Oxygen Mass Flow Rate Generated For Monitoring Hydrogen Peroxide Stability

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H. Richard Ross
Lockheed Martin / GB Tech
NASA John C. Stennis Space Center
Stennis Space Center, MS 39529-6000

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Abstract

Recent interest in propellants with non-toxic reaction products has led to a resurgence of interest in hydrogen peroxide for various propellant applications. Because peroxide is sensitive to contaminants, material interactions, stability and storage issues, monitoring decomposition rates is important. Stennis Space Center (SSC) uses thermocouples to monitor bulk fluid temperature (heat evolution) to determine reaction rates. Unfortunately, large temperature rises are required to offset the heat lost into the surrounding fluid. Also, tank penetration to accommodate a thermocouple can entail modification of a tank or line and act as a source of contamination.

The paper evaluates a method for monitoring oxygen evolution as a means to determine peroxide stability. Oxygen generation is not only directly related to peroxide decomposition, but occurs immediately. Measuring peroxide temperature to monitor peroxide stability has significant limitations. The bulk decomposition of 1% / week in a large volume tank can produce in excess of 30 cc / min. This oxygen flow rate corresponds to an equivalent temperature rise of approximately 14 millidegrees C, which is difficult to measure reliably. Thus, if heat transfer were included, there would be no measurable temperature rise. Temperature changes from the surrounding environment and heat lost to the peroxide will also mask potential problems.

The use of oxygen flow measurements provides an ultra sensitive technique for monitoring reaction events and will provide an earlier indication of an abnormal decomposition when compared to measuring temperature rise.

Background

NASA with cooperation of the Air Force has taken the first steps to develop low cost upper stage technologies with the initiation of the Upper Stage Flight Experiment (USFE) with Orbital Sciences. A unique aspect of the USFE is the integration of a reusable hydrogen peroxide engine with a composite tank structure.

The USFE engine is a pressure fed H202 / JP8 design, which is totally focused on low cost expendable components. The engine has undergone hot test firings at Stennis Space Center and has achieved good results: Demonstrated C* efficiencies greater than 0.97; multiple
restarts; accumulated over 700 seconds of run time on silver based catalyst screens without performance degradation.

The nozzle construction is based on the on the ablative engine nozzle developed at Marshall Space Flight Center for the LOX / Fastrac engine. The chamber produces a vacuum thrust of 10,000 lbf using a 40:1 throat nozzle expansion. An USFE engine test is shown in Figure 1.

Figure 1. Orbital USFE 10K Engine Test at Stennis Space Center E Complex

Another unique aspect of the USFE is the composite storage tank. One of the key goals for the tank is to store peroxide for more than one year. Consequently, proper material selection is necessary to achieve long-term peroxide stability. Further validation of the tank design through subscale development is also ongoing. Real time monitoring to warn of accelerated decomposition is also needed to know when to dump the peroxide or when to take corrective measures to prevent a runaway reaction.

Detailed experiments conducted by Orbital Sciences show the peroxide decomposition rates of a subscale tank over a 34-week period. The experimental data shown in Graph 1 is based on subscale tank testing with 7 gallons fill volume of high-test peroxide.

Graph 1. Concentration in Weight % vs. Time for H2O2 in Subscale Tank from 2/19/99 through 10/1/99
The initiation point and decomposition rate at the curve elbow (dump limit for onset of a runaway reaction) were determined from the data in graph 1. The decomposition slope at the elbow region is 0.75% / week and provides a reference point to monitor peroxide reactions based on the flow of evolved oxygen from the tank vent line. The decomposition rate also accounts for the convective heat transfer (lost) from the vessel.

**Analytical Evaluation**

Analytical simulations based on subscale tank experiments performed by Orbital Sciences were conducted to: (1) determine if the mass flow rate of oxygen generated from the H$_2$O$_2$ tank at SSC can monitor decomposition and warn if a runaway reaction is imminent; (2) determine if temperature or O$_2$ is the most sensitive to monitor abnormal decomposition.

Stennis Space Center (SSC) uses thermocouples to monitor bulk fluid temperature (heat generation) to determine reaction rates. Unfortunately, large temperature rises are required to offset the heat lost into the surrounding fluid. Also, tank penetration to accommodate a thermocouple can entail modification of the tank and act as a source of contamination.

