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The Impact of Ozone on the Lower Flammable Limit of Hydrogen in Vessels Containing Savannah River Site High Level Waste

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Abstract

The Savannah River Site, in conjunction with AREVA Federal services, has designed a process to treat dissolved radioactive waste solids with ozone. It is known that in this radioactive waste process, radionuclides radiolytically break down water into gaseous hydrogen and oxygen, which presents a well defined flammability hazard. Flammability limits have been established for both ozone and hydrogen separately; however, there is little information on mixtures of hydrogen and ozone. Therefore, testing was designed to provide critical flammability information necessary to support safety related considerations for the development of ozone treatment and potential scale-up to the commercial level. Since information was lacking on flammability issues at low levels of hydrogen and ozone, a testing program was developed to focus on filling this portion of the information gap. A 2-L vessel was used to conduct flammability tests at atmospheric pressure and temperature using a fuse wire ignition source at 1 percent ozone intervals spanning from no ozone to the Lower Flammable Limit (LFL) of ozone in the vessel, determined as 8.4%(v/v) ozone. An ozone generator and ozone detector were used to generate and measure the ozone concentration within the vessel *in situ*, since ozone decomposes rapidly on standing. The lower flammability limit of hydrogen in an ozone-oxygen mixture was found to decrease from the LFL

of hydrogen in air, determined as 4.2 % (v/v) in this vessel. From the results of this testing, Savannah River was able to develop safety procedures and operating parameters to effectively minimize the formation of a flammable atmosphere.

1. Introduction

The SRS waste tanks are carbon steel vessels, each approximately 4 million liters in volume. The 51 tanks, with various minor modifications in size, design and materials of construction, have been used since the 1950s to collect the high level nuclear waste generated as part of the national defense effort that supplied nuclear material for weapons, medicine, NASA and nuclear research campaigns. Currently, in support of the Federal Facilities Agreement Act, the tanks are being emptied, cleaned and grouted; and the waste permanently dispositioned in a series of specialized treatment processes. To date, of the original inventory of 400 million curies of radioactivity, approximately 40 million curies have been removed from the tanks. Most waste tanks have/had 3 distinct physical phases, a high pH supernatant top layer, a solid salt layer and a “sludge” layer (approximately 30 volume % solids in 70 volume % liquid). The solids are mainly metal hydroxides and oxides of radionuclides, primarily isotopes of plutonium and uranium, in addition to sodium, iron and aluminum. In general, the majority of the waste removal is accomplished by a Bulk Waste Removal (BWR) campaign which empties the tank of easily accessible liquid supernatant and other liquid, followed by salt dissolution/removal and, finally, heel removal. At the end of the BWR campaign, fewer than 20,000 liters of sludge (less than 2 inches depth) remains in the tank. Currently, this final residual material is cleaned from the tank during a process called Bulk Oxalic Acid Cleaning (BOAC), whereby heated, 6 weight percent oxalic acid is added to the tank to a sufficient level to enable mixing. The solution is then vigorously mixed, encouraging soluble material to be dissolved into solution and the insoluble material to be entrained in the rapidly moving fluid. The resulting slurry is transferred out, usually in a 3 strike campaign, to a receipt tank where it is neutralized prior to further processing. While BOAC has been effective in sludge dissolution and removal, the metal oxalates formed during oxalic acid dissolution cause downstream complications during evaporation (e.g. foaming) in addition to requiring excessive sludge washing (thereby greatly increasing the overall volume of waste to be dispositioned) to meet feed qualifications of the Defense Waste Processing Facility. This prompted research, testing and acceptance of a treatment process that utilized the proven effectiveness of oxalic acid for sludge dissolution and mobilization, yet removed the offending metal oxalates from the solution without adding liquid volume or contaminants. The Enhanced Chemical Cleaning (ECC) process was thus developed to replace BOAC stage of waste removal.

The Enhanced Chemical Cleaning (ECC) process uses ozone to promote the oxidation of metal oxalates produced during the dissolution of sludge in the Savannah River Site (SRS) waste tanks. The process is held at 70°C to improve decomposition kinetics and 10 psig to improve ozone solubility. A simplified depiction of the ECC process is shown in Figure 1, below.

