Theoretical Analysis of the Condensation of Hydrogen peroxide Gas and Water Vapour as used in Surface Decontamination.

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Introduction

For some time there has been two schools of thought about gaseous hydrogen peroxide surface decontamination. The traditional thinking as described in European Patent EP 0 486 623 B1 is that hydrogen peroxide gas decomposes according to a half-life rule and that decontamination is a dry gas process. Condensation should therefore be avoided as it causes the process to become uncontrollable. The other school of thought states that away from catalytic surfaces the gas is stable and condensation is unavoidable given the usual operating parameters. The second school of thought also believes that condensation is the primary method of causing the decontamination. The second process is described in detail in two UK Patent Applications numbers GB 2 354 443A and GB 2 351 664 A.

This paper is an analysis of the equations governing the vapour pressures, and the mass and energy balances of hydrogen peroxide and water mixtures in the dynamic environment of a chamber undergoing hydrogen peroxide decontamination. It establishes the point during the process at which condensation will occur and the profile of the gas concentration as further amounts of hydrogen peroxide solution are flash evaporated and added to the system after the saturation point has been reached. Finally the changes in gas concentration during the aeration phase are calculated and the theoretical results compared with results obtained from experimentation.

Typical Hydrogen Peroxide Equipment and Decontamination Cycle

Most commercially available hydrogen peroxide generators are closed loop devices. With such equipment the generator is connected to the chamber to be decontaminated in a sealed fashion, such that the volume of air or air and gas that is delivered to the chamber is equal to that returned to the generator. Closed loop systems have the advantage of containing the hydrogen peroxide vapour that is generated as they may be made pressure tight.

The hydrogen peroxide and water vapour is generated by flash evaporation on a heated plate, which is in excess of the boiling points of the components of the solution. This ensures that the ratio of hydrogen peroxide and water are the same in the vapour phase as in the liquid that is evaporated.

Hydrogen peroxide decontamination in isolators or rooms and other similar closed chambers is usually performed in four phases. The first phase of the decontamination cycle is to stabilise the equipment temperature and where necessary to adjust the relative humidity inside the closed chamber to a predetermined level. The next phase is to flash evaporate hydrogen peroxide solution into a heated air stream and pass the vapours into the chamber to raise the gas concentration to the required level to cause decontamination.
During the third phase liquid is still evaporated into the air stream, often at a lower rate in order to maintain the required gas concentration inside the chamber. The fourth and final stage is to pass clean air into the chamber to remove the hydrogen peroxide vapour by dilution.

**Equilibrium Vapour Pressures**

The equilibrium vapour pressure of pure water and pure hydrogen peroxide can be calculated from two polynomial equations.

Water vapour pressure is calculated from the following equation that has been fitted to the vapour pressure temperature data by Keyes (1):

\[ \log p_w(T) = G + A/T + B\log T + CT + DT^2 + ET^3 + FT^4 \]  

(1)

Where \( T \) is the absolute temperature and \( A, B, C, D, E, F, \) and \( G \) are constants, \( A = -2892.3693, B = -2.892736, C = -4.9369728 \times 10^{-3}, \) \( D = 5.606905 \times 10^{-6}, E = -4.645869 \times 10^{-9}, F = 3.7874 \times 10^{-12}, \) and \( G = 19.3011421. \)

Hydrogen peroxide vapour pressures may be calculated from a second equation by Scatchard (2), which is:

\[ \log p_H(T) = DT + A/T + B\log T + CT \]  

(2)

where \( A, B, C \) and \( D \) are constants, \( D = 44.5760, A = -4025.3, B = -12.996 \) and \( C = 4.6055 \times 10^{-3} \)

With ideal mixtures the vapour pressure of each component may then be calculated using Raoult’s law:

\[ p_w = x_w p_w^0 \quad \text{and} \quad p_H = x_H p_H^0 \]  

(3)

Where \( p \) is the vapour pressure exerted in the mixture, \( x \) is the liquid phase mole fraction and \( p^0 \) is the vapour pressure that the pure component would exert at the same temperature with the subscripts \( W \) and \( H \) referring to water and hydrogen peroxide respectively. The mole fraction is the number of molecules of a component in the two-component mixture divided by the total number of molecules in the solution.

