Low Temperature Start & Operation Capability of 82% Hydrogen Peroxide Gas Generators*†

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Monopropellant Gas Generators find use in applications that demand high power density for time periods which are generally in excess of one minute. Additionally, the system level requirements are such that a complex bi-propellant system is not warranted. This paper seeks to document recent testing involving a monopropellant gas generator using 82% H_2O_2 under low temperature conditions involving both the fluid temperature and the initial hardware temperature. It is demonstrated that the Gas Generator design was able to achieve nominal start transient rates and C* efficiencies greater than 98%. Start and steady state operation was achieved with fluid and initial hardware temperatures of around zero (0°) Fahrenheit. This temperature is just above that of the freezing point of 82% H_2O_2 suggesting that the operational limit is the freezing point of the H_2O_2 solution. Comparisons are made with other liquid monopropellant gas generators systems, in particular hydrazine. The experimental test data opens operating conditions previously thought inaccessible to liquid monopropellant gas generators.

* This work was performed at Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under Contract DE-AC04-94AL85000.
† This work was sponsored by Defense Advanced Research Projects Agency STO, under the Strategically Hardened Facility Defeat Program. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressly or implied, of the Defense Advanced Research Projects Agency or the U.S. Government.
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Nomenclature

APU = Auxiliary Power Unit
C^* = Characteristic Exhaust Velocity (ft/s)
GG = Gas Generator
H_2O_2 = Hydrogen Peroxide
N_2H_4 = Hydrazine
RCS = Reaction Control System

I. Introduction

Rocket propellant driven gas generators (GG) find application primarily in aerospace and defense systems where short operational duration and high power density are a requirement. Additionally, gas generators are usually used to drive turbomachinery or similar equipment and consequently the exhaust products are generally held below 1700 °F[1]. These requirements are a natural fit for liquid monopropellant GGs which has historically been covered by hydrogen peroxide and hydrazine. Recently a GG using 82-81% H_2O_2 was developed and tested for low temperature start and operation. This paper covers the development testing and then compares the results with historical H_2O_2 monopropellant systems and also with historical hydrazine monopropellant systems.

II. Test Equipment Description

Hot fire testing was conducted at Purdue University's Zucrow Labs during December 2007 & January 2008. The test apparatus was a pressure fed test stand and a horizontally mounted test article (see Figures 1 & 2). The test stand comprises a 14 gallon (53 liter) run tank with a 1.0 inch (2.54 cm) horizontal exit run line into a 0.25 inch (0.635 cm) ball valve which acts as the fire valve. The fire valve is pneumatically driven with an estimated full open rate of around 100 ms. The ball valve exit is close-coupled to a manifold, which contains a venturi and is the physical mount for the GG. The manifold also contains ports for the purge check valve, the venturi inlet pressure port and the gas generator inlet port. The pressure transducers on both the venturi inlet and GG inlet are snubbed to prevent possible damage from water hammer. The purge pressure is set low enough to automatically stop during a hot fire run. The typical test is 10 seconds (100 seconds for endurance tests) in duration, with the purge on 1 second before and off 1 second after the fire valve is opened/closed for the test duration. Gaseous Nitrogen was used for both purge gases and as the primary pressurant in the run tank. The gas generator is P/N: GK-PD039-201-003 (see Figure 3) and has aft penetrations (four, equally spaced) for measurement of chamber pressure and chamber temperatures.

The test plan included gas generator wear-in followed by performance mapping of a single GG over various operating parameters which included low temperature propellant and hardware start. After performance mapping the GG was then endurance tested at the nominal conditions for a total accumulated time of 20 minutes. Nominal test conditions are shown in Table 1. Subsequent to the endurance testing it was found that there was sufficient propellant to further investigate the cold limits of the device.

Table 1 Nominal Gas Generators Test Conditions

Parameter	Value (English)	Value (SI)
Chamber Pressure	~1400 psia	~96 bar
Oxidizer Flow Rate	1.40-1.45 lbm/s	0.64 kg/s
GG Start Temperature	85+/-10 F	~30 °C
H_2O_2 Temperature	85+/-5 F	~30 °C
H_2O_2 Concentration	81-82% wt	

In summary a single GG was hot fire tested with:

- Wear-In
- Performance Mapping of 20 tests of 10 seconds each
- Endurance Testing (~100 sec each) to an accumulated test time of 20 minutes.
- Cold Limit Testing with tests of 10 seconds each.

The next section primarily covers the test performed during the Cold Limit portion of the test campaign. Data presented is taken at 1000 samples per second and is unfiltered. Derived parameters are adjusted for temperature effects on theoretical performance.

III. Cold Limit Experimental Test Results

Initial performance mapping tests suggested that the GG could operate with fluid temperatures below 35 °F (1.7 °C) and as such the final set of "Cold Limit" tests were conducted to investigate this. A natural lower barrier to investigate would be to get as close as possible to the freezing point of the H2O2 solution. Figure 4 shows the liquid-solid phase diagram for H_2O_2-H_2O solutions. As can be seen from the figure the minimum eutectic temperature occurs at a concentration of roughly 62% H_2O_2 around -67 °F (-55 °C). It is also noteworthy from the figure that H_2O_2 solutions will readily undergo significant supercooling. As noted from reference 7: "Tanks of hydrogen peroxide have been stored, without freezing for many years in climates where the temperature frequently is 10 to 15 °F (-5 to -8 °C) below the true freezing point. However, do not rely on the hydrogen peroxide supercooling during weeks of cold temperatures or where the solution must be transported or pumped at low temperatures." Also worth mentioning is that when concentrated H_2O_2 solutions do freeze, slush is first formed from the H_2O_2 which becomes thicker as the temperature is decreased. What occurs is that pure H_2O_2 crystals form which then lowers the concentration of the remaining solution and hence the freezing point until complete solidification occurs at the lower eutectic (-67 °F).[7] For the present test data the range of H_2O_2 tested was between 82-81% wt. Table 2 shows the range of freezing point as read from the data found in Figure 4. In particular for the final tests the solution was 81.3% H_2O_2 and as can be see from Table 2 this translates into a freezing point between roughly -4 °F (-20 °C) and -7 °F (-21.7 °C). During temperature conditioning of the H_2O_2 within the run tank with LN_2 it was noted that the temperature inside the run tank would pause at around -4 °F. This may have been an erroneous observation but was cause for notionally putting the "freezing point" at -4 °F (-20 °C). For operational simplicity and for a good round number lower target temperatures for the fluid and the hardware (GG) were put at 0 °F (-18 °C).