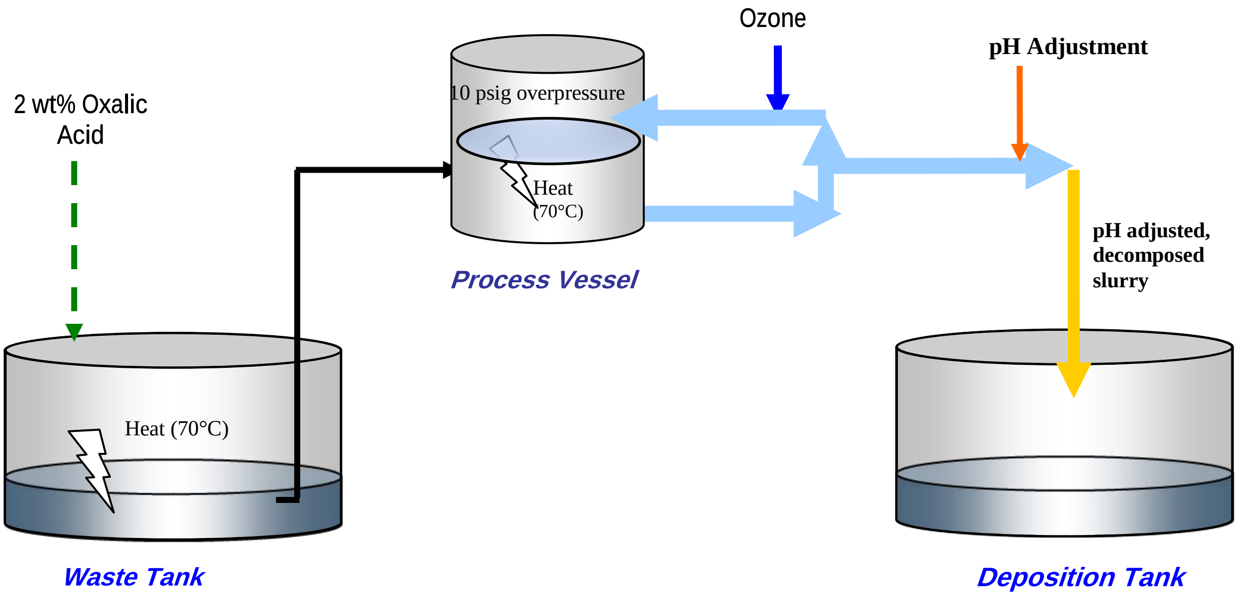


Figure 1: Schematic of the Enhanced Chemical Cleaning Process

In this process, the ozone reacts with the metal oxalates to form metal oxide and hydroxide precipitants, and the CO_2, O_2, H_2O and any unreacted O_3 gases are discharged into the vapor space. The major chemistry employed in the ECC process vessel is the reaction of ozone with the metal oxalates to form metal oxides, metal hydroxides, CO_2 and H_2O by the reactions shown below:

$$O_3 + H_2O \rightarrow O_2 + 2OH\bullet$$
$$Fe_2(C_2O_4)_3 + 6\ OH\bullet \rightarrow 6CO_2 + Fe_2O_3 + 3H_2O$$
$$H_2C_2O_4 + O_3 \rightarrow 2CO_2 + H_2O + O_2$$

While only the Iron oxalate reaction is listed above, formation of the powerfully reactive hydroxyl radical initiates many oxidizing reactions, effectively putting most waste constituents into their highest oxidation state.

In addition to the non-radioactive metals in the waste, however, the SRS radioactive waste also contains a variety of radionuclides, hence, hydrogen gas is also present in the vapor space of the ECC system. In order to prevent a buildup of hydrogen, and, hence, a flammability/explosion concern, waste tanks are purged and the hydrogen concentration monitored to ensure that the vapor space of each waste tank and all related processing equipment remains below the Lower Flammability Limit (LFL) of hydrogen. Furthermore, a comprehensive flammability control program is utilized to ensure that the LFL of the vapor space of a waste tank will not be attained for at least 7 days without forced ventilation. Because the use of ozone/oxygen in the processing equipment may also introduce ozone/oxygen into the vapor space of the waste tanks, the impact of this gas stream on the LFL of hydrogen must be understood for all possible operating scenarios of both normal and off-normal situations, with particular emphasis at the elevated temperatures and pressures of the typical process operating conditions. Oxygen is a known accelerant in combustion reactions, but while there are data associated with the behavior of hydrogen/oxygen environments, relevant studies addressing the effect of ozone on the flammability limit of hydrogen proved scarce. Further, discussions with industry experts verified the absence of data in this area and indicated that laboratory testing, specific to defined operating parameters was needed to comprehensively address the issue. Testing was thus designed and commissioned to provide the data necessary to support safety related considerations for the ozone treatment process.

2. Experimental

2.1 Flammability Apparatus

In order to ensure consistency between this testing and other documented flammability testing, the test methodology utilizes the guidelines established in ASTM E-918-83 (2005), "Standard Practices for Determining Limits of Flammability of Chemicals at Elevated Temperature and Pressure" [1]. Using this standard as the testing basis, a test setup was developed and is given in Figure 2.

