RESEARCH ON THE OZONE STERILIZATION AND REMAINDER POLLUTION IN CLEANROOM AIR

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ABSTRACT
The high-concentration ozone can be used as disinfectant to kill germ and virus, but the high-concentration ozone has the injury of human body and respiratory organ. After sterilized by ozone in one room, the concentration of the leftover ozone should paid more attention. In this experiment, the ozone was generated continuously by an ozone generator and transferred to a biological cleanroom through the duct of the air-condition system until the ozone concentration of the cleanroom was reached to the sterilizing value for indoor disinfection. After disinfection period, the air-conditioning and ventilation system were carried out to dilute the indoor ozone to a safe limit. The indoor ozone concentration was monitored continuously. In theory, the mass-balance equation and the first-decay model are opted to predict the ozone concentration of the generation-decay, and the study gets the theoretical decay curve. Furthermore, comparing the theoretical curve with the measuring curve, this paper analyzes the differences and gains the impacted factors of indoor ozone concentration. During the ozone sterilization period, the more attentions should be paid to protect workers in workshops. Through measuring the ozone concentration of the sterilized cleanroom, the research suggests 30 minutes is the safe interval for the indoor ozone concentration to reach the health safe limit (80 parts per billion GBT18883-2002).

INDEX TERMS
Ozone, Cleanroom, Sterilization, Pollution

INTRODUCTION
In recent years, ozone technology is already successfully used in many fields, such as medical, chemical production, atmospheric purification and sterilized the drinking water and so on. Because of its strong oxidize ability, ozone can destroy the cell wall as disinfectant, and then make it lose vitality. On one hand, the high-concentration ozone can be used to kill virus. On the other hand, the high-concentration ozone has the injury of human body and respiratory organ. After disinfected by ozone in one room, the concentration of the remainder ozone should be paid more attention to in the HVAC (heating, ventilation, air-conditioning) field.

Many studies were conducted to the ozone decay in many fields. In the stainless steel chamber, the ozone decay in the surface and ozone emission was obtained by experiment (J.L. Niu 2001). To predict the ozone injury, many experts (Golam Sarwar 2002; Heinz-Jorn Moriske 1998; Martin Kraenzmer 1999) used the different models to predict the ozone concentration, and testified the feasibility of the models.

RESEARCH METHODS
Ozone-Concentration-Predict Model
In the theory, the following equation was normally opted to predict the ozone concentration of the generation-decay:

\[
V \frac{dc}{dt} = S + S_f - S_e - KVC
\]

Where:
- \( K \): the decay constant due to the various decomposition of the surface, m/s;
- \( C \): the indoor concentration of the ozone, ppm;
- \( S \): the ozone source, g/h;
- \( S_f \): the ozone of the fresh-air, g/h;
- \( S_e \): the exhausted ozone, g/h;

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V: the volume of measured clean room, m$^3$;
T: time, min.

The general solution of the equation (1) is:

$$C = S \frac{\left(1 - e^{-Kt}\right)}{KV} + C_0 e^{-Kt}$$  \hspace{1cm} (2)

Where:

$$S = S + S_f - S_e$$

$C_0$: the initial ozone concentration in the measured volume.

When no ozone emission is present, i.e., when the ozone generator was off, $S_e = 0$, and then the equation (1) become:

$$\left(\frac{dc}{dt}\right) = -KC$$  \hspace{1cm} (3)

The solution is:

$$C = C_0 e^{-Kt}$$  \hspace{1cm} (4)

This is an ozone decay model using to predict the ozone concentration during the decay time.

**Model Used In This Ozone Sterilization Research**

The calculation described here is based on a mass-balance equation, i.e., what is supplied to a volume is equal to the sum of what is removed and what is stored in the volume. Equation (1) is a mass-balance equation with a source term.

$$K_s (Q_f c_f + Q_r c_r + S) / Q_{in} = V dc / dt + K_a VC + Q_e c$$  \hspace{1cm} (5)

Where:

$$c_r = K_s c$$

$Q_f$: the flow rate of fresh air, m$^3$/h;
$Q_r$: the flow rate of return air, m$^3$/h;
$Q_s$: the flow rate of the supply air in the investigated workroom, m$^3$/h;
$Q_{in}$: the total flow rate of the supply air in the investigated AHU (air handling unit), m$^3$/h;
$Q_e$: the flow rate of exhaust air in the investigated workroom, m$^3$/h;
$C$: the ozone concentration of the investigated workroom, ppm;
$C_f$: the ozone concentration of the fresh air, ppm;
$C_r$: the ozone concentration of the return air, ppm;
$V$: the volume of the investigated workroom, m$^3$;
$S$: the source of the ozone generation, g/h;
$K_d$: the decay constant due to the ozone natural decay and due to the various decomposition of the surface, h$^{-1}$;
$K_s$: the decay constant due to the ozone reactant in the duck, h$^{-1}$;

When the ozone generator was turned off, $S=0$, the decay model was used to calculate the ozone concentration. The decay model was described in the following equation (6):

$$K_s (Q_f c_f + Q_r c_r) / Q_{in} = V dc / dt + K_a VC + Q_e c$$  \hspace{1cm} (6)