Table 2 Freezing Point Experimentally Determined Limits of 82-81% H2O2 Solutions[2]

H_2O_2	Lower Curve	Upper Curve
81.0%	-23.2 °C (-9.8 °F)	-20.7 °C (-5.3 °F)
81.3 %	-6.5 °F	-4.6 °F
82.0%	-21.4 °C (-6.5 °F)	-19.4 °C (-2.9 °F)

Prior tests (wear-in, performance mapping & endurance) had established a baseline of understanding of the nominal performance of the GG. The primary parameters of interest derived from measured data are: start time (time from initial chamber pressure rise to 90% of steady state), C* efficiency, catalyst bed pressure drop (difference between GG inlet pressure and chamber pressure), chamber pressure roughness (3 sigma zero to peak of mean). It was determined that the start times are between 450-350 ms, C* efficiencies > 98%, pressure drop around 50 psid and roughness < 1.5%. All of the these parameters are indicative of a well performing GG and as such if significant deviations were noted during testing for the cold limit, the testing would then indicate the lower limit. All of the prior tests were conducted with propellant above 35 °F (1.7 °C) which produced an exhaust temperature around 1000 °F (538 °C). Hence the first test to determine the cold limit was to lower the fluid to around 20 °F (- 6.7 °C) and heat up the GG to around 150 °F (65.5 °C), which would help the start condition. Subsequent tests decreased the fluid temperature and then followed by lowering the GG start temperature until performance significantly deviated.

Table 3 shows an overview of the last endurance test conducted (PU010808_002) and all of the cold limit tests. As can be seen from the table the GG was able to smoothly start and maintain operation without impacting the performance at 0 °F and GG start temp of 100 °F. Figures 5, 6 & 7 show the measured pressure and temperature response from the 10 second steady state run of test PU010808_005. The figures show smooth operation with no deviation from nominal performance other than the reduced exhaust gas temperature. From the data in Table 3 the reduced exhaust temperature decreases roughly 1.6 °F (0.89 °C) for every 1.0 °F (0.56 °C) reduction in H_2O_2 temperature. The venturi inlet temperature starts at a temperature between that of the conditioned H_2O_2 and the GG, and rapidly drives to the H_2O_2 temperature at startup as the cold fluid runs through the system.

Table 3 Cold Limit Temperature Conditions & Measured Performance

Test #	Fluid Temp	GG Start Temp	Start Time	C* Efficiency	Gas Temp Exhaust, Centerline	Comments
PU010808_002	86 °F (30 °C)	92 °F (33.3 °C)	~440 ms	98.9%	1025 °F (552 °C)	Lastendurance test Nominal start
PU010808_003	19 °F	150 °F	~350 ms	98.8%	992 °F	First cold test Nominal start
PU010808_004	2 °F	153 °F	~325 ms	98.5%	892 °F	Nominal start
PU010808_005	0 °F	104 °F	~400 ms	98.6%	886 °F	Nominal start
PU010908_001	0 °F	48 °F	~270 ms	98.9%	886 °F	Slight effect on start
PU010908_002	0 °F	35 °F	~175 ms	98.8%	884 °F	Some effect on start One light overshoot
PU010908_003	5 °F	0 °F	~520 ms	98.7%	890 °F	More pronounced effect on start Two slight overshoot

For test PU010908_001 the GG start temperature was again lowered (~50 °F) while maintaining the H_2O_2 temperature of ~ 0 °F. Although the pressure trace is not provided the GG did start and operate acceptably. The start time appears reduced, which is merely an artifact of a very mild hard start such that the first chamber pressure rise to be over 90% of steady state but not greater than the steady state value.

The subsequent test (PU010908_002) was with the GG start temperature further reduced to around the freezing point of water (conditioned with ice packed around the exterior) while keeping the fluid temperature at ~0 °F. The pressure and temperature responses are shown in Figures 8 & 9 and show that the GG started with a little spike and operated acceptably for the remainder of the test. Figure 10 & 11 show views of the plume during the start transient and during steady state. The start transient picture shows a plume of atomized fluid (assumed to be water) which is rapidly followed by a very nice looking exhaust plume. Note the ice wrapped around the exterior of the GG is visible in the photos.

The final test (PU010908_003) was to find the lower limit on temperature of 0°F/0°F on H_2O_2 and GG start temperature. Unfortunately, the actual H_2O_2 was a little higher, at around 5 °F. Figure 12 shows the GG prior to test with frost on the outside of the housing and nozzle. Figures 13 & 14 show the pressure and temperature response from the test in which the start transient has two spikes. The maximum peak is only about 20% greater than steady state values. Prior performance mapping showed that reduced valve rates can be used to reduce and likely eliminate the mild hard starts. Hence, it is concluded that the GG will start and operate nominally and is fully functional at start conditions of 0 °F & 0 °F for H_2O_2 and GG temperature. Or rather, that the lower operating temperature limits on hardware and fluid is just above the freezing point of the fluid.

IV. Comparison to Other Liquid Monopropellant Systems

The results from the Cold Limit tests discussed in the previous section seemed to be a new record for low temperature operation of hydrogen peroxide. A short literature review was conducted for comparison. The only other liquid monopropellant of significant historical use, hydrazine, was also investigated for comparison purposes. Table 4 shows the results of the literature search.