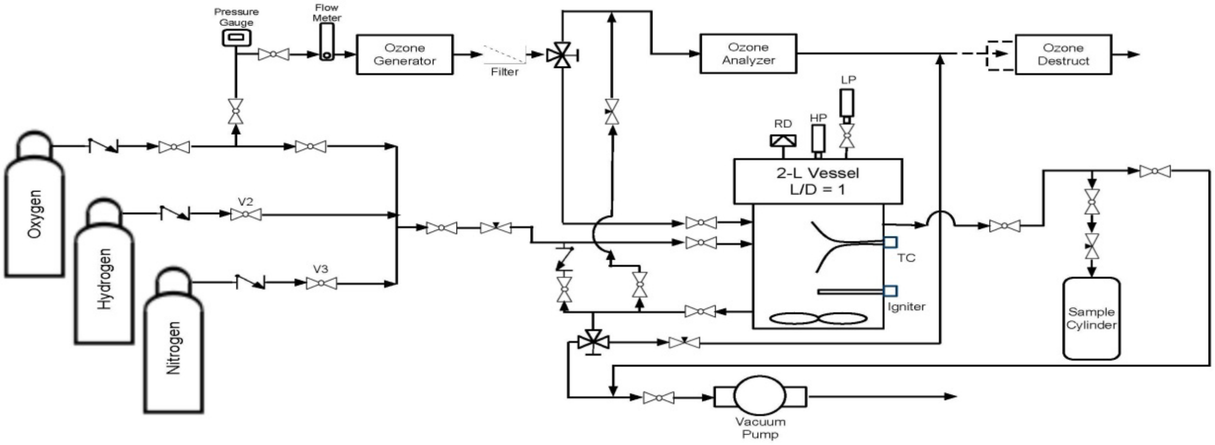


Figure 2: Test Apparatus for Testing the Lower Flammability Limit of Specified Gas Mixtures

The testing was conducted in a 2-L vessel rated to 3,000 psi at 500°C with an L/D ratio of one. There are two pressure transducers mounted on the vessel: a high accuracy (0.05% full scale) low range pressure transducer (0-25 psia) used for preparing the gas mixtures by partial pressure and a high accuracy (0.05% full scale) high range pressure transducer (0-200 psia) used to monitor the pressure after the mixture is ignited. High purity research grade gases were used for the preparation of the gas mixtures: nitrogen (99.9999%), oxygen (99.999%), and hydrogen (99.9999%). Two thermocouples were placed in the vessel to measure the temperature at the center and at the upper area of the vessel. A stir bar was placed at the bottom of the vessel to provide mixing of the gases. The gas mixture was ignited using an exploding fuse wire positioned a third of the way from the bottom. The energy provided by the fuse wire was approximately 10 joules. An ignition energy of 10 J was chosen because it produces very little wire spatter and a cylindrical shock wave is formed upon the vaporization of the wire because it is above the 5 J/cm threshold [2].

Ozone is generated on-site using a high ozone concentration generator. The ozone concentration of the ozone/oxygen stream is analyzed with an in-line UV absorption unit designed to enable accurate measurements of ozone from 0.01 wt. % ozone in oxygen to 20 weight percent.

In order to minimize undesired ozone decomposition, the materials used for this testing were carefully chosen. The test vessel, tubing, and fittings are all made of 316 stainless steel and passivated per ASTM A967 [3]. The packing material and/or seals for the valves were made of PTFE or fluorocarbon FKM.

2.2 Experimental Method

Prior to testing, the thermocouples, pressure transducers, ozone analyzer, and data acquisition instrumentation are checked to ensure they are functioning properly. The 2L vessel is opened and wiped down with acetone. A 10mm 40 gauge tinned copper wire is wrapped around the igniter electrodes. The vessel is sealed and checked for leaks through pressurizing the vessel. This is followed by a vacuum and pressure purging procedure with a diluent gas (N_2 or O_2) depending on the test conditions. The gas manifold and piping are vacuumed and pressure purged with the respective gas prior to addition into the vessel. The purging helps minimize trace contamination of other gases as well as to remove residual moisture.

By assuming that these gases behave ideally, the gas concentration is determined based on partial pressure addition. Prior to gas filling, the vessel is evacuated down to approximately 0.2 psia. The magnetic stirrer is turned on to provide mixing during the gas filling step. Each gas is added slowly to the desired concentration based on the partial pressure calculation. During addition, there is a slight temperature rise due to the compression of the gases; therefore, after each gas addition, the mixture is allowed to reach equilibrium. The gas manifold and piping are purged with the subsequent gas prior to being added to the mixture.

For the ozone tests, oxygen is fed into a corona discharge ozone generator. A potentiometer on the unit controls the power to the elements. Thus, by adjusting the oxygen flowrate through the generator and tuning the potentiometer, the precise ozone/oxygen ratio specified in the test matrix can be produced. The ozone concentration is measured with an in-line ozone analyzer that is placed on the outlet line of the vessel.

Early scoping tests performed to optimize the test setup indicated that if ozone was added to the test vessel while the vessel was under a vacuum, the ozone decomposed very rapidly, making it difficult to establish the desired test conditions. By feeding the ozone/oxygen mixture through the process vessel at atmospheric pressure, then monitoring the ozone concentration at the discharge, an accurate determination of the ozone concentration in the test vessel, just prior to the addition of hydrogen, may be made. The test vessel can then be evacuated just enough to add the prescribed volume of hydrogen for the test, minimizing loss of ozone.

Once the mixture has been prepared, the magnetic stirrer is turned off. The mixture is allowed to relax prior to ignition so that a quiescent mixture is tested rather than a turbulent mixture. The low pressure transducer valve is closed and the data collection is started. The mixture is manually ignited using the fuse wire providing a nominal 10 joules. The data acquisition records the pressure and temperature time traces in the vessel. A mixture is considered to be flammable if the pressure rise after the ignition event is greater than or equal to 7% in accordance with ASTM E918. The procedure is repeated until there are a minimum of two demonstrations conducted at the lowest fuel concentration to be considered flammable and three at the highest fuel concentration considered non-flammable.

