Oxygen Mass Flow Rate Generated For Monitoring Hydrogen Peroxide Stability

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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.

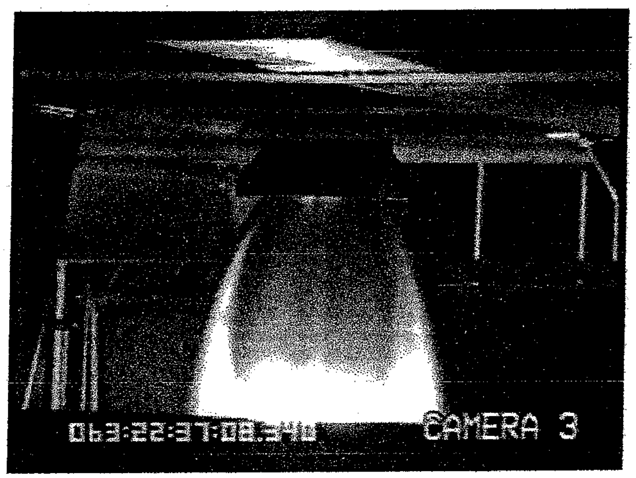
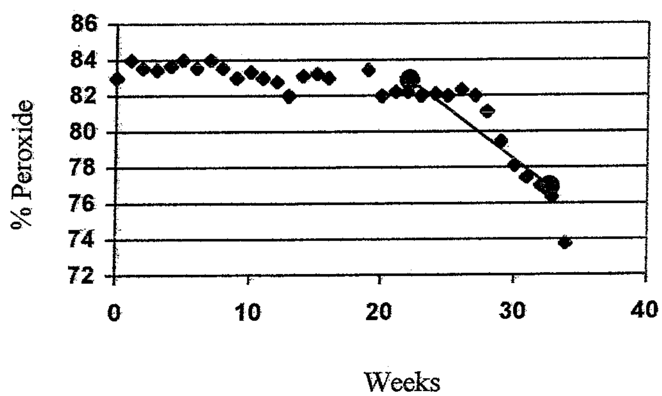


Figure 1. Orbital USFE 10K Engine Test at Stennis Space Center E Complex

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 H202 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_2O_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_2O_2 to an incremental fill volume (total mass H_2O_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_2O_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_2O_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_2O_2 available, temperature, impurity types and concentration, surface area of the tank, and the condition of the wetted surfaces in contact with H202.

Decomposition Reaction

$$2\,H_2O_2 \longrightarrow 2H_2O + O_2$$

Every two moles (68 grams) of H_2O_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_2O_2 and water, the proportion of water that remains in solution depends on the temperature and the H_2O_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.

$$90\%\ H_2O_2 + 10\%\ H_2O \longrightarrow 88\%\ H_2O_2 + 10\%\ H_2O + 2\%\ (0.53\ H_2O + 0.47\ O_2) \quad \textbf{(1)}$$

or

$$90\%\ H_2O_2 + 10\%\ H_2O \longrightarrow 88\%\ H_2O_2 + 10\%\ H_2O + (1.06\ \%\ H_2O + 0.94\%\ O_2) \quad \textbf{(2)}$$

or

$$90\%\ H_2O_2 + 10\%\ H_2O \longrightarrow 88\%\ H_2O_2 + 11.06\ \%\ H_2O + 0.94\%\ O_2 \quad \textbf{(3)}$$

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%.

$$90\%\ H_2O_2 + 10\%\ H_2O \longrightarrow 88.83\%\ H_2O_2 + 11.17\%\ H_2O \quad \textbf{(4)}$$

Analytical Simulation # 1

Determine the O_2 generated in SCCM from 276lbs of 90% H_2O_2 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 1.105×10^7 sccm (Reference: PE USFE 009-010)

Warning Alarm Point (1% H_2O_2 Lost / Month)

Approach 1

276lbs of 90% H_2O_2 = 248.4 lbs of H_2O_2

1% (248.4 lbs of H_2O_2) / Month = 1% (116.748 lbs O_2 + 131.652 lbs H_2O) / Month

1% (248.4 lbs of H_2O_2) / Month = (1.17lbs O_2 + 1.32 lbs H_2O) / Month

$$H_2O_2 \longrightarrow H_2O + 1/2O_2$$

O_2 = (1.17 lbs of O_2 / Month) (1000cc/L) (11.2L / 0.5 Mole)) (0.5 Mole O_2 / 16 Mole grams) (453.59g / lb) (Month / 30 Days) (1 Day / 24 hrs) (1 hr / 60 min) (298 K / 273 K)

O_2 = 9.4cc/min

Approach 2 (Validation)

O_2 = (1000cc/L) (22.4L / Mole) (Mole O_2 / 2 Moles H_2O_2) (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)

$O_2 = 9.4$ cc/min

Dump Alarm Point (0.75 % H2O2 Lost / Week)

Approach 1

0.75 % (248.4 lbs of H_2O_2) / Week = 0.75% (116.748 lbs O_2 + 131.652 lbs H_2O) / Week