It has been demonstrated that, due to hydrogen bonding, hydrogen peroxide and water does not obey Raoult’s law, as the molecules interact with each other providing a system that is far from the ideal model. In such a situation an activity coefficient has to be inserted into Raoult’s law. The activity of the component is defined as the product of an activity coefficient, \( \gamma \), and the mole fraction.

\[ p_w = \gamma_w x_w p_w^0 \quad \text{and} \quad p_H = \gamma_H x_H p_H^0 \]  

(4)
Activity coefficients for water and hydrogen peroxide have been calculated and published by Schumb et al (3) and are as follows:

\[ \gamma_w = \exp \left\{ \frac{(1-x_w)^2}{RT} \left[ B_o + B_1 (1-4x_w) + B_2 (1-2x_w)(1-6x_w) \right] \right\} \]  

(5)

And

\[ \gamma_H = \exp \left\{ \frac{x_H^2}{RT} \left[ B_o + B_1 (3-4x_H) + B_2 (1-2x_H)(5-6x_H) \right] \right\} \]  

(6)

Where \( B_o, B_1 \), and \( B_2 \) are constants, \( R \) is the universal gas constant and \( T \) is the absolute temperature. \( B_o = -1017 + 0.97T \), and \( B_1 = 85 \) and \( B_2 = 13 \)

By substituting equations (1) and (5) in equation (4) it is possible to calculate the equilibrium vapour pressure of water at any hydrogen peroxide aqueous concentration and temperature from the freezing to the boiling point. By a similar technique and using equations (2) and (6) it is possible to calculate the equilibrium vapour pressure of hydrogen peroxide for the same range of conditions. Figs 1 and 2 are the vapour concentrations of hydrogen peroxide and water at various aqueous solution strengths and temperatures. A plot of
the equilibrium liquid and vapour mole fractions of hydrogen peroxide solutions at 20°C is shown in Fig 3 and helps in understanding why the vapour and condensate concentrations are always in a state of change.

It is important to note that at all concentrations less than pure hydrogen peroxide that the mole fraction of the vapour is less than that of the liquid.

**Gas Concentration in a Sealed Chamber**

Consider what will happen if we take a closed chamber of known volume containing air at a known value of relative humidity (RH) and flash evaporate hydrogen peroxide solution of a known mass and concentration inside the chamber. For the purposes of theoretical reasoning it must be assumed that the volume of the chamber will expand to maintain the internal pressure at exactly 1 atmosphere. In practice the change in pressure of a perfectly sealed chamber would be very small. The term “dynamic equilibrium” is used because at any moment in time the vapours and any condensate that has formed will be in equilibrium. As the conditions change, either because of the addition of more water and hydrogen peroxide vapour or a shift in temperature, the equilibrium state will also change.

The hydrogen peroxide and water vapour concentration will rise inside the chamber until dew point is reached, at which time a dynamic equilibrium will be established between the vapour phase and the liquid. Because hot gasses are being added to the system the temperature will rise, the rate of heat loss depends on the size and construction of the enclosure. If the rate of temperature rise is known this may be incorporated into the calculations by adjusting the temperature term in equations (1), (2), (5) and (6). For simplicity it will be assumed that the temperature inside the chamber remains constant.
The process may be analysed at a specific point in time, after the first droplet of condensation has formed. It is possible to establish the mass balance inside the chamber, at the specific equilibrium conditions.

The mass of water in the chamber will be made up from the water content of the air inside the chamber at the start of the evaporation process and the water content of the evaporated liquid. The mass of hydrogen peroxide will be known from the mass of evaporated liquid. Once the first droplet of condensation has formed the hydrogen peroxide and water will be distributed between the liquid phase (condensate) and the gaseous phase, and the mass balance may be evaluated and checked against the mass of water and hydrogen peroxide present. Starting with the total known masses of each component, which may be expressed as follows:

\[
W_{(T)} = W_{(RH)} + W_{(S)} \quad \text{and} \quad H_{(T)} = H_{(S)}
\]

Where \( W \) and \( H \) are the masses of water and hydrogen peroxide and the suffix \((T), (RH), \) and \((S)\) stand for Total, Relative Humidity and Solution respectively. The mass of each component will be distributed either as a liquid or as a vapour, hence:

\[
W_{(V)} = W_{(L)} \quad \text{and} \quad H_{(V)} = H_{(L)}
\]

Where the suffixes \((V)\) and \((L)\) stand for vapour and liquid respectively.