3. Results and Discussion

3.1 Hydrogen Lower Flammable Limit

The lower flammable limit for initially quiescent hydrogen-air mixtures was determined in order to validate the test equipment setup and the procedure. The LFL for hydrogen in air was determined as 4.2 volume percent based on the ASTM 7% pressure rise criteria. A comparison of this result to data obtained by other researchers is summarized in Table 1.

TABLE 1: Hydrogen LFL in Air, this testing compared to others

Source	**Hydrogen Concentration (vol. %)**	**Comments**
LFL using 5% pressure rise criteria		
SAFEKINEX [4]	4.1	2.8-L vessel
	3.9	6-L vessel
	4.1	14-L vessel
	4.7	40-L vessel
	5.8	1250-L vessel
	4.1	2000-L vessel
LFL using 7% pressure rise criteria		
Present Work	4.2 ± 0.1	2-L vessel (L/D = 1)
Crowl and Jo [5]	5.7	20-L spherical vessel
Cashdollar et al. [6]	5.0 ± 0.5	8-L chamber
	6.0 ± 0.5	20-L chamber
	6.5 ± 0.5	120-L spherical vessel
LFL using a visual criterion		
Coward and Jones [7]	4.0	Flammability Tube

The experimentally measured LFL is in close agreement with the accepted lower flammable limit of 4 vol. % which was obtained through visual criterion [7]. Many other researchers have shown that it is difficult to obtain this value using the 7% pressure rise criteria. This has been explained through hydrogen’s high diffusivity as compared to oxygen and nitrogen [6].

The majority of tests using the pressure rise criteria are performed with the ignition source in the center of the vessel. Central ignition is used for the determination of the explosion severity of flammable mixtures because it gives the maximum rate of pressure rise and the maximum overpressure. However, central ignition may not be useful when determining the limits of flammability. It has been shown that ignition source location has an impact on the flammability limits of methane [8]. As the location of the ignition source is lowered, a larger percentage of the combustible mixture participates in the reaction with minimal heat loss to the vessel wall. This results in a higher explosion overpressure, thereby widening the flammable region. The present work uses an ignition source placed approximately one-third from the bottom of the vessel.

3.2 Ozone Lower Flammable Limit

Initially, tests were conducted to determine the extent of ozone decomposition over time inside the combustion vessel at ambient conditions. This was accomplished by preparing an ozone-oxygen mixture and holding the mixture in the combustion vessel for approximately 30 minutes while stirring. After the specified hold time the ozone concentration was measured. It was found that there were negligible amounts of ozone decomposition that occurred in the vessel.

The LFL of ozone in oxygen was determined as 8.4 volume percent. Previous studies on the flammability of ozone in oxygen are presented in Table 2.

TABLE 2: Ozone LFL in Oxygen, this testing compared to others

Source	Ozone Concentration (vol. %)	Comments
Present Work	8.40 ± 0.17	2-L vessel (L/D = 1)
Mizutani et al. [9]	10.5	1-L cylindrical vessel, Electric spark
Koike et al. [10]	10.0	1-L cylindrical vessel, 1 J electric spark
Cook et al. [11]	9.5 ± 0.5	10 cm i.d. glass bulb, 0.47 J electric spark

The present work reveals that the explosion limit of ozone in oxygen is consistent with previously reported values; however, it is lower than other literature data which can be attributed to the differences in the experimental method and procedure. The lower explosion limit obtained in this work is most likely a result of a combination of factors: the type of ignition source, location of the ignition source, and vessel size and geometry. In these tests, the ignition source energy was setup to give approximately 10J which is much greater than that used in previous work. Flammability limits are a function of ignition energy, thus, by increasing the strength of the ignition source the flammable limits tend to widen [12]. There also tends to be some variation in the flammable limits which is influenced by the type of ignition source: a fuse wire as compared to an electric spark [13]. This may be an effect of the energy density provided by each type of ignition source and the amount of energy actually being transferred to the mixture. As discussed previously, the ignition source location may be playing a part in the lower value obtained.

The differences in the size and dimensions of the explosion vessels could have affected the lower flammable limit [13]. As the vessel size is increased, the heat losses to the wall become negligible. Through minimizing heat losses to the vessel wall, more heat is transferred to the combustion reaction, therefore, promoting flame propagation. This will result in a widening of the flammable region and combustion can occur at lower temperatures.

3.3 Lower Flammable Limit of Hydrogen in Ozone/Oxygen Mixtures

The experimental results for the lower flammable limits of hydrogen in the ozone/oxygen concentrations defined in the test matrix are shown in Figure 3. The solid circles represent a flammable mixture and the open circles represent a non-flammable mixture.

