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Analysis of Removal and Decomposition Pathways of Vaporized Hydrogen Peroxide (VHP) for Aircraft Decontamination Operation

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In response to possible terrorist attacks and epidemic/pandemic diseases, there is a need for efficient infection control and sanitization of airliners. Use of vaporized hydrogen peroxide (VHP) is a promising method to achieve the goal. However, the impact of disposed VHP on atmospheric environment after decontamination operation needs to be fully understood to avoid any detrimental consequence caused by airliner decontamination. This paper analyzed the removal and decomposition pathways of VHP in the atmosphere, including physical and chemical pathways. Absorption by water droplets in atmosphere and photolytic decay mechanisms have been investigated. The results show that the uptake to water droplets in the air appears to be a major pathway for the removal of VHP.

Nomenclature

H_2O_2	=	Hydrogen peroxide
$HO*$	=	Hydroxyl
SO_2	=	Sulfur Dioxide
VHP	=	Vaporized Hydrogen Peroxide

I. Introduction

Modern civil aviation provides unprecedented systems for rapid transport, and the industry is growing by 5% each year. However, there are significant ongoing concerns over routine air travel and these concerns are vastly magnified in the event of an epidemic/pandemic/terrorist attack using chemical and biological agents because:

A).air travel transports infected individuals to new locations;

B).aerosol person to person transmission can occur within the cabin;

C). transmission can occur via cabin surfaces;

In all three cases, efficient infection control strategies are needed such as decontamination or sanitization of aircraft. Aircraft Decontamination consists of delivering VHP (Vaporized Hydrogen Peroxide) through a stand-alone system, in an efficient way, without requiring bulky vaporizers or other heavy equipment within the cabin, such that the system is capable of delivering controlled quantities of VHP to achieve sporicidal conditions throughout the cabin. In this process, hydrogen peroxide from a concentrated liquid source (35 % hydrogen peroxide) is flash vaporized and delivered to the space to be decontaminated in the vapour phase. Some hydrogen peroxide decontamination processes can employ hydrogen peroxide aerosols. However, the design objective in the VHP process is to deliver hydrogen peroxide in the vapour phase. Thus for the purpose of the present paper aerosolization during initial delivery to the aircraft in neglected. The concentrations (120-170 ppm) employed for the aircraft are far below the dew point and the VHP process is nominally all vapour phase. At the end of the operation, the concentration of VHP was reduced to 1 ppm and then

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released to atmosphere. Some hydrogen peroxide decontamination processes can employ aerosols. However, the design objective in the VHP process is to deliver hydrogen peroxide in the vapour phase. Thus for the purpose of the present paper, aerosolisation during initial delivery to the aircraft is neglected.

In seeking industry and government input on the deployment of VHP for civil aviation applications, two key concerns were raised frequently in workshops and consultations:

- Compatibility with aircraft materials and systems.
- The extent to which any environmental release of hydrogen peroxide presents a safety threat to adjacent aviation operations.

The first of these issues was addressed in earlier work by one of the authors[1, 2]. However, the second remains a key concern and this is the motivation for this paper.

There are two scenarios for the release of hydrogen peroxide by the VHP aircraft decontamination operations: normal release (1 ppm) and accident release ((120-170 ppm). These gaseous releases are much harder to manage than a liquid spill so in this paper the focus is on the environmental fate of vapour phase escapes.

The fate of vaporized hydrogen peroxide released to atmosphere from aircraft decontamination operation using VHP involves two aspects: removal and decomposition by physical and chemical processes and dispersion of H_2O_2 in the atmosphere. This work has focused on the removal and decomposition aspects and reviewed major pathways of removal and decomposition of VHP in atmosphere and assessed the fate of disposed VHP and discussed possible interactions with air pollutants in normal operation and accidental leakage of aircraft decontamination.

