ozone solubility [5]. It can be seen that increasing the partial pressure increases the calculated oxygen and ozone solubility dramatically. Even with the use of the advanced ozone generators, gas phase oxygen concentration is still above 80% weight. Therefore, the dissolved oxygen levels exiting a full flow ozone contactor will range between 20 and 30 mg/L.

Once high dissolved oxygen levels are established in the ozone contactor, the residual DO will stay in solution unless it is reduced by demand in solution, oxidation of materials it contacts or if partitioned from solution.

Basic Principals of Dissolved Oxygen Stripping

The application of Henry's law to volatile contaminant stripping can be stated as follows:

When a liquid containing a volatile contaminant is brought into intimate contact with a gas phase, the contaminant will partition between the liquid and gas phases.

This principle can be expressed as a partition coefficient (K), which can be determined from, published Henry's law constant (H) by the following formula:

$$\mathbf{H/Pa = K}$$

where **H =** Henry’s constant (ATM) and **Pa** = Absolute Pressure of the System (ATM).

High Henry's constants facilitate stripping while low constants inhibit stripping. It can be seen that the stripping efficiency of a system is inversely proportional to the absolute pressure of the system. Compounds with low Henry’s constants may require high gas to liquid ratios, agitation, increased surface area and or recirculating configurations through a particular treatment process for adequate removal efficiency.

Temperature also affects the effective Henry's law constant. High temperature promotes stripping while low temperature retards stripping. Thermodynamic equations are available for estimating the change in a Henry's constant value from the published temperature to a system temperature.

Complex mathematical formulas and computer programs utilizing the basic Henry’s Law formula and published constants have been developed and employed in system design and process evaluation. In depth discussion of these formulas is beyond the scope of this paper.

VacGDT™ Process

Numerous volatile stripping system configurations have been designed and employed in water and wastewater treatment over the years. Designs include simply bubbling air through a water column, forced draft counter current flow packed towers, multiple tray forced air strippers and thermal spray or tray deaerators [6]. Most commercial stripping systems operate at atmospheric to slightly positive pressure conditions as in the case of a gas bubbled through a water column. Each process has its strengths and weakness related to capital and operating cost, size (floor foot print) and height requirements, fouling characteristics and operator training and support needed.

The VacGDT™ process is a unique modification of the GDT™ process, which is typically used as a high efficiency ozone mass transfer system operating under positive pressure [7]. As stated previously, the absolute pressure of the treatment system affects the rate of volatile partitioning. The VacGDT process operates under negative pressure conditions to increase partitioning of volatile compounds in a small geometry.

In the VacGDT process detailed in **Figure 4**, shows the liquid flow to be treated entering a patented Mazzei® injector under pressure. This pressure can be as low as 5-15 psig, equivalent to the static head of most atmospheric ozone contacting systems.

The available pressure sets the motive flow rate through the process and establishes suction capacity for the stripping gas to be used. The injectors aspirate the stripping gas under vacuum conditions, where the stripping gas expands into the liquid, resulting in violent small bubble gas - liquid mixing. The dynamic gas - liquid mixing that occurs at the injector allows volatile partitioning and rapid equilibrium attainment in the two-phase flow leaving the injector. The flow then travels to the GDT degas separator (DS) for rapid volatilized entrained gas removal.

As the entrained gas/water mixture enters the degassing separator, it is accelerated to a velocity that exerts 4-10 times gravity in a lateral force creating a water film at the separator wall and a gas vortex at the central, gas extraction core. This journey of a few seconds has the ability to extract 98% of the entrained gases within the water stream.

A degas relief valve controls the flow of separated gas under the vacuum created by a vacuum pump designed for the specific gas to liquid ratio needed to attain the desired volatile removal rate. A pump at the outlet of degas separator boosts the pressure from the vacuum condition within the process to the desired pressure for further treatment or distribution.

Figure 4 below, is representative of the actual system used to develop the data presented in **Figure 5.**