Items of note concerning the comparisons:

- Limited to US systems as the data was readily available. Russia uses a significant amount of 82% H_2O_2 but is not included here as the authors know little of their operational limits.
- All data is for catalytic decomposition of the monopropellants. Liquid, non catalytic gas generators are not considered.
- All hydrazine data is with Shell 405 as the catalytic material.
- Both hydrazine and hydrogen peroxide contract on freezing[7, 3] and do not burst containers like water. However, care must be taken to assure that no trapped cavities are created with frozen propellant in either case.

Inspection of the hydrazine portion of Table 4 suggests that the temperature of the fluid can be successfully driven to 5-10 °F above the freezing point. However, the lower limit for the catalyst is somewhere around 70-100 °F. As noted by the TRW study: "The results indicated that ignition delay increased rapidly below 100 °F … and the ignitions were accompanied by large overpressures"[5] Also starting from the lower temperature of 70-100 °F appears to have detrimental effect on the Shell 405 catalyst as noted in the Aerospace Corp study: "Some early work at the The Aerospace Corporation in a small scale reactor indicated that both low catalyst bed temperature (<70 °F) and low propellant temperature (40 °F) increased ignition delay time, resulting in large overpressure spikes and pulverization of the catalyst"[5]. As such for missions which require a great many pulses, the hydrazine catalyst bed lower limits are generally greater as suggested by Reference 4 & 5 at anywhere from 200 to 600 °F.

Table 4 Comparison of Hydrazine and Hydrogen Peroxide Lower Operating Limits

System	Fluid	Freezing Pt Fluid	Fluid Lower Limit	Hardware Lower Limit	Comment
Shuttle APU	N_2H_4	34 °F (1.3 °C)	45 °F	190 °F	Ref 4
TRW	N_2H_4		-	>100 °F	1967 Study, Ref 5
Aerospace Corp	N_2H_4		40 °F	70 °F	1969 Study, Ref 5
Pioneer Jupiter Probe	N_2H_4		-	> 70 °F	Ref 5
Fleetsatcom	N_2H_4		-	> 600 °F	Ref 5
Project Mercury	90-91% H_2O_2	11 °F[2] (-11.7 °C)	35-50 °F Flood-out Limit	35-50 °F Flood-out Limit	1960 Study, Ref 6 Matched Fluid & Hardware Temps
X-1B	90-91% H_2O_2		> Freezing	Trickle Preheat	Ref 10
X-15	90-91% H_2O_2		Heated Possible > 59 °F	Heated Possible > 59 °F	Ref 9
Scout	90-91% H_2O_2		40 °F	Probable Pulse Preheat	Ref 8
FMC	90-91% H_2O_2		> 50 °F	> 50 °F	Ref 11
GK-Sandia	81.3% H_2O_2	-5 °F (-20.6 °C)	~ 0 °F (-17.4 °C)	~ 0 °F (-18 °C)	Present Study Comparison Only

The historical H_2O_2 applications noted in Table 4 utilize 90-91% H_2O_2 and have lower fluid temperature limits of roughly 20-30 °F above the freezing point. It appears that utilizing separate thermal conditioning of the H_2O_2 and the catalytic device was not studied. Additionally, alternate methods of heating the catalytic devices were employed such as trickle preheat on X-1B. Reference 10 states that the feed lines were fed from the mother craft with a flow rate of 0.05 lbm/s with 80 +/-10 °F H_2O_2 such that the system stayed above freezing before the X-1B reached altitude of use for the RCS thrusters. Further Reference 8 suggest by the mass properties that H_2O_2 was used to pulse preheat the thrusters on stages 2 &3. Although not explicitly stated Reference 9 suggests that the entire system was kept above 59 °F using heaters to guard against the cool liquid oxygen onboard the vehicle. And finally, FMC standard design criteria calls for keeping both fluid and catalytic device above 50 °F.

Hence it seems that the present experimental study has established a new low record for operation with hydrogen peroxide, that of being just above the freezing point for both fluid and catalytic device conditioning. In addition, the device has demonstrated mild hard starts, which based upon historical evidence might not be possible with hydrazine.

V. Conclusion

Recent experimental work conducted at Purdue University utilizing 81-82% Hydrogen Peroxide on a new single gas generator has yielded the following results:

- Total accumulated on time in excess of 20 minutes with no adverse effects on gas generator performance.
- C* efficiencies in excess of 98% with low catalyst bed pressure drop.
- Chamber pressure roughness less than 1.5% on a 3 sigma basis (zero-to-peak of mean).
- Successful start and operation with 0 °F & 0 °F for H_2O_2 temperatures and gas generator start temperatures.
- The 0 °F low test limit is just above the freezing point of 82% H_2O_2 and appears to be a new record for low temperature operation of a liquid propellant monopropellant.

Acknowledgments

General Kinetics Inc and Sandia National Labs would like to thank DARPA for funding and guiding this project. Additionally, thanks to the staff at Purdue University Zucrow Lab who assisted greatly this testing. Specifically, the Zucrow Lab members: Scott E. Meyer, Jonathon Kubiak, Mark James & Vince Werner.

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Figure 1 – View Looking Into Test Cell of Test Stand (Blue Frame and White Insulation Blanket Over Run Tank). Test Article (Gas Generator) is Mounted Horizontally (Approximately Picture Center).