**Assumptions**

The analytical evaluation will consider 276 lbs. of 90% H$_2$O$_2$ to an incremental fill volume (total mass H$_2$O$_2$) present in the tank. The analysis assumes an overall bulk decomposition at an approximate temperature of 25deg C. Temperature rise is assumed uniform and adiabatic. All O$_2$ generated from decomposing H$_2$O$_2$ is measured as a gas flow rate at the tank vent line. A linear decomposition rate is applied. A constant decomposition rate over a time interval is considered. The normal decomposition of H$_2$O$_2$ for a Class 1 material is approximately 1% / year. The first (warning) alarm point is 1 wt % / month. The second (dump) alarm point is 0.75 wt % / week.

O$_2$ formation rate is dependent on total mass of H$_2$O$_2$ available, temperature, impurity types and concentration, surface area of the tank, and the condition of the wetted surfaces in contact with H2O2.

**Decomposition Reaction**

\[ 2 \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]

Every two moles (68 grams) of H$_2$O$_2$ yields one mole (32 grams) of O$_2$ gas and an energy release of 97.4kJ mole$^{-1}$. The equivalent heat of decomposition is 1240 BTU / lb.

As decomposition occurs in a liquid phase solution of H$_2$O$_2$ and water, the proportion of water that remains in solution depends on the temperature and the H$_2$O$_2$ concentration. For highly concentrated hydrogen peroxide solutions at temperatures near ambient, most of the water of the reaction remains in solution and the oxygen is evolved as a gas. The mole fraction of evolved oxygen and water of reaction is 47% and 53% respectively. The decomposition reactions are illustrated in equations 1 through 4.
90% H₂O₂ + 10% H₂O  \rightarrow  88% H₂O₂ + 10% H₂O + 2% (0.53 H₂O + 0.47 O₂) \ (1)

or

90% H₂O₂ + 10% H₂O  \rightarrow  88% H₂O₂ + 10% H₂O + (1.06 \% H₂O + 0.94\% O₂) \ (2)

or

90% H₂O₂ + 10% H₂O  \rightarrow  88% H₂O₂ + 11.06 \% H₂O + 0.94\% O₂ \ (3)

A 1% drop in H₂O₂ corresponds to 0.47% active oxygen lost. Since the oxygen is evolved as a gas, the true peroxide concentration in solution will actually decrease by 1.17% and not by 2%. The actual H₂O₂ concentration becomes 88.83%, not 88.00%.

90% H₂O₂ + 10% H₂O  \rightarrow  88.83\% H₂O₂ + 11.17\% H₂O \ (4)

**Analytical Simulation # 1**

Determine the O₂ generated in SCCM from 276lbs of 90% H₂O₂ that is decomposing at 1% per Month (Abnormal Flow Rate) and at 0.75% / Week (Exceptionally High Flow Rate). The maximum mass flow rate allowable by the tank venting system is 1.105 x 10⁷ sccm (Reference: PE USFE 009-010)

**Warning Alarm Point (1% H₂O₂ Lost / Month)**

**Approach 1**

276lbs of 90% H₂O₂ = 248.4 lbs of H₂O₂

1% (248.4 lbs of H₂O₂) / Month = 1% (116.748 lbs O₂ + 131.652 lbs H₂O) / Month

1% (248.4 lbs of H₂O₂) / Month = (1.17lbs O₂ + 1.32 lbs H₂O) / Month

H₂O₂  \rightarrow  H₂O + 1/2O₂

O₂ = (1.17 lbs of O₂ / Month) (1000cc/L) (11.2L / 0.5 Mole) (0.5 Mole O₂ / 16 Mole grams) (453.59g / lb) (Month / 30 Days) (1 Day / 24 hrs) (1 hr / 60 min) (298 K / 273 K)

O₂ = 9.4cc/min

**Approach 2 (Validation)**

O₂ = (1000cc/L) (22.4L / Mole) (Mole O₂ / 2 Moles H₂O₂) (2 Moles H₂O₂ / 68 grams) (453.59g / lb) (0.9 * 276 lb) (0.01 / Month) (1 Month / 30 Days) (1 Day / 24 hrs) (1 hr / 60 min) (298 K / 273 K)
O₂ = 9.4 cc/min

**Dump Alarm Point (0.75% H₂O₂ Lost / Week)**

*Approach 1*

0.75% (248.4 lbs of H₂O₂) / Week = 0.75% (116.748 lbs O₂ + 131.652 lbs H₂O) / Week