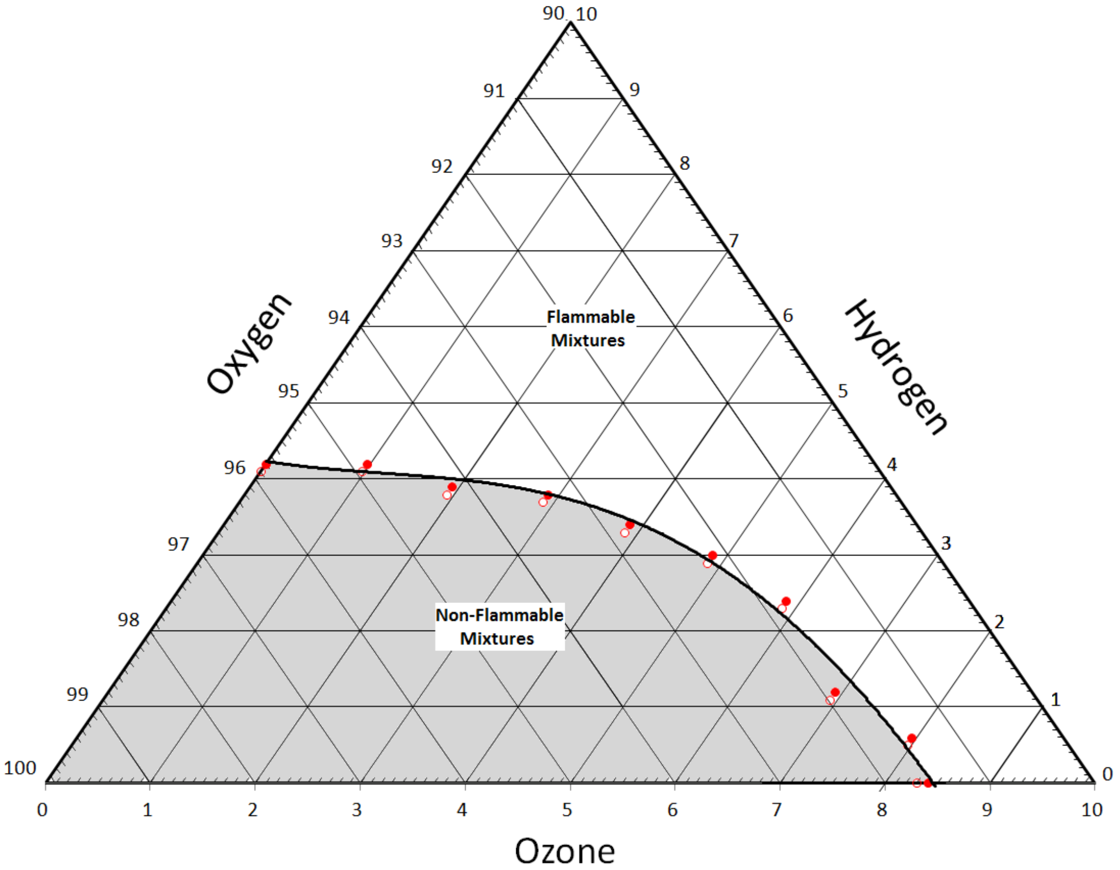
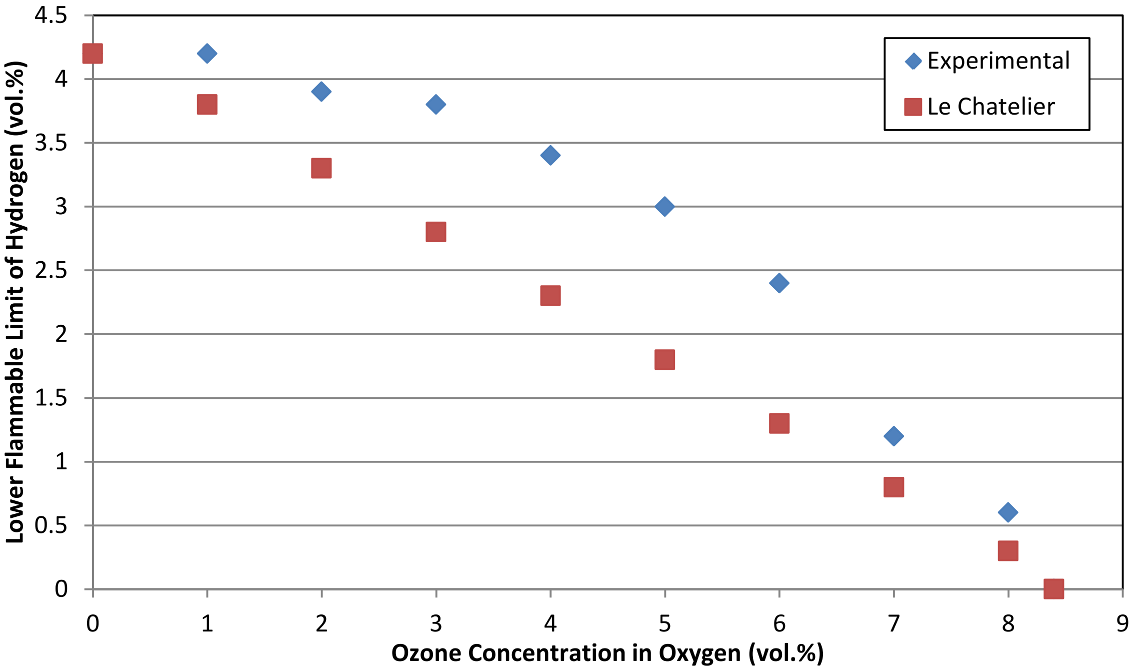


Figure 3: Flammability envelope for hydrogen/ozone/oxygen mixtures (all values are in volume percent).