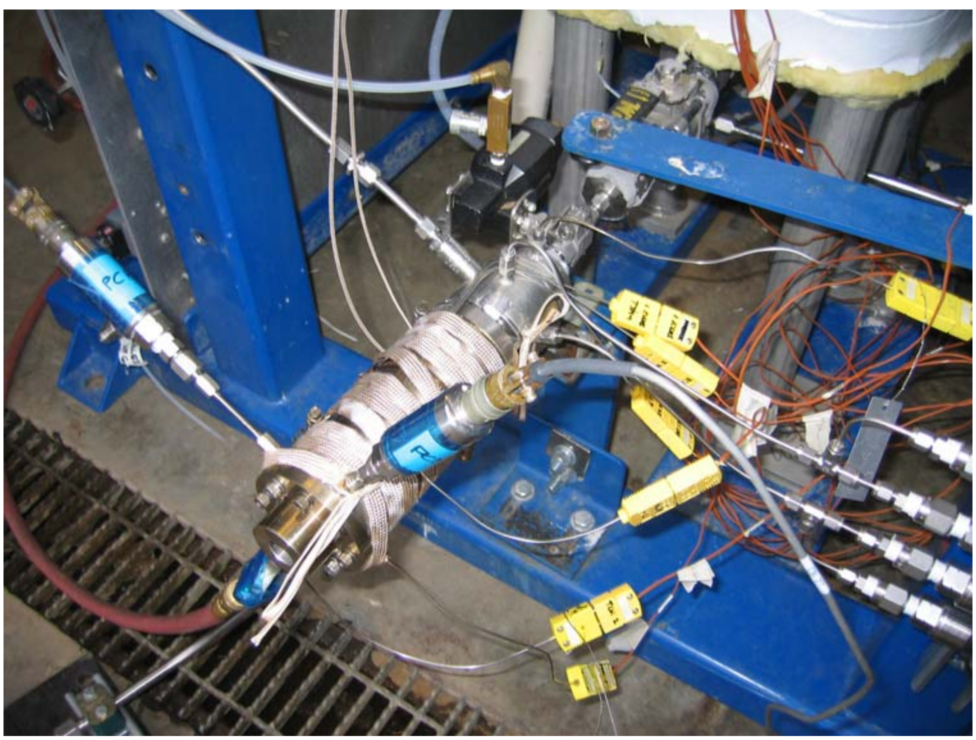

Figure 2 – Closer View of Gas Generator Wrapped With Tape Heater. Nozzle Is Bolted Onto GG In Lower Left of Picture. Upstream of GG is a Manifold (Where Tape Heater Ends) Which Houses the Flow Venturi and GG Inlet Pressure, Venturi Inlet Ports and Close Coupled Purge Check Valve (In Order).

Figure 3 – 82-81% H2O2 Gas Generator P/N: GK-PD039-201-003. GG is ~3 Inches (7.6 cm) in Diameter. Bottom is Exhaust End, One of the Four Instrumentation Ports are Shown In Photo.