We can simplify the equation (6) as form as equation (2) and solute it as follows:

$$C = E \frac{\left(1 - e^{-K't}\right)}{KV} + C_0' e^{-K't}$$  \hspace{1cm} (7)

where:

$$E = \frac{K_s Q_f c_f / Q_{in}}{Q_e}$$  \hspace{1cm} (7-a)

$$K' = K_d + \frac{Q_e}{V} - \frac{K_s^2 Q_f Q_r}{Q_{in} V}$$  \hspace{1cm} (7-b)

$C_0'$: the ozone concentration when the ozone generator was turned off.
Ozone Generation
During the generated period, the ozone was produced continuously with an ozone generator, which generates 60g ozone in one hour. The ozone generator was placed in the terminal section of the air-handling unit. The generated ozone was introduced into the sterilized biological cleanroom with the supply air. The location of the ozone generator was shown in fig. 1. It is worth noting that the parts of heating and humidifying in the air handling unit must be turned off which the ozone generator was turned on in the original design. However, because of some controlled reasons, they can’t be turned off in this measurement.

![Diagram of air handling unit]

Figure 1. the location of the ozone generator in the air-handling unit

Measured Location
The size of this measured infected cleanroom is 9.0(Long)×2.0(Wide)×2.6(High) m in a Tianjin biological pharmaceutical. The surface of this cleanroom is color steel plate. It has five supply air inlets, one return air outlet and one exhaust outlet from a controlled central air conditioning system, the ozone sampling location is near the return air outlet 1.0m and above the floor 1.5m.

Measurement Of The Ozone Concentration
The ozone concentration in the infected cleanroom was measured continuously by a UV-photometer of the brand ZX-01, connected to a computer that was used for automatic record of the ozone concentration. Generally, a program that a concentration was recorded every 6 seconds was made in the computer. According to the manufacture, the detection limit of ozone for this instrument is 2 ppb. The indoor ozone concentration was monitored from the highest value till to the lowest value.

RESULTS
The parameters in the equation (5) ~ (7) were gained through the design of the air handling unit. Their values were described as follows:
\[ Q_f = 7154 \text{m}^3/\text{h}; \; Q_r = 12722 \text{m}^3/\text{h}; \; Q_i = 2811 \text{m}^3/\text{h}; \; Q_t = 19876 \text{m}^3/\text{h}; \; Q_e = 2173 \text{m}^3/\text{h}; \]
\[ C_f = 0.015 \text{ppm}; \; C_0 = 0.004 \text{ppm}; \; C_0' = 1.545 \text{ppm}; \]
\[ S = 60 \text{g/h}; \; V = 9 \times 2.2 \times 2.6 \text{m}^3; \]

With the regression of the ozone concentration of generating, the decay constant \(K_c\) is regarded as 0.6. The standard limit of disinfected ozone concentration is 10ppm (Ministry of Health of China). The sterilization persistent period must be more than 1 hour.

After sterilization period, the ozone generator will be turned off and the indoor ozone concentration will decay with the indoor ventilation. The ozone concentration is shown in figure 2 based on the predicted model. Seen from the fig. 2, after ten minutes ozone concentration of the measured cleanroom decreased to the indoor air quality standard value, 0.08ppm (GB/T18883-2002). The decay time should shorter than the suggested safe entering interval. In the theory, 10 min. is the safe interval when there is no ozone remainder pollution after sterilization.
During the ozone sterilization period, because the heating and humidifying can’t be turned off, the sterilization ozone concentration didn’t reach 10ppm. The reason is ozone is a more active matter that is influenced by the air relative humidity, temperature. The ozone concentration is far lower than the sterilization limit even if the ozone generator capacity is enough.

The ozone concentration in the cleanroom kept the level of 1.5ppm finally in the experiment. The predicted and measured ozone concentrations are shown in the fig.3.

The measured and predicted curve has the similar trend, but the measured ozone decay is slower than the predicted one. Compared with the predicted time 6 minutes in theory, the indoor ozone concentration reached the 0.08ppm actually after 13.5 minutes. The reason is that the value of the decay constant Kc. Practically, because ozone is a more active matter, many factors influenced the decay constant Kc, such as the air relative humidity, temperature, filter, duck, surface and so on. To study the ozone remainder after sterilization, much work should be done to give a more precise decay constant. 30 minutes (more than the predicted one 13.5 minutes) according to measured trend is a reasonable suggested value for health safety interval of ozone sterilization and personnel entering.

CONCLUSION AND IMPLICATIONS
The feasibility of the first-decay model to predict the ozone concentration in the ozone- sterilization area is testified because the measured and predicted curve has the similar trend. But the parameter of the model is not simply to give one value, more attentions should be paid to decay constant. More studies should be done to avoid the ozone remainder pollution and protect the workers’ health, who work in the ozone-sterilization area. It is proved in the measuring more than 30 minutes is a reasonable suggested value for health safety interval of ozone sterilization and personnel entering.
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