Typically, it is of interest to estimate the flammability limits of multi-component mixtures. In the absence of experimental data, estimation methods can be useful if the flammable limits of pure components are known. Le Chatelier [14] developed an empirical equation for predicting the flammable limits of fuel mixtures,

Eq. [1]

where



Lower Flammable Limit of Hydrogen (vol.%)
Ozone Concentration in Oxygen (vol.%)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
0
1
2
3
4
5
6
7
8
9
Experimental
Le Chatelier

as 90% decomposition when the ozone concentration was 11.2% in the mixture [11]. In any case, additional work is needed to fully understand the nature of these experiments.

3.4 Temperature and Pressure Effect on the Lower Flammable Limit of Hydrogen-Ozone-Oxygen Mixtures

It has been reported previously that the ozone decomposition rate increases at the temperature of its environment increases [16]. Therefore, stability tests were performed again to determine the extent of ozone decomposition at the elevated test conditions. This time it was found that the ozone decomposition rate could not be considered negligible. With initial mixtures containing 5 vol.% ozone in oxygen at approximately 75°C, the ozone decomposition rate was approximately 0.1 vol.% ozone every 10 minutes.

The results from the tests performed at elevated temperatures and pressures are shown in Figure 5. It was found that as the temperature is increased the LFL decreases and the opposite was observed when the pressure was increased.

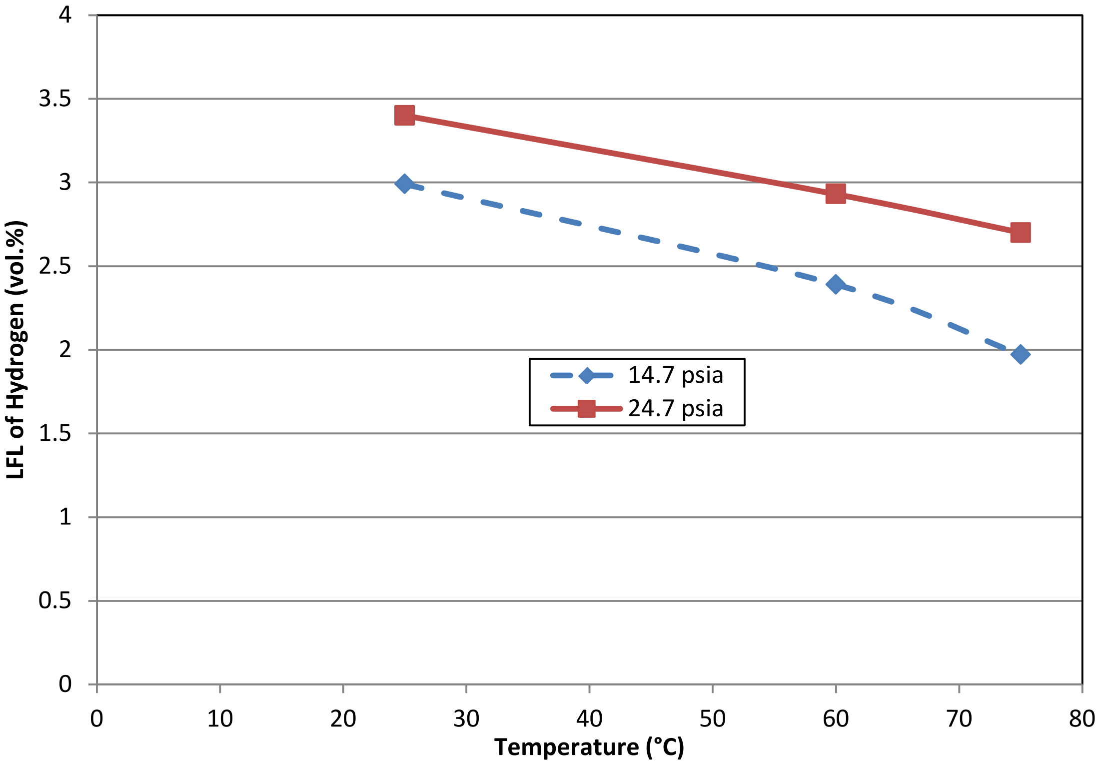


Figure 5: Effect of temperature and pressure on the flammability limits of hydrogen-ozone-oxygen mixtures. Tests were performed with 5 vol.% ozone in oxygen.

The increase in the LFL as a result of the increase in pressure is generally not characteristically observed for flammable gases; however, this is a characteristic of hydrogen flammability [17]. This result leads to the conclusion that the reaction mechanism responsible for the increased LFL as the pressure is increased for hydrogen is still the dominate mechanism when ozone is added. Furthermore, it is noticed that as the temperature is increased the decrease in the LFL is fairly linear throughout the range of temperatures tested. The LFL results from these tests show that the LFL is more susceptible to elevated temperatures when compared to results of hydrogen-air or hydrogen-oxygen. One explanation for this is that at the increase temperatures more of the ozone participates in the reactions that occur in the vessel. Previous research on ozone decomposition has found that only a part of the ozone decomposes when the ozone concentration is below its LFL. At the higher temperatures, the reaction rates increase as well as the instability in the ozone molecule.