0.75% (248.4 lbs of H_2O_2) / Week = (0.876 lbs O_2 + 1.32 lbs H_2O) / Week

O_2 = (0.876lbs of O_2 / Week) (1000cc / L) (11.2 L / 0.5 Mole) (0.5 Mole O_2 / 16 grams) (453.59g / lb) (1 Week/ 7 Days) (1 Day / 24 hrs) (1 hr / 60 min) (298 K / 273 K)

$O_2 = 30$ cc/min

Approach 2 (Validation)

O_2 = (1000cc/L) (22.4L / Mole) (Mole O_2 / 2 Moles H2O2) (2 Moles H2O2 / 68 grams) (453.59g /lb) (0.9 * 276 lb) (0.0075 / Week) (1 Week / 7 Days) (1 Day / 24 hrs) (1 hr / 60 min) (298 K / 273 K)

$O_2 = 30$ cc/min

Analytical Simulation #2

Determine the Bulk Temperature Rise for a 60 Minute Period of 276lbs 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 276lbs of 90% H2O2 that is decomposing at 0.75% per Week (Dump Alarm Point).

Calculations

The Specific Heat for 90% H_2O_2 is 0.66cal / g ^{0}C. 0.66 calories of heat energy is required to change the temperature of 1 gram of 90% H_2O_2 by 1 degree C. The heat released (Δ Q) from the peroxide is shown in equation 5. (Ref: CRC Handbook of Chemistry and Physics).

The Heat of Decomposition (ΔH) for 90% H_2O_2 is 1,108.4 BTU/ lb of solution or 620 calories per gram of solution; for 100% H_2O_2, the ΔH is 1,240.1 BTU / lb or 693 calories per gram (Ref: H_2O_2 Physical Properties, FMC Technical Bulletin No. 67, 1969)

$$\Delta Q = (M)\,(C)\,(\Delta T) \qquad (5)$$

Δ 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

Δ T = Temperature Rise

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

$$\Delta T = \{(1/M)(1/C)\}\ \Delta Q \quad \textbf{(6)}$$

Temperature Rise from 1.0 % H202 Decomposition Per Month @ a 60 Minute Interval

H_2O_2 Decomposed = (276lbs) (1% Lost / Month) (60 min) (Month / 30 Days) (1 Day / 24 hrs) (1 hr / 60 min)

H_2O_2 Decomposed = 0.00383 lbs. in a 90% H_2O_2 Solution

ΔH for 90% H_2O_2 = 1,108.4 BTUs/lb

Δ Q = (0.00383 lbs) (ΔH)

Heat Energy Released = 4.24 BTUs

ΔT = (4.24 BTU) (1/276lbs) (g^0C / 0.66 cal) (252 cal / 1 BTU) (1lb / 453.59g)

Temp Rise = 0.013 ^0C

Approach 2 (Validation)

H_2O_2 Decomposed = (0.9)(276lbs) (453.59 g / lb) (1% Lost / Month) (60 min) (Month / 30 Days) (1 Day / 24 hrs) (1 hr / 60 min)

H_2O_2 Decomposed = 1.563g

ΔH for 100% H_2O_2 = 1240.1 BTU / lb (693 calories / gram)

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

Heat Energy Released = 1083.16 calories

ΔT = (1083.16 cal) (g^0C / 0.66 cal) (1/276lbs) (1lb / 453.59g)

Temp Rise = 0.013 ^0C

Temperature Rise from 0.75% H202 Decomposition Per Week @ a 30 Minute Interval

H_2O_2 Decomposed = 276lbs (0.75% Lost /Week) (30min) (Week / 7 Days) (1 Day / 24 hrs) (1 hr / 60 min)

H_2O_2 Decomposed = 0.00616lbs

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

ΔT = (6.83 BTU) (1/276lbs) (g^0C / 0.66 cal) (252 cal / 1 BTU) (1 lb / 453.59g)

Temp Rise = 0.17 ^0C

Temperature Rise from 0.75% H202 Decomposition Per Week @ a 60 Minute Interval

ΔT = (0.17 ^0C / 30 Min) (60 Min)

Temp Rise = 0.34 ^0C

Analytical Simulation # 3

Determine gas generated for a decomposition rate that would produce a localized 3 ^0C temperature rise for a volume of 90% Peroxide in a 1″ Diameter x 12″ Length pipe in 1 minute.

<u>Calculations</u>

Density of 90% H2O2 = 11.57 lbs/ gal or 86.7lbs/ ft^3

Mass of H2O2 = (86.7 lbs /ft^3) (π) (0.5^2) (12) (ft^3/1,728in^3)

Mass of H2O2 = 0.473 lbs

Energy required for a 3 ^0C Temperature Rise

ΔQ = 3 ^0C (0.473lbs) (0.66cal /g ^0C) (1 BTU / 252cal) (453.59 g / lb)

ΔQ = 1.686 BTU

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

Mass of Peroxide Decomposed = 0.00152lbs

Convert Decomposed H_2O_2 to SCCM of O_2

9.4 cc/min = Flow Rate Produced from 276lbs of 90% H_2O_2 that is decomposing at 1% per Month

0.00383 lbs = H_2O_2 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 $\simeq$ 224 sccm

Results

Three different scenarios were evaluated. The first evaluation assumes an overall bulk decomposition of a drum (276lbs) 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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