0.75% (248.4 lbs of H₂O₂) / Week = (0.876 lbs O₂ + 1.32 lbs H₂O) / Week

O₂ = (0.876 lbs of O₂ / Week) (1000 cc / L) (11.2 L / 0.5 Mole) (0.5 Mole O₂ / 16 grams)

(453.59 g / lb) (1 Week / 7 Days) (1 Day / 24 hrs) (1 hr / 60 min) (298 K / 273 K)

O₂ = 30 cc/min

*Approach 2 (Validation)*

O₂ = (1000 cc / L) (22.4 L / Mole) (Mole O₂ / 2 Moles H₂O₂) (2 Moles H₂O₂ / 68 grams)

(453.59 g / lb) (0.9 * 276 lb) (0.0075 / Week) (1 Week / 7 Days) (1 Day / 24 hrs) (1 hr / 60 min) (298 K / 273 K)

O₂ = 30 cc/min

**Analytical Simulation #2**

Determine the Bulk Temperature Rise for a 60 minute period of 276 lbs of 90% H₂O₂ that is decomposing at 1% per month (Warning Alarm Point) and validate the finding.

Determine the Bulk Temperature Rise for 30 and 60 minute periods of 276 lbs of 90% H₂O₂ that is decomposing at 0.75% per week (Dump Alarm Point).

**Calculations**

The Specific Heat for 90% H₂O₂ is 0.66 cal / g °C. 0.66 calories of heat energy is required to change the temperature of 1 gram of 90% H₂O₂ by 1 degree C. The heat released (ΔQ) from the peroxide is shown in equation 5. (Ref: CRC Handbook of Chemistry and Physics).

The Heat of Decomposition (ΔH) for 90% H₂O₂ is 1,108.4 BTU/lb of solution or 620 calories per gram of solution; for 100% H₂O₂, the ΔH is 1,240.1 BTU/lb or 693 calories per gram (Ref: H₂O₂ Physical Properties, FMC Technical Bulletin No. 67, 1969)

\[
\Delta Q = (M) (C) (\Delta T) \quad (5)
\]

\(\Delta Q = \) Heat Supplied to the Peroxide Solution from the Thermal Energy Released by Decomposition (Released Heat Energy)

M = Mass of the Peroxide
C = Specific Heat of the Peroxide

\[ \Delta T = \text{Temperature Rise} \]

By rearranging equation 4, the temperature rise from the heat generated by the peroxide decomposition can be calculated. The computation for \( \Delta T \) is shown in equation 6.

\[ \Delta T = \{(1/M)(1/C)\} \Delta Q \quad (6) \]

**Temperature Rise from 1.0 % H2O2 Decomposition Per Month @ a 60 Minute Interval**

\[ \text{H}_2\text{O}_2 \text{ Decomposed} = (276\text{lbs}) (1\% \text{ Lost / Month}) (60 \text{ min}) (\text{Month / 30 Days}) (1 \text{ Day / 24 hrs}) (1 \text{ hr / 60 min}) \]

\[ \text{H}_2\text{O}_2 \text{ Decomposed} = 0.00383 \text{ lbs. in a 90\% H}_2\text{O}_2 \text{ Solution} \]

\[ \Delta \text{H for 90\% H}_2\text{O}_2 = 1,108.4 \text{ BTUs/lb} \]

\[ \Delta \text{Q} = (0.00383 \text{ lbs}) (\Delta \text{H}) \]

Heat Energy Released = 4.24 BTUs

\[ \Delta T = (4.24 \text{ BTU}) (1/276\text{lbs}) (\text{g}^0\text{C} / 0.66 \text{ cal}) (252 \text{ cal / 1 BTU}) (1\text{lb / 453.59g}) \]

Temp Rise = 0.013 \text{ 0\degree C} \]

**Approach 2 (Validation)**

\[ \text{H}_2\text{O}_2 \text{ Decomposed} = (0.9)(276\text{lbs}) (453.59 \text{ g / lb}) (1\% \text{ Lost / Month}) (60 \text{ min}) (\text{Month / 30 Days}) (1 \text{ Day / 24 hrs}) (1 \text{ hr / 60 min}) \]

\[ \text{H}_2\text{O}_2 \text{ Decomposed} = 1.563\text{g} \]

\[ \Delta \text{H for 100\% H}_2\text{O}_2 = 1240.1 \text{ BTU / lb (693 calories / gram)} \]

Heat Released = (1.563g)(693cal/g)