Although there has been research on the atmospheric behavior of hydrogen peroxide[3-12], this work differs in that the source hydrogen peroxide concentration is much high, which has implications for the fate of the hydrogen peroxide.

II. Removal and Decomposition Pathways of Released Hydrogen Peroxide

A. Overview of Pathways

In general, released hydrogen peroxide from aircraft decontamination could be removed from atmosphere in two pathways: physical and chemical pathways. Absorption to water droplets is a typical physical pathway though there are chemical reactions occurring after absorption in the aqueous phase. The chemical pathways include spontaneous decomposition (photolytic decay) and reactions with those sink compounds[5]. These pathways could happen in both gaseous and aqueous phase. The third one, reactions with sink compounds, has particular implications for aviation because the aircraft decontamination would be operated at the airport vicinity, which could be a polluted area especially at major airports. The chemical reactions could happen between hydrogen peroxide and engine and combustion emitted pollutants such as SO_2 and NOx. SO_2 is well known as a major sink for hydrogen peroxide[5]. However, the mechanism of reactions between hydrogen peroxide and these compounds is complicated and the parameters that affect the sinking effect are multiple. Moreover, as the aviation fuels have been reducing their sulfur content and SO_2 concentrations in the airports are therefore getting lower and lower (this is also due to the reduction from power generations), the effect of SO_2 as a sink for hydrogen peroxide is less significant. So in this paper the pathways due to reactions with pollutants are not discussed and will be reported in a separate paper.

The pathway of the removal and decomposition of hydrogen peroxide can be classified and expressed in Fig. 1 below:
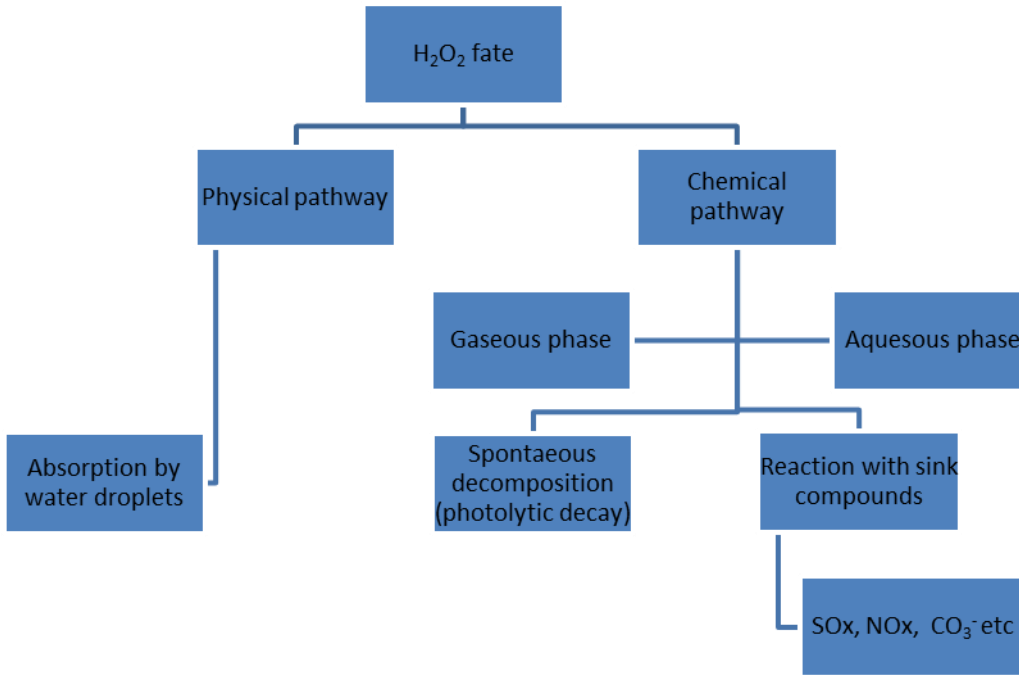
Figure 1.   The fate of hydrogen peroxide released from aircraft decontamination.