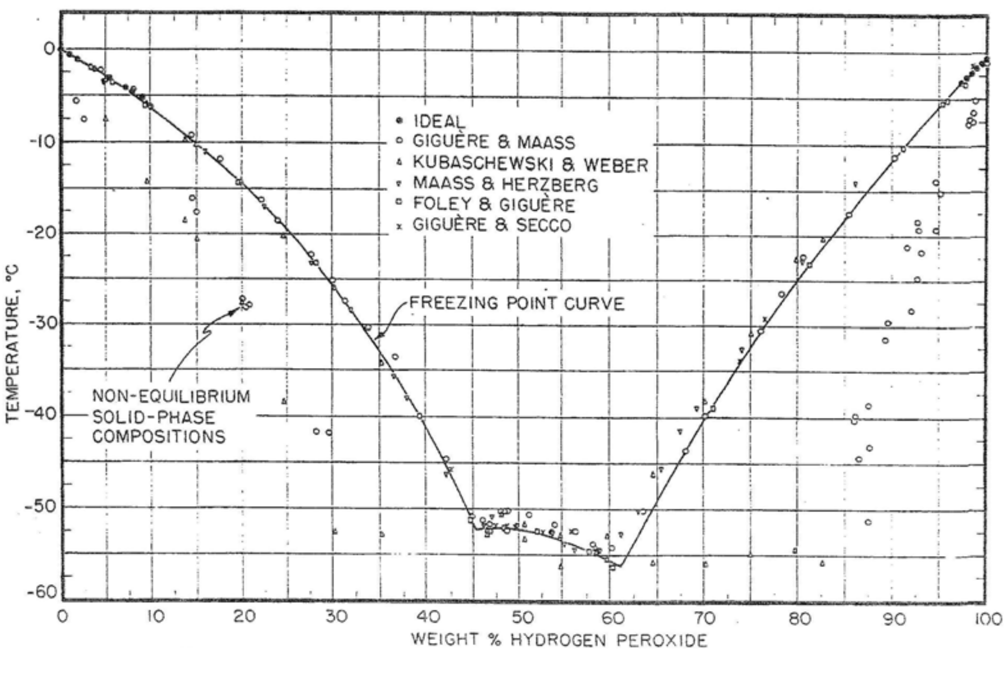

Figure 4 – Freezing Point of H_2O_2-H_2O Solutions, Ref. 2

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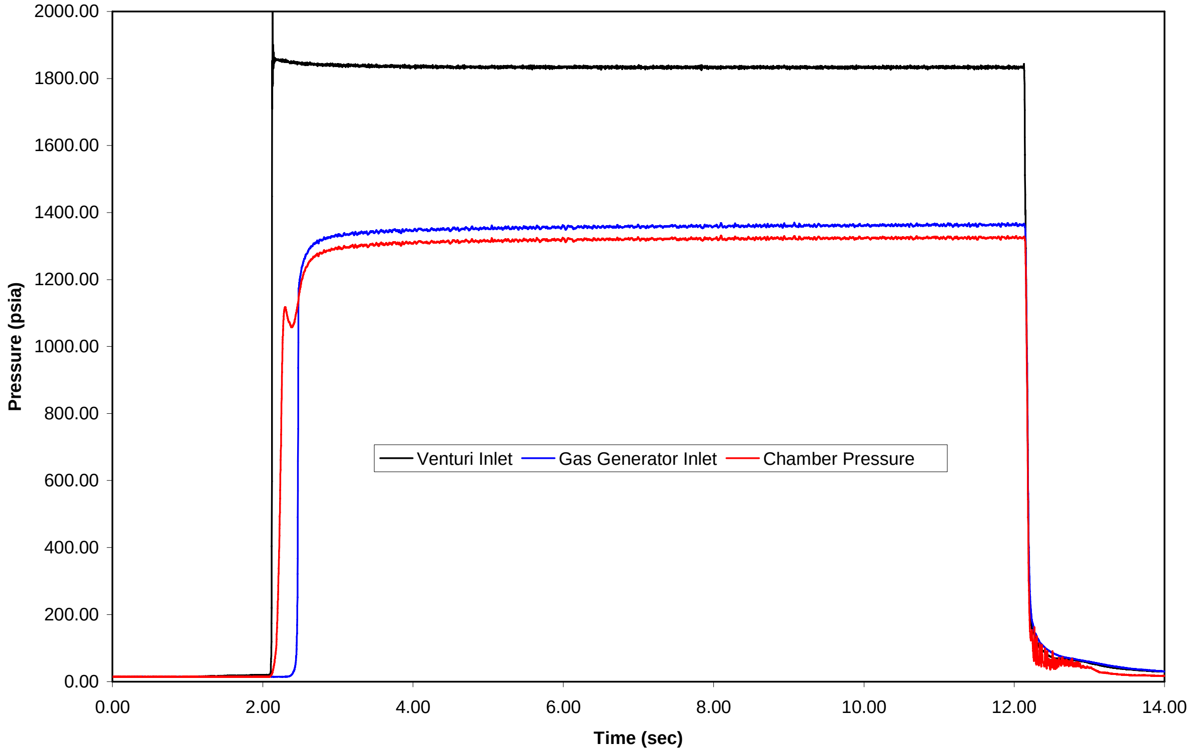

Figure 5 – Pressure Trace From Cold Limit Test PU010808_005. H_2O_2 Temperature ~ 0 °F and GG Start Temperature ~ 100 °F.

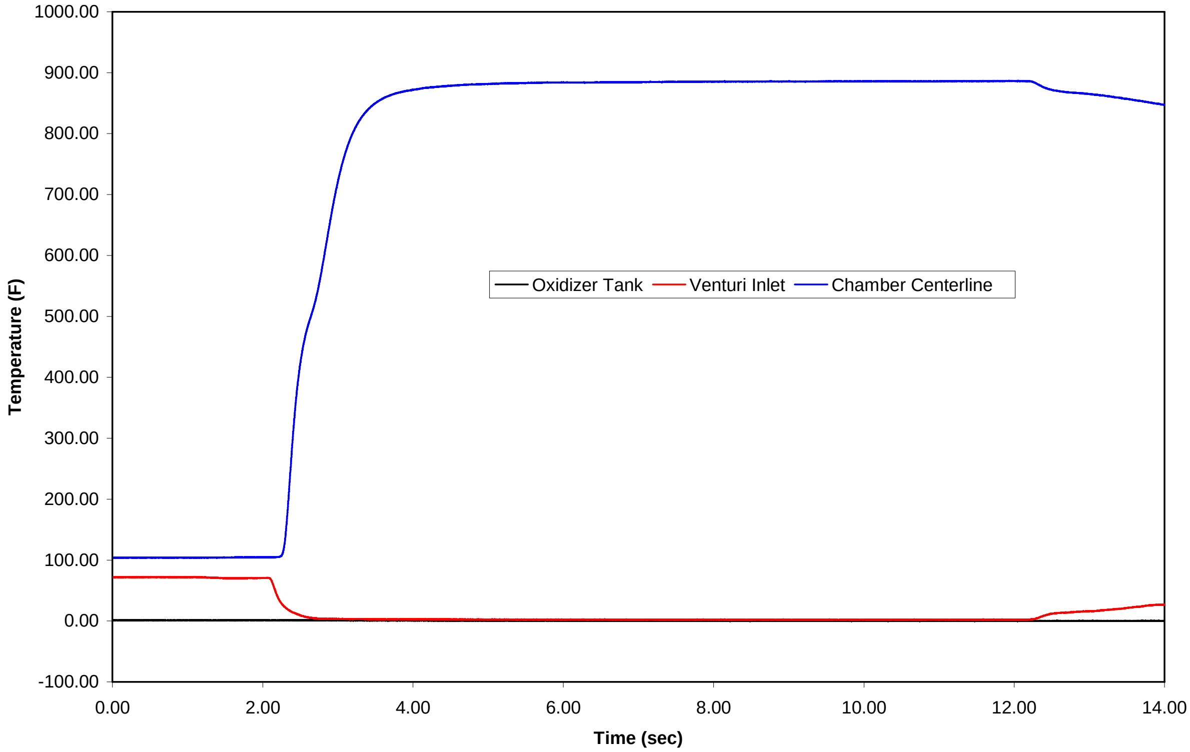

Figure 6 – Temperature Trace From Cold Limit Test PU010808_005. H_2O_2 Temperature ~ 0 °F and GG Start Temperature ~ 100 °F.