If an estimate of the mole fraction \((x_H)\) of hydrogen peroxide in the condensate is made it is then possible to calculate the mass of hydrogen peroxide vapour in the chamber as the liquid and vapour will be in equilibrium. By substituting equation (2) and (6) in equation (4) it is possible to establish the gas concentration \((p_H)\).

Once the value of \((p_H)\) has been established it becomes possible to calculate the mole fraction in the vapour phase from: -

\[
p_H = y_H P
\]

where \( y_H \) is the vapour mole fraction and \( P \) is the atmospheric pressure. Then from a knowledge of the volume of the chamber and hence the number of mols of gas in the chamber it is possible to calculate the number of mols of hydrogen peroxide in the vapour phase: -

\[
N_H = y_H N_C
\]

where \( N_H \) is the number of mols of hydrogen peroxide in the vapour phase and \( N_C \) is the total number of mols of gas in the chamber.

A similar calculation may then be performed to find the number of mols of water \( N_W \) in the vapour.
The total number of mols of water and hydrogen peroxide in the chamber may then be calculated by dividing \( W_T \) and \( H_T \) from equation (7) by 34.02 and 18.02 respectively.

The mole fraction of the condensate may then be calculated:

\[
\text{Calculated } x_H = \frac{H_T/34.02 - y_H N_C}{\left(\frac{H_T}{34.02} - y_H N_C\right) + \left(\frac{H_T}{18.02} - y_H N_C\right)} \quad (11)
\]

The calculated value of \( x_H \) may then be compared with the estimated value used at the start of the calculation. If they do not match a revised estimate is used and the calculation repeated until a match is achieved.

This calculation may be repeated for different masses of evaporated liquid to establish the profile of the gas concentration, and also to establish the importance of the initial RH in the chamber. If required it is also possible to perform the same calculation at different temperatures.

**Gas Concentration during Aeration**

The gas concentration during the aeration or fourth phase may be calculated using a similar technique as that described above. During aeration clean dry air is passed through the chamber reducing the gas concentration by a dilution effect, making it possible to estimate the amount of gas being removed at any instant in time and hence to recalculate the mass balance.

This calculation may be performed using a step technique. If it is assumed that the gas concentration remains constant during a short time interval then it is possible to estimate the loss of water and peroxide during the period. This loss of gas may then be deducted from the mass at the start of the interval and a new mass balance calculated. The accuracy of this calculation is improved as the time interval is shortened and is best calculated using a computer program.

**First Bead of Condensation in the Chamber**

It is not possible to use the mass balance technique to establish the point at which the first bead of condensation will form. At the moment of formation of the first bead the mass of condensate is zero and hence all of the hydrogen peroxide and water are in the vapour phase.

To overcome this difficulty a different technique has been developed to establish the point at which the first bead would form.

Using the vapour concentration expression in terms of mole fraction and the vapour concentration derived from Raoult's law and the activity coefficient for substance \( A \):

\[
p_A = y_A P \quad \text{and} \quad p_A = y_A x_A p_A^o(T) \quad (12)
\]
Where \( P \) is the atmospheric pressure, \( y_A \) is the mole fraction in the vapour phase and \( p_A^o(T) \) is the equilibrium vapour pressure of the pure component at the absolute temperature \( T \).

Then by substitution and subsequent rearranging of equation (12), the liquid phase mole fractions of a multi-component substance can be calculated for a given temperature:

\[
x_A = \frac{y_A P}{\gamma_A p_A^o(T)}
\]  

(13)

For the purposes of this calculation the requirement is to locate the first point at which condensation occurs, and the dew-point can be calculated by determining the point at which the mole fractions of the condensable components equal 1, for a two component system this is given by: -

\[
x_A + x_B = 1 \quad \text{or} \quad x_H + x_W = 1
\]  

(14)

Substituting equation (13) into equation (14), where only water and hydrogen peroxide are considered to be condensable components, yields:

\[
\frac{y_W P}{\gamma_W p_W^o(T_{dp})} + \frac{y_H P}{\gamma_H p_H^o(T_{dp})} = 1
\]  

(15)

Where \( T_{dp} \) is the temperature of the dew point.