B. Physical Pathway - Uptake to Water Droplets
1. Partition between gaseous and aqueous phase

Hydrogen peroxide has excellent solubility in water and can be dissolved in water in any ratio. This made uptake to water droplets become a major pathway for the removal of gaseous hydrogen peroxide. Olszyna[3] and Jacob et al[4] measured the ambient H_2O_2 concentrations at different weather conditions. They observed a significant decrease of gas phase H_2O_2 during the formation of clouds and rainfall, which proved that the absorption of gaseous H_2O_2 to water droplets was a major pathway for the removal of gaseous H_2O_2.

The solubility of H_2O_2 in water droplets is determined by the Henry's law, which can be expressed as follows[13]:

$$K_{H,(cp)} = C_{H2O2(aq)} / P_{H2O2(g)} \tag{1}$$

Henry's Law can also be written in other forms, with different definition of the constant K_H and different dimensional units. For example:

$$K_{H,(cc)} = C_{(H2O2aq)} / C_{H2O2(g)} \tag{2}$$

Where:
- $C_{H2O2(aq)}$ is the molar concentration of H_2O_2 in a solution which is in equilibrium with the gas phase, mol/L.
- $C_{H2O2(g)}$ is the molar concentration of H_2O_2 in gaseous phase, mol/L.
- $P_{H2O2(g)}$ is the gas phase partial pressure of H_2O_2 in equilibrium with its aqueous solution.
- $K_{H,(cp)}$ is the proportionality constant (the Henry's Law constant) in mol/L· atm. $K_{H,(cp)}$ is a function of temperature (given by the van't Hoff equation below), pressure and the chemical composition of the system. The pressure dependence of $K_{H,(cp)}$ is normally neglected because the pressure effect on the condensed phase is small.
- $K_{H,(cc)}$ is the proportionality constant (the Henry's Law constant) dimensionless.

The relation between $K_{H,(cp)}$ and $K_{H,(cc)}$ is given in equation (3) below:

$$K_{H,(cp)} = R* T *K_{H,(cc)} \tag{3}$$

Where, R is gas constant, 8.314 J/mol. T is the ambient temperature in Kelvin.

Henry's law constant is a function of temperature, which has been investigated by Martin et al[14] and can be expressed in equation (4) below:

$$K_{H,(cp)} = e^{(a/T-b)} \tag{4}$$

Where:

T is the ambient temperature in Kelvin,

a=7024,

b=11.97

The correlation between ambient temperature and Henry's law constant $K_{H,(cc)}$ for hydrogen peroxide is calculated as shown in Fig. 2. Overall, the value of Henry's Law constant of H_2O_2 is high, showing that the ratio of $C_{H2O2(aq)}$ to $P_{H2O2(g)}$ or $C_{H2O2(g)}$ is high and this indicates that the H_2O_2 has a strong tendency to be present in aqueous phase. As a result the large proportion of gaseous phase H_2O_2 released to the atmosphere would be dissolved in the water droplets, clouds or raindrops in humid weather. The results in Fig. 2 showed that solubility of H_2O_2 in aqueous phase decreases as the ambient temperature rises.
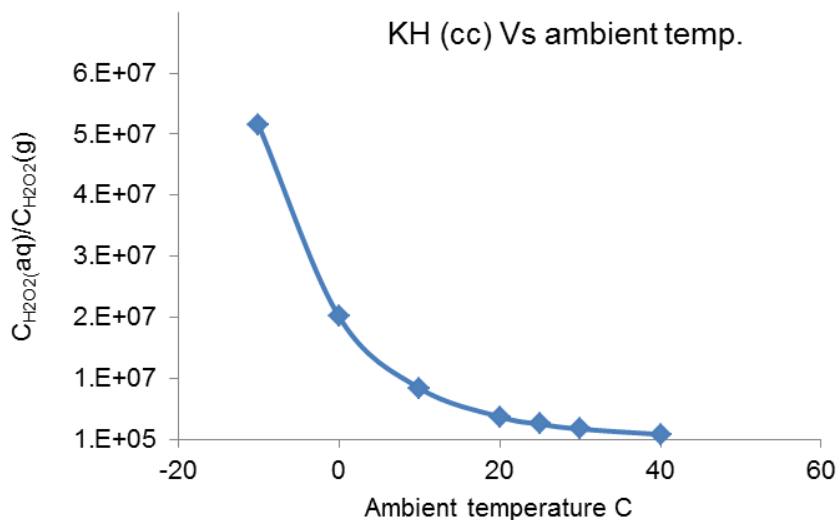