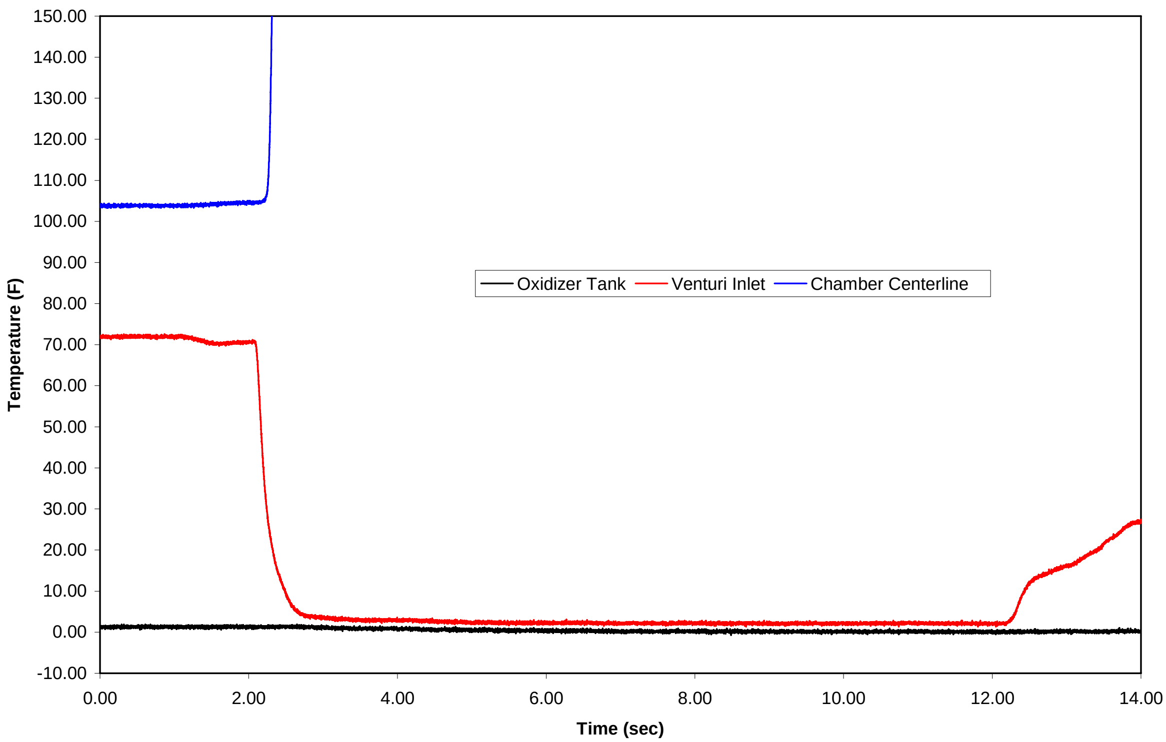

Figure 7 – Temperature Trace From Cold Limit Test PU010808_005. H_2O_2 Temperature ~ 0 °F and GG Start Temperature ~ 100 °F.

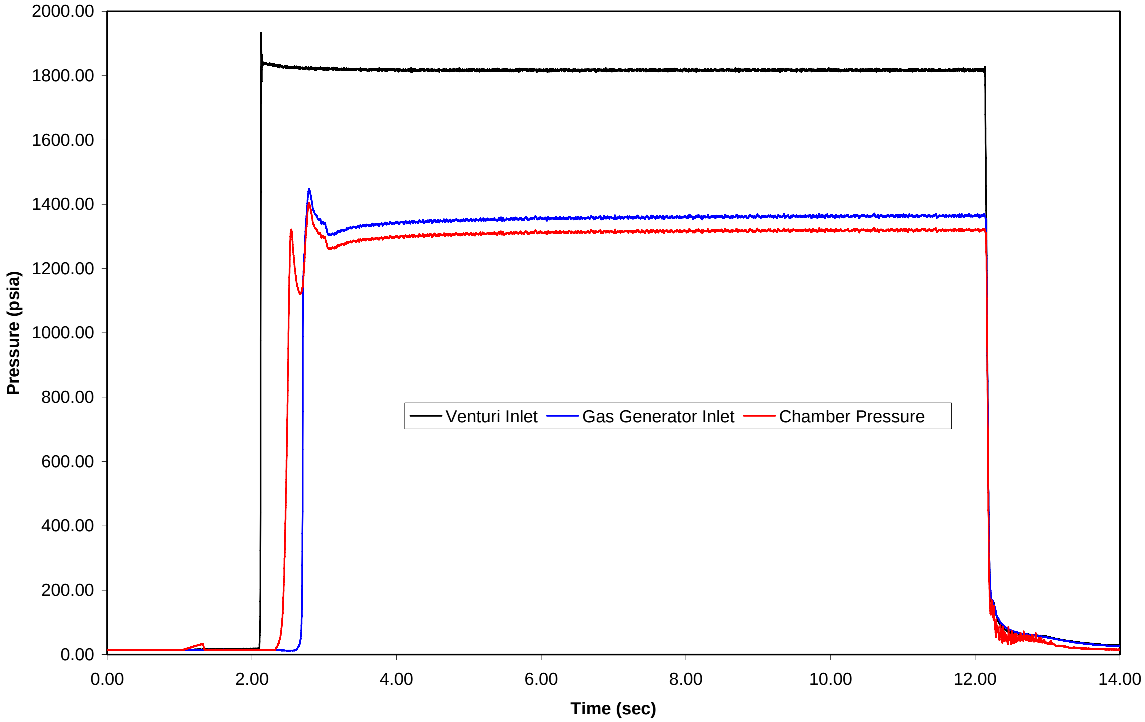

Figure 8 – Pressure Trace From Cold Limit Test PU010908_002. H_2O_2 Temperature ~ 0 °F and GG Start Temperature ~ 35 °F.