Calculation of water vapour concentration comprises the residual vapour from atmospheric conditions (RH) plus the water vapour present from the liquid injected during the flash evaporation process.

From equation (9) and using the RH as a ratio component the concentration of water vapour due to RH can be calculated thus:

\[
y_{W,RH} = \frac{p_W^o(T) \times RH}{100}
\]  

(16)

Calculation of the total concentration of the water vapour in the system uses equation (16) plus the mole fraction of the water injected into the system as part of the flash evaporation process, hence:

\[
y_W = y_{W,RH} + \frac{(1 - (C/100) \times Fl_{tot})}{N_C}
\]  

(17)

Where \( C \) is the concentration of peroxide within the injected fluid, and \( Fl_{tot} \) is the total amount of liquid injected.
The equation for hydrogen peroxide is similar although lacks the initial conditioning component, due to the assumption that no hydrogen peroxide is present in the system at the start of the flash evaporation process:

\[ y_H = \frac{(C / 100) \times Fl_{tot}}{N_C} \times \frac{34.02}{100} \]  

(18)

By substitution and subsequent rearrangement of equations (15), (17) and (18) the total amount of hydrogen peroxide solution needed to cause the first bead of condensation can be calculated.

\[ Fl_{tot} = \frac{p_w^o (T_{dp}) y_w}{P} - y_i \times \left( \frac{1 - (C / 100)}{18.02 \times N_C} + \frac{(C / 100)}{34.02 \times N_C} \times \frac{p_w^o (T_{dp}) y_w}{p_H^o (T_{dp}) y_H} \right) \]  

(19)

The calculation of the concentration of hydrogen peroxide in the first bead of condensation cannot be calculated directly. A value for \( x_{H} \) must be assumed and then the calculation performed to find the value of \( x_{H} \). If the assumed value and the calculated value are equal this is the concentration at which the first bead of condensation will form.
The calculation of \( x_H \), (i.e. \( C \)) the solution concentration, is performed by a specially developed computer program using an iterative loop until the assumed value and the calculated value are equal. A flow chart depicting this process can be seen in Fig 4.

**Calculated Values of the Gas Concentration in a Chamber.**

The above techniques have been used to calculate the gas concentration in a 1m³ chamber at 22°C with a starting RH of 10%, 30% and 50% with a liquid injection rate of 35% w/w solution of hydrogen peroxide of 2 grams/minute. The results of the calculations shown in Fig 5 assume that the temperature throughout remains constant. As stated earlier it is possible to perform the same calculation but against a changing temperature profile. The initial peak in gas concentration is at the point when condensation first occurs and is dependent upon the initial relative humidity in the chamber. After the first bead

N.B. equations (17) and (18) cannot be calculated until \( F_{\text{TOT}} \) is calculated in equation (19). Hence the order shown must always be followed.

**Fig 4**

N.B. equations (17) and (18) cannot be calculated until \( F_{\text{TOT}} \) is calculated in equation (19). Hence the order shown must always be followed.
of condensation has formed the gas concentration falls very rapidly towards the equilibrium value of the evaporated liquid, but on aeration the gas concentration is again seen to rise.

The rise in concentration during aeration is caused by a change in the concentration of the condensate. Because water has a higher vapour pressure than hydrogen peroxide it evaporates more rapidly causing the condensate to become more concentrated. The increase in concentration of the condensate leads to a higher hydrogen peroxide gas concentration.

The hydrogen peroxide gas concentration will continue to rise until all of the condensate has evaporated at which point the gas concentration will start to fall through dilution.

A further set of calculations has been performed to establish the affect of the chamber temperature and initial relative humidity on the peak gas concentration. The results of these calculations are shown in Fig 6.