Figure 2. The partition between aqueous and gas phase H$_2$O$_2$ as a function of ambient temperature.

2. Uptake capability of hydrogen peroxide by air at different relative humidity and ambient temperatures

The strong tendency of H_2O_2 dissolving in the water droplets means that the amount of water available in the air is one of the key parameters affecting uptake of H_2O_2 from aircraft decontamination operation. Another important parameter is temperature. The relations between the amount of gaseous H_2O_2 (1ppm scenario) absorbable by 1 m^3 air, relative humidity and ambient temperature of air were modelled by calculating the available amount of water vapour in 1 m^3 air at each relative humidity and ambient temperature, assuming a concentration of H_2O_2 in aqueous phase 50% after absorption. Figure 3 shows that the absorption of H_2O_2 in water vapour has a good linear relationship with relative humidity of air and increases as the ambient temperature rises. In a hot humid summer day (e.g. above 22°C), 1 volume of air could absorb at least ten volumes of H_2O_2. However, under cold weather conditions such as 10C or below, the absorption capability of water droplets is much reduced even at high relative humidity. The ambient temperature has significant influences on the absorption capability of water droplets to hydrogen peroxide. The relationship between air humidity and absorption capability of hydrogen peroxide depended on ambient air temperatures. At low ambient temperatures, the humidity of air has much less impacts on absorption of hydrogen peroxide. This indicated that the removal of H_2O_2 by water droplets in cold weather is a slow process whatever the air humidity is.
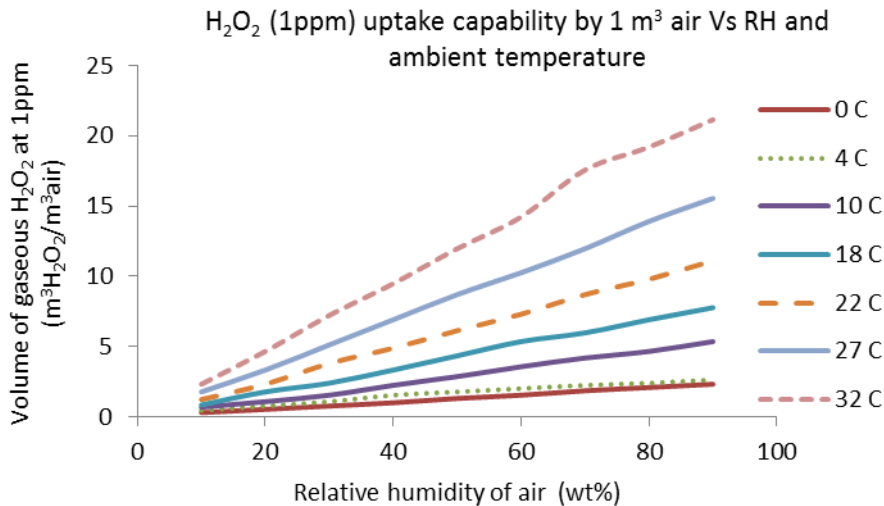
Figure 3. Volume of gaseous H_2O_2 (1ppm) that can be absorbed by 1 m^3 of air as a function of relative humidity and ambient temperature.