3.5 Effect of Relative Humidity on the Lower Flammable Limit of Hydrogen-Ozone-Oxygen Mixtures at Elevated Temperatures and Pressure.

Tests conducted with the addition of water vapor have shown a slight increase in the LFL as shown in Figure 6. Since there is an additional component (water vapor) added to the mixture, the results should be compared on a total combustibles (hydrogen plus ozone) basis rather than just on the concentration of hydrogen in the mixture. This is because as more water vapor is added to the mixture, the concentration of ozone decreases; therefore, even if more hydrogen was needed to be added to the mixture, the total amount of combustibles may have remained constant to produce a flammable mixture.

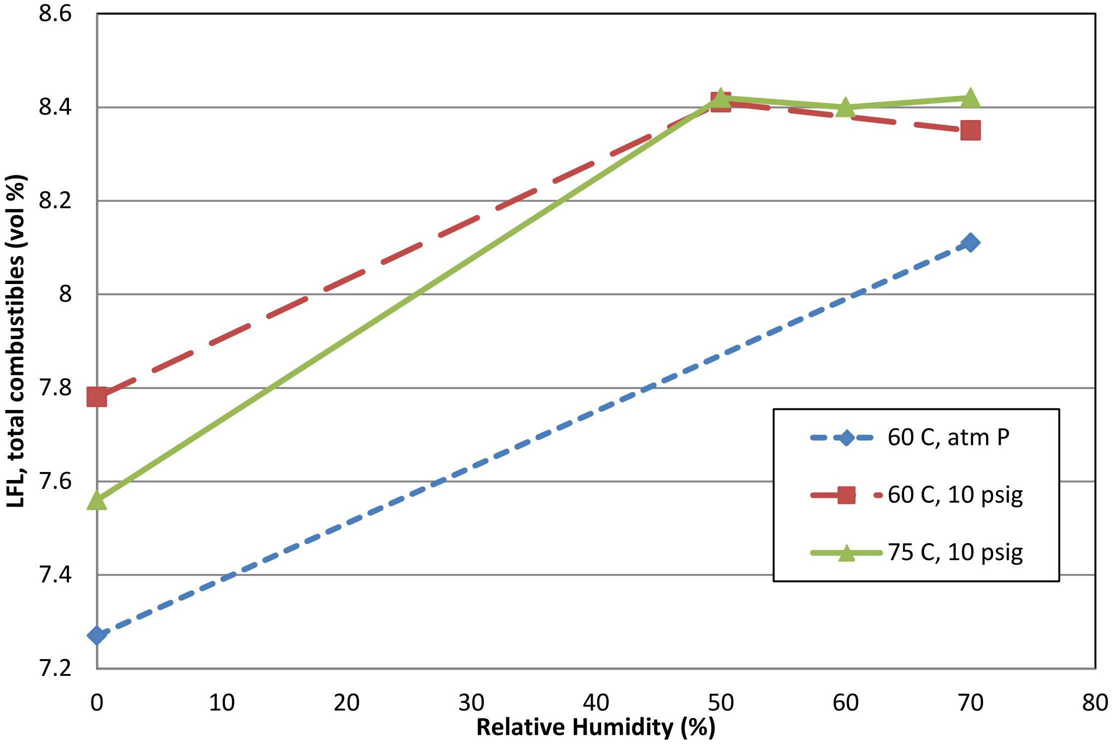


Figure 6: Effect of relative humidity on the LFL of hydrogen-ozone-oxygen mixtures. Tests were performed with 5 vol.% ozone in oxygen.

The slight increase in the LFL could be a result of either the addition of the water vapor or decrease in ozone concentration. The addition of water vapor to the mixture helps extract heat from the reactions occurring in the vessel (combustion or decomposition), thereby, quenching the flame propagation by lowering the reaction rate. Furthermore, the observed increase in the LFL could be a result of a decrease in the ozone concentration. It is known that both hydrogen and water act as a catalyst for ozone decomposition; therefore, the actual concentration inside the vessel prior to igniting the mixture is lower than the reported concentrations.

4. Impact on Operation

This testing was designed to provide data under the conditions considered most optimal to produce a deflagration. The geometry and materials of construction of the testing vessel; the location of the fuse wire; the magnitude of the supplied energy; the careful minimization of diluents and other contaminants; and meticulous procedural detail to maintain integrity of the ozone to the maximum extent practical, result in data that reflect not the expected process conditions, but those that enhance the possibility of flame propagation. For this reason, there is believed to be considerable conservatism in the indicated results. Per the vendor, the maximum possible ozone concentration producible by the planned ECC Ozone generator is 8 volume percent (typical maximum expected concentration is 6.8 vol%), less than the 8.4 minimum volume % concentration shown to be flammable in a pure O_2 environment at the optimally conservative conditions established in this testing. As both water vapor and nitrogen, together constituting approximately 6.5 % of the actual feed stream, are powerful diluents, it is believed not credible that deflagration can occur at this maximum feed concentration condition. In addition, once the ozone stream contacts the waste stream, the many simultaneous oxidizing reactions will rapidly decompose available ozone to well below flammable levels. Further, because the radiolytically generated hydrogen quantity is negligible compared to the supplied ozone/oxygen stream (0.0004 moles per minute H_2 vs 76 moles per minute ozone/oxygen), even the total H_2/O_3 mixture, without crediting decomposition reactions, does not approach flammable concentrations. Finally, even at the “end” of the ECC batch cycle, when most of the metal oxalates have been decomposed, testing has indicated that the ozone concentration in the vapor space of the ECC process vessel reaches a concentration of no more than 3 vol%, remaining well below concentrations of concern.