Heat Energy Released = 1083.16 calories

\[ \Delta T = (1083.16 \text{ cal}) (\text{g}^0\text{C} / 0.66 \text{ cal}) (1/276\text{lbs}) (1\text{lb / 453.59g}) \]

Temp Rise = 0.013 \text{ 0\degree C} \]

**Temperature Rise from 0.75% H2O2 Decomposition Per Week @ a 30 Minute Interval**

\[ \text{H}_2\text{O}_2 \text{ Decomposed} = 276\text{lbs} (0.75\% \text{ Lost /Week}) (30\text{min}) (\text{Week / 7 Days}) (1 \text{ Day / 24 hrs}) (1 \text{ hr / 60 min}) \]
H₂O₂ Decomposed = 0.00616 lbs

ΔQ = (0.00616 lbs) (1,108.4 BTU/lb) = 6.83 BTU

ΔT = (6.83 BTU) (1/276lbs) (g°C / 0.66 cal) (252 cal / 1 BTU) (1 lb / 453.59 g)

Temp Rise = 0.17 °C

**Temperature Rise from 0.75% H₂O₂ Decomposition Per Week @ a 60 Minute Interval**

ΔT = (0.17 °C / 30 Min) (60 Min)

Temp Rise = 0.34 °C

**Analytical Simulation # 3**

Determine gas generated for a decomposition rate that would produce a localized 3 °C temperature rise for a volume of 90% Peroxide in a 1" Diameter x 12" Length pipe in 1 minute.

**Calculations**

Density of 90% H₂O₂ = 11.57 lbs/ gal or 86.7 lbs/ ft³

Mass of H₂O₂ = (86.7 lbs /ft³) (π) (0.5²) (12) (ft³/1,728in³)

Mass of H₂O₂ = 0.473 lbs

Energy required for a 3 °C Temperature Rise

ΔQ = 3 °C (0.473 lbs) (0.66 cal /g°C) (1 BTU / 252 cal) (453.59 g / lb)

ΔQ = 1.686 BTU

Mass of Peroxide Decomposed = (1.686 BTU) / (lb / 1,108.4 BTU)

Mass of Peroxide Decomposed = 0.00152 lbs

Convert Decomposed H₂O₂ to SCCM of O₂

9.4 cc/min = Flow Rate Produced from 276 lbs of 90% H₂O₂ that is decomposing at 1% per Month

0.00383 lbs = H₂O₂ Decomposed at a 1.0 % Decomposition Rate Per Month for 60 Minutes

O₂ sccm = (0.00152lbs /1min) (60 Min) (9.4 sccm) / (0.00383 lbs)

O₂ sccm = 223.8 = 224 sccm
Results

Three different scenarios were evaluated. The first evaluation assumes an overall bulk decomposition of a drum (276 lbs) of 90% peroxide. Temperature rise is assumed uniform and adiabatic. Results show that for an oxygen generation of 9.4 cc/min (first indication of abnormal decomposition) the temperature rise is less than 0.02 deg C. This is an immeasurable temperature rise. The second analytical evaluation is the same as the first except it assumes an oxygen flow of 30 cc/min (peroxide tank dump limit as proposed by OSC). The calculated temperature rise for this measured flow rate is 0.2 deg. C. Again, nearly immeasurable. The last scenario assumes a localized decomposition confined to a 1’ x 12” pipe, in which a 3 deg C temperature rise is measured in a period of 1 minute. The calculated oxygen flow rate is nearly 225 sccm, clearly exceeding the proposed alarm and dump limits.

Conclusion

The analysis study shows the advantage of monitoring oxygen flow for assessing peroxide stability. Oxygen generation is not only directly related to peroxide decomposition, but can be measured in real time. Measuring peroxide temperature as a means of monitoring peroxide stability has significant shortcomings. The first is that a bulk decomposition of 0.75% / Week (Dump Limit) from 276 lbs of 90% peroxide at 25 deg C. produces 30 sccm. This flow rate corresponds to an equivalent temperature rise of approximately 14 millidegrees C, which is difficult to measure reliably. Thus, if heat transfer were included, there would be no measurable temperature rise. Secondly, temperature changes from the surrounding environment and heat lost to the peroxide will also mask potential problems. As shown in the last study, a 3 deg C temperature rise may show an indication of a problem. When peroxide decomposition rate is monitored by oxygen generation, the oxygen flow rates are a factor of 20 higher than the first alarm (warning) point.

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**Author(s):**
Richard Ross

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