C. **Chemical pathways**

3. *Spontaneous decomposition (Photolytic decay)*

The decomposition of hydrogen peroxide is a spontaneous process at room temperature. The rate of the reaction is increased by the presence of light. However, the research on the detailed rate of photolytic decay reaction of hydrogen peroxide in atmosphere has been limited, especially for high concentration scenarios. Jacobi et al[15, 16] investigated the photochemical decomposition of H_2O_2. They measured the decay rate of H_2O_2 in the artificial snow made in lab under the influence of highly intensive UV and visible radiation. They found that H_2O_2 in the gas and liquid phase significantly absorb solar radiation and thus photolytic reactions are good sinks for H_2O_2 in the atmosphere. A first order photolytic decomposition reaction of hydrogen peroxide was observed as described below in reaction (R1) and equations (5) and (6):

$$H2O2 + hv \rightarrow 2OH^* \tag{R1}$$

$$d[c]/dt = -k[c] \tag{5}$$

$$\ln([c]/[c_0]) = -kt \tag{6}$$

Where, [c] is the concentration of hydrogen peroxide at t time, mol/L.
$[c_0]$ is the initial concentration of hydrogen peroxide, mol/L.
k is the rate constant, here corresponding to the photolysis rate, h^{-1}.

Jacobi et al[16] measured the k values for various initial concentrations of hydrogen peroxide and found a value of 0.48 h^{-1} at a radiation intensity of 1200 W m^{-2}. However this radiation intensity was under lab condition. In reality, the light radiation is affected by weather, location, season and many other parameters. Burgess[17] reported measured clear day solar radiation in South England in June, September and December and found a fourfold difference between June and December. He also reported clear day solar radiations at three latitudes in the UK (50°N: Penzance; 55°N: Newcastle, and 60°N: Shetland) and found that the major difference was in winter and there was little gap in summer between different locations. The maximum radiation intensity observed at 52°N was 800 W m^{-2} in June and 150 W m^{-2} in December for clear days. As the k is a function of radiation intensity and the measured radiation intensity in the UK was weaker than that of the lab conditions, the k values for typical UK conditions accordingly were a fraction of laboratory determined values (0.48 h^{-1}). Two k values, one for summer and the other for winter scenario, were obtained as 0.32 h^{-1} and 0.16 h^{-1} based on 800 W m^{-2} and 150 W m^{-2} radiation intensity. From these two k values, decay rates in terms

of percentage relative to the initial hydrogen peroxide concentration (1 and 170 ppm) for June and December scenarios were calculated as a function of time using equation (6) and shown in Figs. 4 and 5. The results show that it will take approximately ~8 hours in June and ~40 hours in December for 90% of hydrogen peroxide to decompose by photolysis, indicating that the photolytic decay mechanism is a slow process for the decomposition of hydrogen peroxide.
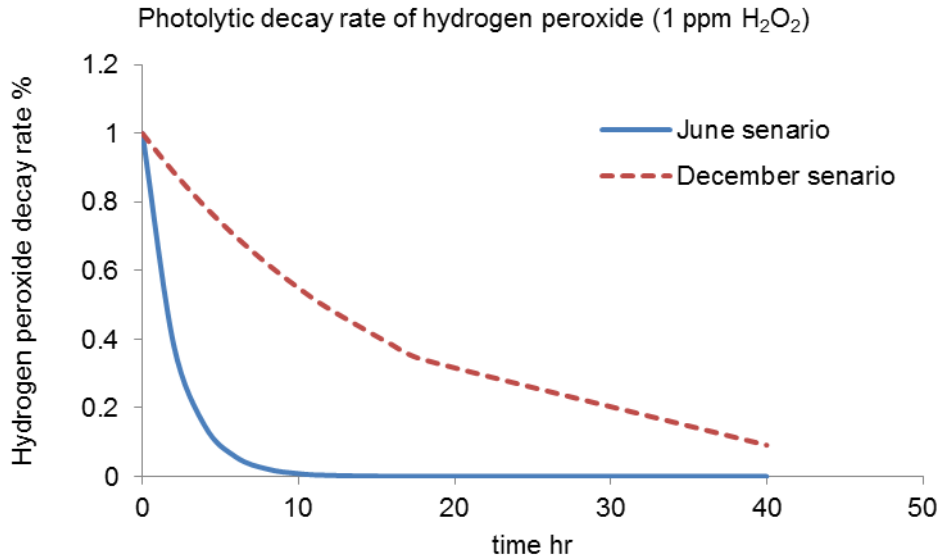