The major issue for the ECC operation established by this testing is the impact of the data when applied to off normal conditions. While it is possible to discontinue ozone addition to the reaction vessel at any time, the radiolytic hydrogen generation rate continues, varying slightly as ambient pressures and temperatures change. Relative to the data generated and analyzed in this testing, the ECC hazards analysis team will re-evaluate off normal conditions (e.g. those during which process exhaust ventilation is lost) such that issues involving mixtures of hydrogen and ozone in the vapor space can be appropriately controlled.

5. Conclusion

The LFL of hydrogen in air was determined and is in good agreement with the literature data. Ozone-oxygen mixtures were found to be flammable at concentrations above 8.3 vol.% based on the ASTM E918 7% pressure rise criteria for flame propagation. This result is lower than previously reported values which can be explained through the variations in the test setup and procedure. It is believed that the lower values obtained in this work are a result of improvements of the test methodology. Tests performed with hydrogen in various concentrations of ozone in oxygen have shown that the LFL of hydrogen decreases as the concentration of ozone in the mixture increases.

6. References

[1] ASTM. (2005). ASTM E 918-83 Standard Practice for Determining Limits of Flammability of Chemicals at Elevated Temperature and Pressure. Philadelphia, PA: American Society for Testing and Materials.

[2] Mashuga, C. V. (1999). *Determination of the Combustion Behavior for Pure Components and Mixtures using a 20-Liter Sphere.* Phd Thesis. Michigan Technological University. Ann Arbor: UMI Company.

[3] ASTM. (2005). ASTM A967-05, Standard Specification for Chemical Passivation Treatments for Stainless Steel Parts. Philadelphia, Pa: American Society for Testing and Materials.

[4] Project SAFEKINEX, Contract No. EVG1-CT-2002-00072, Deliverable No.8, *Report on experimentally determined explosion limits, explosion pressures and rates of explosion pressure rise – Part 1: methane, hydrogen, and propene,* March 2006.

[5] Crowl, D. A., & Jo, Y.-d. (2009). A Method for Determining the Flammable Limits of Gases in a Spherical Vessel. *Process Safety Progress , 28* (3), 227-236.

[6] Cashdollar, K. L., Zlochower, I. A., Green, G. M., Thomas, R. A., & Hertzberg, M. (2000). Flammability of methane, propane, and hydrogen gases. *Journal of Loss Prevention in the Process Industries , 13*, 327-340.

[7] Coward, H. F., & Jones, G. W. (1952). *Limits of Flammability of Gases and Vapors.* BuMines, 503.

[8] Van den Schoor, F., Norman, F., & Verplaetsen, F. (2006). Influence of the ignition source location on the determination of the explosion pressure at elevated initial pressure. *Journal of Loss Prevention in the Process Industries* , 459-462.

[9] Mizutani, T., Matsui, H., Sanui, H., & Yonekura, M. (2001). Decomposing detonation and deflagration properties of ozone/oxygen mixtures. *Journal of Loss Prevention in the Process Industries , 14*, 559-565.

[10] Koike, K., Nifuku, M., Izumi, K., Nakamura, S., Fujiwara, S., & Horiguchi, S. (2005). Explosion properties of highly concentrated ozone gas. *Journal of Loss Prevention in the Process Industries, 18,* 465-468.

[11] Cook, G. A., Spadinger, E., Kiffer, A. D., & Klumpp, C. V. (1956). Explosion Limits of Ozone-Oxygen Mixtures. *Industrial and Engineering Chemistry , 48* (4), 736-741.

[12] Bartknecht, W. (1981). *Explosions, Course Prevention Protection.* New York: Springer-Verlag.

[13] Project SAFEKINEX, Contract No. EVG1-CT-2002-00072, Deliverable No. 2, *Report on the experimental factors influencing explosion indices determination*, September 2003.

[14] Le Chatelier, H. (1891). Note on the Determination of Firedamp by Flammability Limits. *Ann. Mines , 19*, 388-395.

[15] Babrauskas, V. (2003). *Ignition Handbook.* Issaquah: Fire Science Publishers.

[16] Koike, K., Inoue, G., Suzuki, M., Saida, J., & Komatsu, I. (1998). Decomposition Characteristics of Concentrated Ozone. *Journal of Chemical Engineering of Japan , 31* (2), 195-200.

[17] Schroeder, V., & Holtappels, K. (2005). Explosion Characteristics of Hydrogen-Air and Hydrogen-Oxygen Mixtures at Elevated Pressures. *International Conference on Hydrogen Safety*. Pisa.