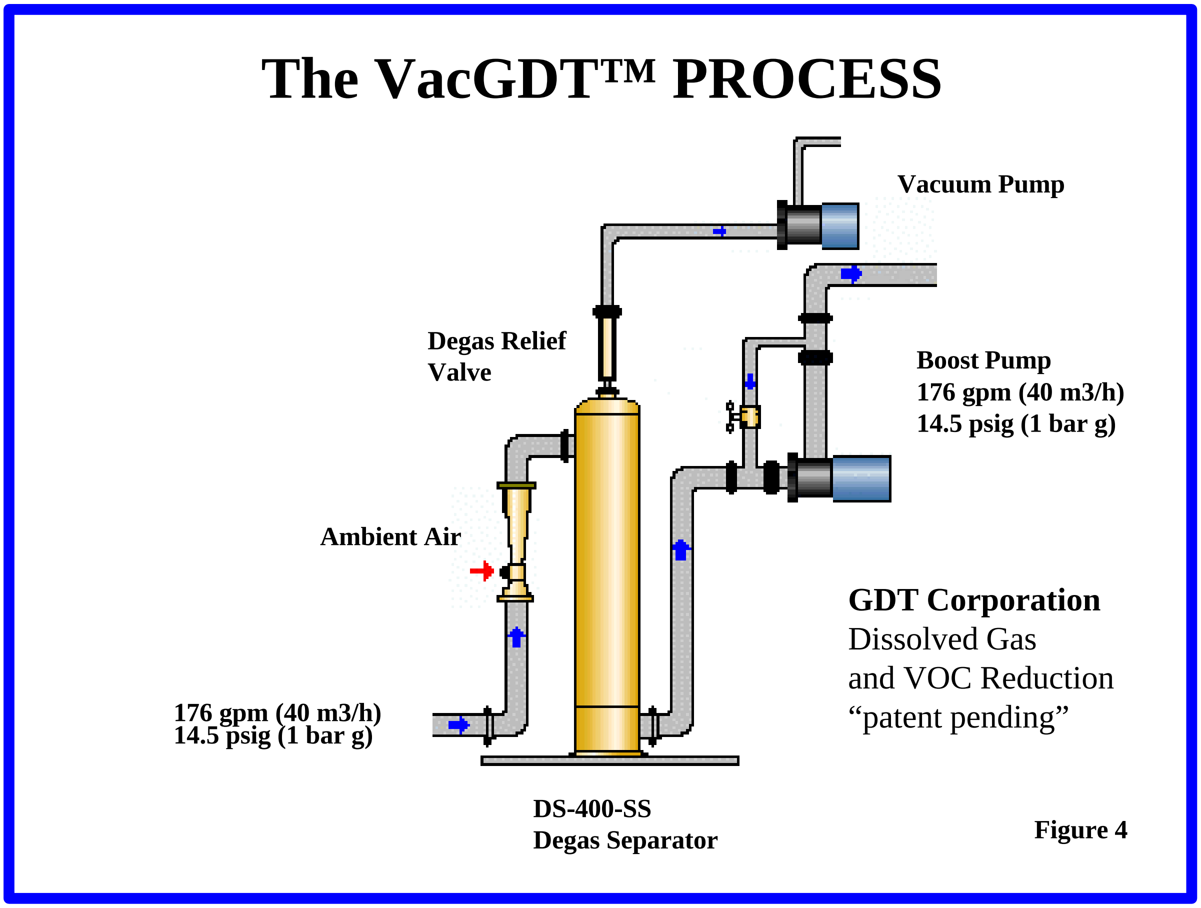


Figure 4

Dissolved Oxygen Reduction Performance

In the case of the VacGDT™ process for oxygen reduction (43,000 ATM at 20°C Henry's constant [7]), ambient air (approx. 21% oxygen and 79% nitrogen), aspirated under vacuum conditions will produce dissolved oxygen levels at or below normal air saturation.

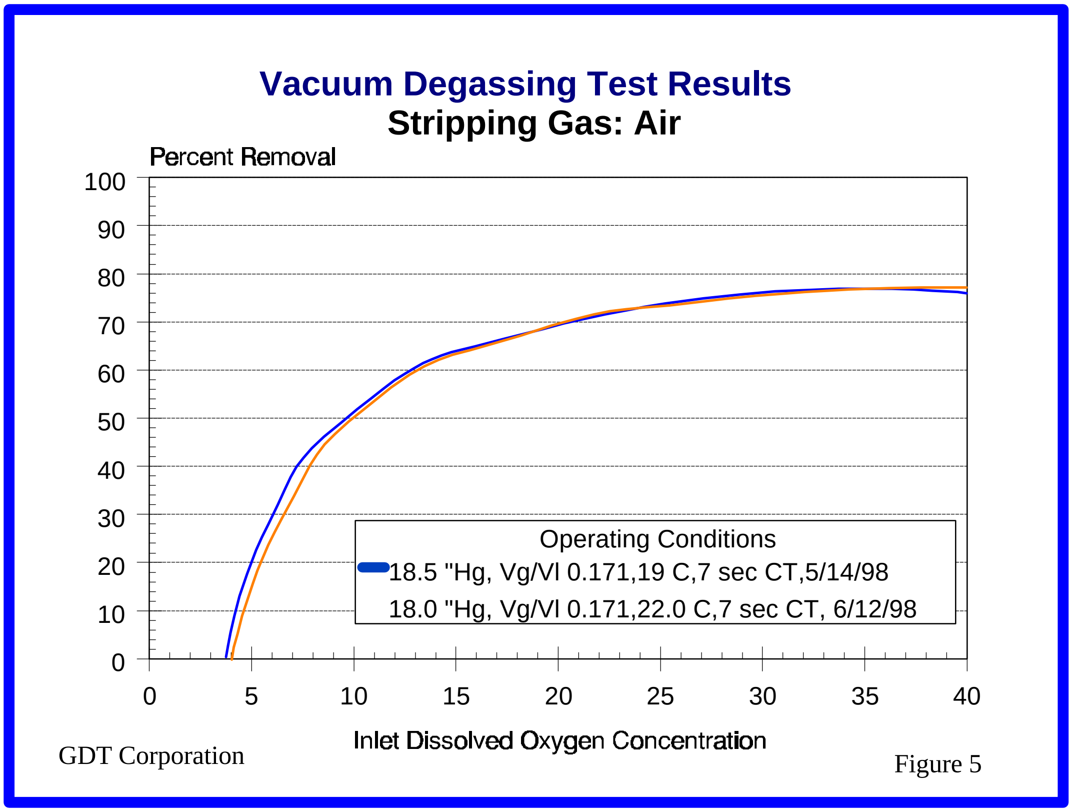


Figure 5

Figure 5 demonstrates the VacGDT process removal efficiency under the conditions specified. The data in **Figure 5** indicate that the stripping efficiency ranged up to 75% with a 30 mg/l DO feed.

Conclusions

- **High dissolved oxygen levels developed within high concentration oxygen fed ozone contactors can create corrosion, down stream process and aesthetic problems with treated water.**

- **The patent pending VacGDT™ process can effectively reduce dissolved oxygen levels in ozonated water by up to 75% in a compact, non-fouling system.**

- **Applications include Deoxygenation of ozone treated water for use as ozone generator cooling water.**

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Key Word

Dissolved Oxygen; Deoxygenation; Mass Transfer; Vacuum; Stripping; Entrained Gas; Deaeration