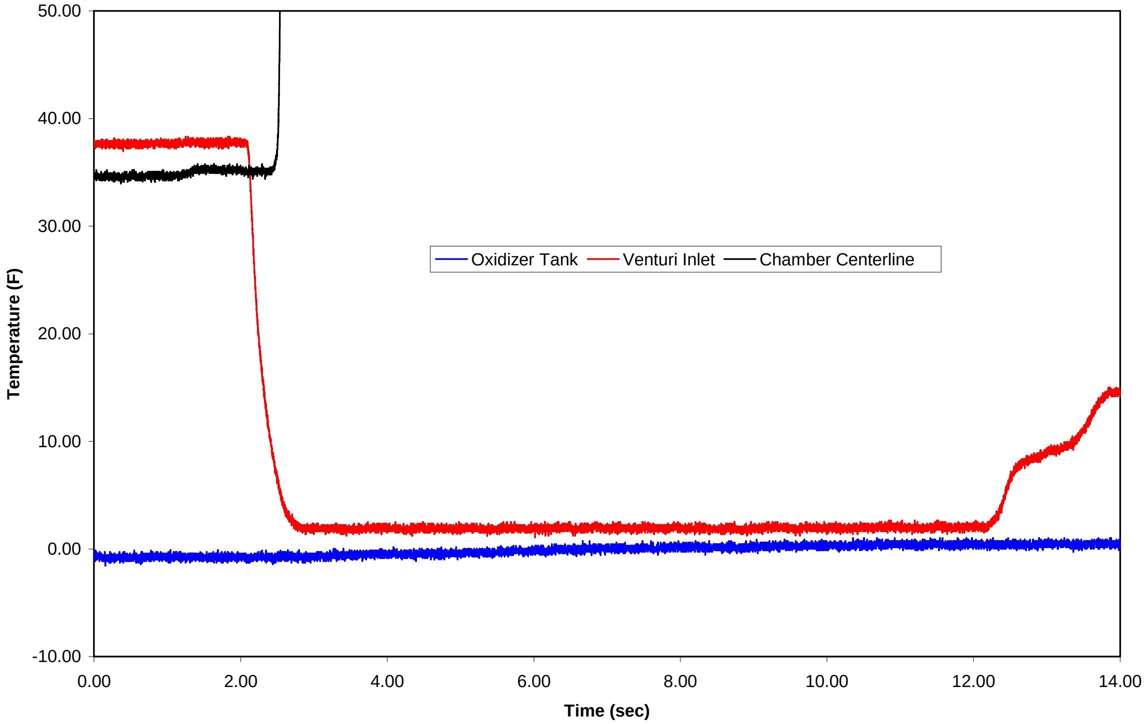

Figure 9– Temperature Trace From Cold Limit Test PU010908_002. H_2O_2 Temperature ~ 0 °F and GG Start Temperature ~ 35 °F.

Figure 10 – Start Transient for PU010908_002 (0 °F H_2O_2, 35 °F GG Start Temp)

Figure 11 – Steady State PU010908_002 (0 °F H_2O_2, 35 °F GG Start Temp)

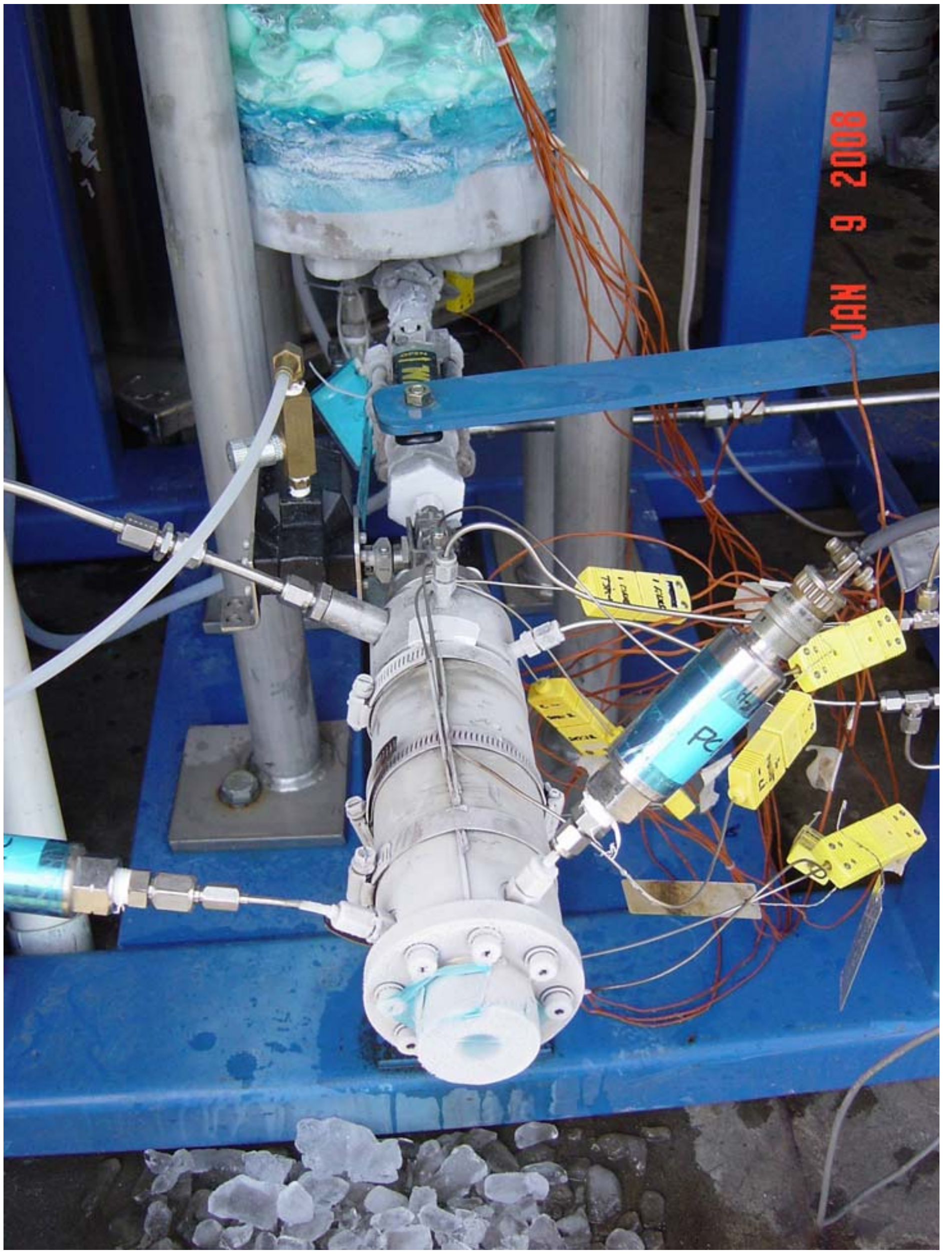

Figure 12 - GG Temperature Conditioned to ~0 F Prior to Test PU010908_003 (Fluid Temperature ~5 °F). Note The Frost On The Feed System and the GG. Also Note Tape Over the Nozzle Exit to Prevent Same Conditions on Interior of GG.