Figure 4.   The rate of photolytic decay of 1 ppm H₂O₂ based on a summer and a winter scenario in the UK.
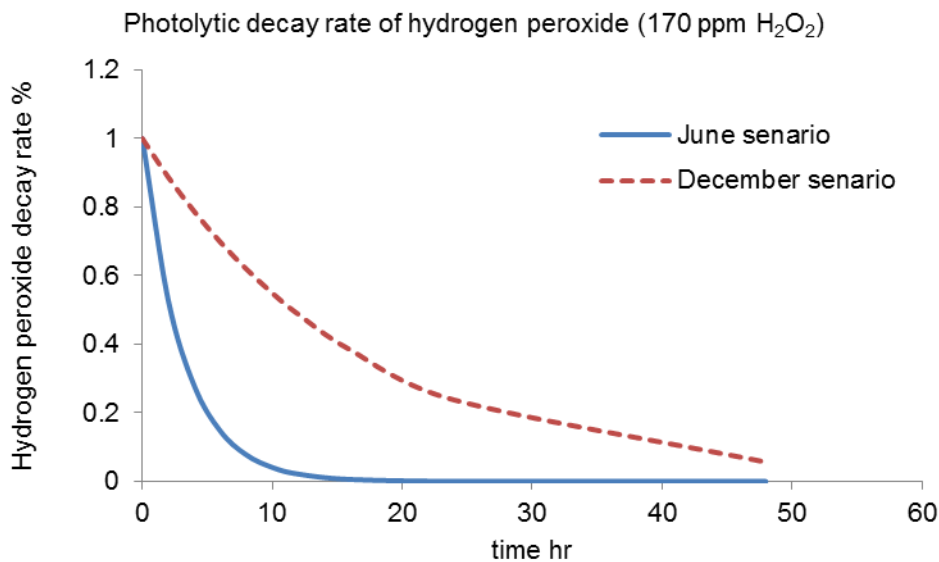

Figure 5.   The rate of photolytic decay of 170 ppm H₂O₂ based on a summer and a winter scenario in the UK.

III. Conclusion

Vaporized hydrogen peroxide (VHP) is a promising method for infection control and sanitization of aircraft. However, there is a concern on the environmental impact and safety threat to adjacent aviation operations by released hydrogen peroxide from decontamination operation. So it is essential to fully understand its impact to avoid any detrimental consequence caused by aircraft VHP decontamination. Two scenarios of VHP release have been considered in the paper: normal operation release (1 ppm VHP) and accidental leak during the operation (170 ppm VHP). The removal and decomposition pathways of VHP in the atmosphere has been analyzed and examined.

In general, the pathway can be classified as physical and chemical pathways. The uptake to water droplets in the air, as a physical pathway, appears to be a major pathway for the removal of VHP due to high Henry's law constant of hydrogen peroxide. The removal efficacy of hydrogen peroxide by water droplets is increased as the ambient temperature and humidity increases.

Photolytic decay, as a chemical decomposition pathway, is a slow process. Based on example scenarios (UK, summer and winter) calculation in the paper, it needs approximately 8 hours in summer and 40 hours in winter for 90% of hydrogen peroxide to decay or decompose.

There are other chemical pathways such as reactions with air pollutants SO_2. The mechanism for that is more complicated and will be reported in a separate paper.

Acknowledgments

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