As would be expected the peak gas concentration is higher when the initial relative humidity is low and when the chamber temperature is high. If condensation were the most important factor in the killing mechanism of microorganisms then from Fig 6 it would be expected that low temperatures and high initial relative humidity would cause faster condensation and hence quicker kills. It should also be noted that the concentration of the first bead of condensation is dependent on the starting RH and the temperature. Set out in Table 1 are the calculated values of the concentration of the first bead of condensation at various values of the starting RH and temperature.
The calculations in Table 1 were performed assuming that the evaporated liquid had a concentration of 35% w/w. It is interesting to note that the concentration of the condensate is significantly higher than the evaporated liquid. Also that the starting RH has a greater influence on the concentration than the temperature.

### Types of Hydrogen peroxide Gas Generators

It was stated earlier that commercial hydrogen peroxide gas generators all use a flash evaporation technique. There is, however, a significant difference between the two main types of generators available. Both are closed loop systems circulating the gas from the generator to the isolator and then back to the generator. In one design the catalyst, dryer and vaporiser are confined in a single loop so that the gas is decomposed on returning to the generator and fresh liquid is evaporated into the air stream. In the other design there is a dual loop. In one branch, used for pre-conditioning and aeration, the returning gas passes over a catalyst and then through a dryer before being returned to the chamber. In the second branch, used for gassing, the returning gas is heated and then more hydrogen peroxide is flash evaporated into the carrier gas. Hence during the gassing phase the returning gas does not pass through the catalyst and the dryer. This Dual Loop system will give results identical to those calculated above assuming there is no decomposition of the gas.
The Single Loop system will have different characteristics because the returning hydrogen peroxide gas is decomposed and the gas stream is dried, then further amounts of sterilant are flash evaporated into the gas stream before it is returned to the chamber. The mass of water and hydrogen peroxide removed from the circulating gas stream will vary depending on the conditions inside the chamber. Also the mass of the water in the air stream being delivered to the flash evaporator will almost certainly be different from the starting RH in the chamber, because it passes through the dryer inside the generator. These factors will alter the mass balance inside the chamber and allowances must be made for the mass of hydrogen peroxide and water removed in the gas mixture returned to the generator and also the condition of the air being fed to the evaporator inside the generator. It is however possible to make some adjustments to the calculation method to allow for the processing of the returning gas. As the volumetric flow, liquid evaporation rate, and the efficiency of the dryer are all known then the condition of the air/gas mixture being supplied to the chamber is also known.

A theoretical calculation may then be made as to the rate of increase or decrease of water vapour and hydrogen peroxide gas inside the chamber assuming perfect mixing of the gasses. The proportion of fluid removed from a chamber is given by the equation:

\[ \text{Fluid removed} = 1 - e^{-N} \]  

(20)

Where \( N \) is the number of fluid changes and is calculated from the volume of the chamber and the fluid flow rate and elapsed time.

This theoretical equation is modified in clean room technology to account for the imperfect mixing of the gas entering the room, and it is assumed that one air change removes half of the original air within the room. It is possible to use either the theoretical or the practical calculation to estimate the rate of change of mass in the chamber. Using the theoretical equation leads to a faster rate of change in both the increase and decrease of the masses within the chamber, but the shape of the gas concentration and mass of condensate curves remain the same.

**Comparison of the Single and Dual Loop Gas Generator Systems**

It is common practice to create a high concentration gas in the generator by flash evaporation at the start of a gassing cycle, typically in excess of 2000 ppm. This high concentration of gas is delivered at an elevated temperature to the chamber where it is dilated and is cooled by the gas already present in the chamber. With the single loop generator some of the gas will be returned to the generator and decomposed in the catalyst.
Using the technique described above it is possible to calculate the time to reach condensation for both types of gas generator. The time will of course depend on the size of the chamber or room, the rate of injection, the temperature in the room and the starting relative humidity. For comparison purposes only, a calculation has been performed assuming a room of 100 m$^3$ and a temperature of 20°C. The impact of the level of relative humidity, at the start of gassing may be seen in Fig 7 below.

![Time to Reach Condensation v Starting Relative Humidity](image)

**Fig 7**

It is interesting to note that decomposing the return gas has a significant effect on the time taken to reach the initial point of condensation.

**Experimental Methods and Results**

Two experiments have been performed to test the accuracy of the derived equations.

Both of these experiments were conducted using isolators that were installed in pharmaceutical manufacturing facilities.