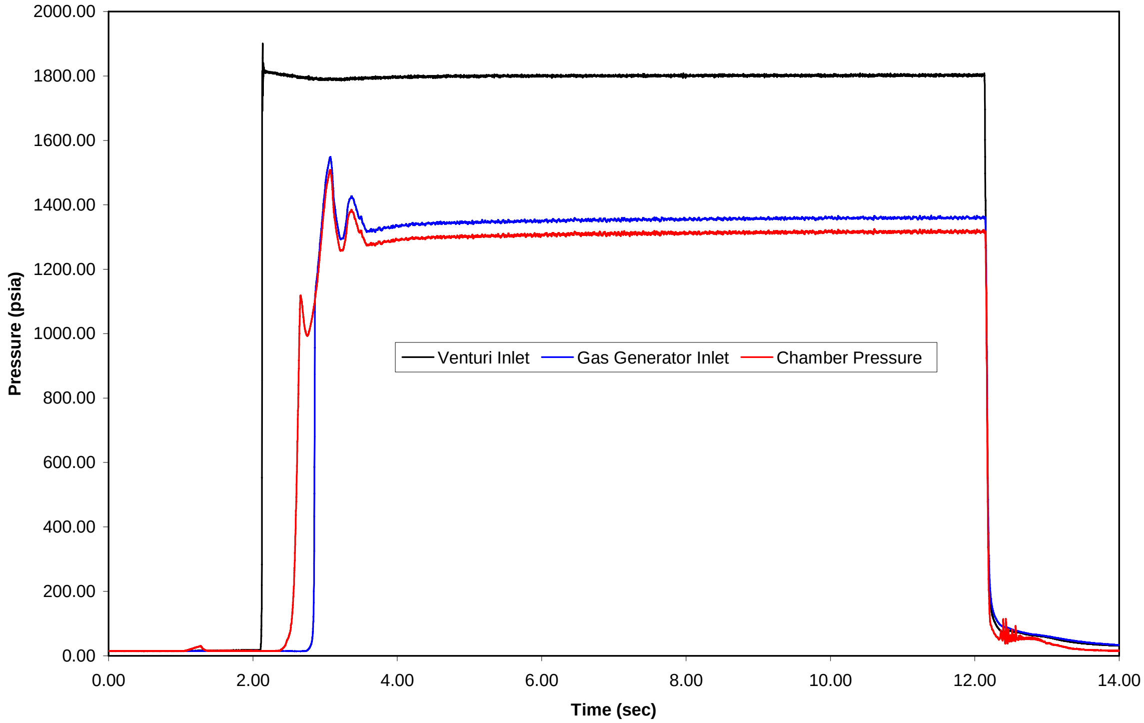

Figure 13 – Pressure Trace From Cold Limit Test PU010908_003. H_2O_2 Temperature ~ 5 °F and GG Start Temperature ~ 0 °F.

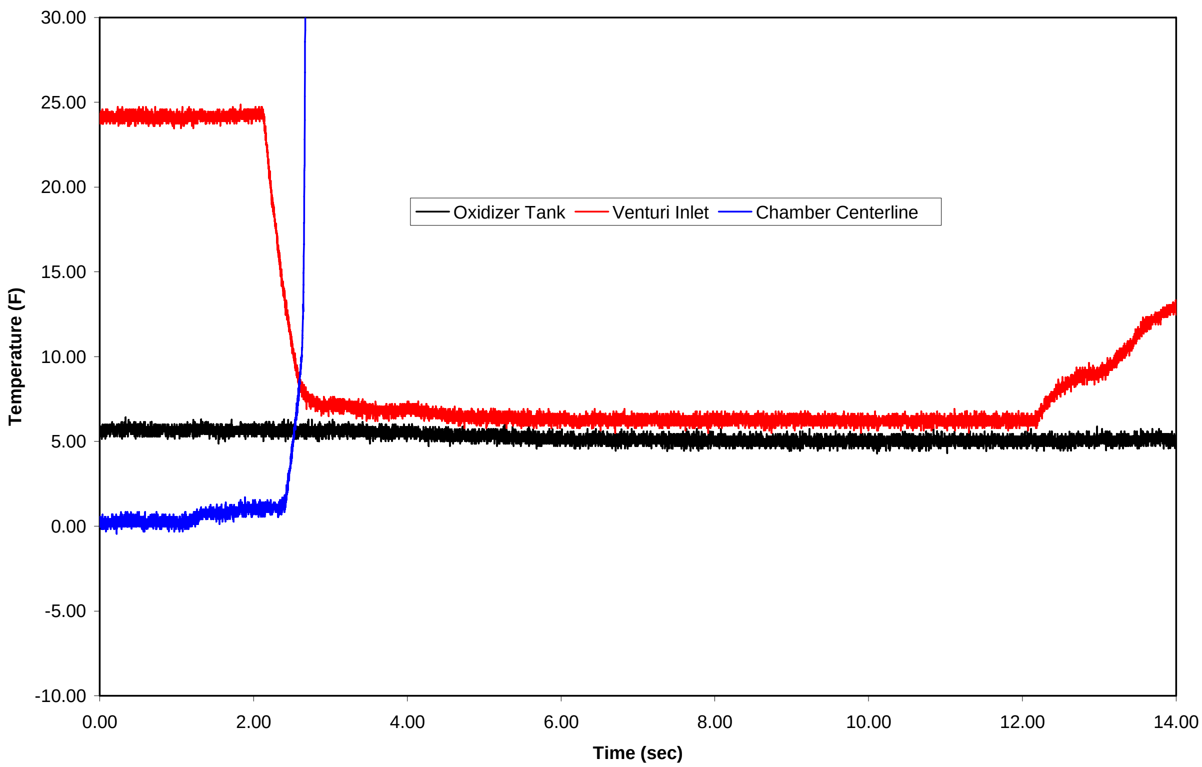

Figure 14 – Temperature Trace From Cold Limit Test PU010908_003. H_2O_2 Temperature ~ 5 °F and GG Start Temperature ~ 0 °F.