The first experiment was conducted using a 6 glove flexible film isolator in a room which was controlled at 20+/-2°C. A dual loop gas generator was connected to the isolator so that the gas was injected directly into the isolator, i.e. not through the isolator filters. The gas generator produced a flow of 30m$^3$/hour with a delivery temperature from the generator of 60°C. The temperature of the gas being injected into the chamber was a little lower at 55°C because of heat loss in the delivery hose and the thorough the insulated inlet filter. The isolator pressure was controlled by the gas generator at about 40Pa.

The conditioning phase of the gassing cycle was set to reduce the relative humidity in the isolator to 40% RH. This was then followed by a gassing phase during which 35% w/w hydrogen peroxide solution was flash evaporated into the carrier gas stream at the rate of 2.5 gms/minute for 10 minutes. There followed a much longer period of 60 minutes during which 1.5 gms/minute were evaporated into the carrier gas stream. At the end of the second gassing phase the generator was switched to aeration mode to remove the hydrogen peroxide from the chamber.
A Siemens PLC controls the Clarus C with the facility to log all of the data from the Clarus instrumentation. This data was then downloaded into Excel and graphs produced of the results.

The technique to calibrate the gas sensor was described by Dr. Brian Webb in the PDA Journal (4). It was noted during the calibration of the sensor that it had a slow response time and that recovery after exposure was also slow. However, this is the only type of cell that has a published calibration technique to a reliable standard, and was therefore used in the experiment.

The actual and calculated gas concentrations are shown in Fig 8 above. It may be seen from the graph of the calculated values that the gas concentration rises rapidly and then falls as condensation forms. The measured gas concentration followed the same rise and fall but because of the response and recovery of the sensor the plot of measured values lags behind the predicted ones. The measured gas concentration also shows a rise at the start of aeration as predicted and illustrated in Fig. 5.

The condensation level as measured by the monitor was also recorded and is shown plotted in Fig 9 and compared with the calculated values. The monitor used has been described by D. Watling at the ISPE Barrier Conference (5) and is based on the work of M. –A. Marcus-Martin (6). There is no direct numerical relationship between the condensation index and the mass of condensate, but Fig 9 clearly shows that the measured and calculated values show similar trends.
The second test was conducted using a single loop gas generator connected to a 4-glove stainless steel sterility test isolator. The isolator was in a clean room at a controlled temperature of 18°±2°C. The generator was configured for direct injection into the main chamber of the isolator and the isolator recirculating fan was left running but with the make-up and exhaust both sealed. Pressure control of the isolator was via the gas generator.

The mass of condensate was predicted and compared with the output from a condensation monitor. The gas generator was set for an initial conditioning/stabilisation phase of 8 minutes. The gassing phase was in two stages, initially at 6.4 grams/minute for 6 minutes reducing to 2.4 grams/minute for the next 16 minutes. The generator then moved to the aeration phase of the cycle. The calculations indicate that condensation should start at about 10 minutes from the start of the cycle i.e. two minutes into the gassing phase, reach a peak at 14 minutes and then fall off as the liquid evaporation rate is reduced. This corresponds to the output from the condensation monitor, which shows condensation starting at 10 minutes, rising to a peak at 14 minutes, and then falling away. The condensation monitor did not finally return to zero until about 22 minutes, probably caused by a lag in the instrument response. The results of this test are shown in Fig.9.

![Graph showing measured and calculated condensation](image)
Conclusion

The use of the standard vapour pressure equations and the application of fundamental chemical engineering process analysis principles allow a better understanding of the processes involved in gaseous hydrogen peroxide decontamination. The results are confirmed by experimentation despite the difficulties of making accurate measurements of the hydrogen peroxide gas concentration.

The analysis of the standard equations for the vapour pressure of aqueous mixtures of hydrogen peroxide show that unless very low concentrations of gas are produced (less than about 700ppm or 1mg/l) then condensation is unavoidable under typical room/isolator operating conditions.

The rate of hydrogen peroxide evaporation and the starting environment in the chamber are the key parameters in determining when and how much condensation will occur.

The concentration of the hydrogen peroxide gas and the liquid in the condensation layer in the enclosure will vary with time from initial transient high levels, and will move towards, but never reach, the equilibrium conditions of the solution that has been evaporated.

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