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Abstract

The several incidents of ozone explosions in cryogenic apparatus in radiation fields are reviewed. It is concluded that the explosions may be avoided if oxygen and/or ozone are excluded from the low-temperature regions where, in static systems, they tend to concentrate by liquefaction. Such provisions would make the proposed circulating N_2 -cooled trap for the N.S. Savannah off-gas system acceptable if the initial oxygen content of the nitrogen coolant is less than 200 ppm. Higher concentrations are undoubtedly safe but the lack of information on such facets of the phenomena as quantities of ozone, required radiation exposure, and explosion-inciting agents does not permit a quantitative definition of the limiting conditions for an explosion.

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General

There are five known instances in which an explosion has occurred in cryogenic apparatus used for experimental work in radiation fields. In each instance the cause of the explosion has been attributed to the rapid reduction of ozone which had been formed as a consequence of the radiation of oxygen. The oxygen in turn had apparently been collected in the equipment since the operating temperature of the experiment or test was below that of the oxygen boiling point. Little is known regarding 1) the rate of production of ozone from oxygen as a function of the gamma or neutron irradiation flux, 2) the amount of ozone that constitutes an explosion hazard, or 3) the inciting mechanism for the explosion. Furthermore, there are numerous instances in which the apparent conditions duplicated those in which the explosions have occurred but in which no explosion occurred. In at least a few⁽¹⁾ such instances ozone is known to have been produced. In view of this history it may be concluded that conditions which will permit the concentration of liquid (or solid) oxygen in the presence of ionizing radiations constitute a hazardous condition and should be avoided except as an experimental necessity and/or where one is prepared to cope with the consequences. In addition to giving rise to an explosion, ozone is a toxic substance and "special precautions must be taken around any equipment with which this material is used."⁽²⁾

Description of Known Incidents

Some pertinent data on the five known incidents of explosions in cryogenic apparatus are listed in Table I.

The three incidents at ORNL all occurred in the same hole in the graphite reactor in which the neutron and gamma flux have been accurately measured.⁽³⁾ The gamma flux is equivalent to $0.7 (+0.1) \times 10^6$ r/hr and the neutron flux is approximately 7×10^{11} thermal and 7×10^{11} fast. Calculation of the dose due to the 0.57-mev protons liberated in the (n,p) reaction with nitrogen indicates that the neutron dose is less than the gamma dose (see Appendix A).

In the first incident listed in Table I the Dewar of liquid nitrogen had been in the radiation field approximately three days during which

Errata for 58-7-97

CF-58-7-97: Ozone Explosion in Irradiated Cryogenic Apparatus and
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Page 3: Last column on right, "Exposure (rad)": reading down,

$\sim 5 \times 10^7$

$\sim 1.4 \times 10^7$

$\sim 4 \times 10^6$

First line of text: beginning,

"time it had received a total exposure of approximately 5×10^7 r
(i.e., 0.7×10^6 r/hr x 72 hr)."

Page 5: 3rd paragraph: beginning line 4,

"bluish cast and the odor associated with ionized air. However,
no explosion occurred...."

3rd paragraph: last line,

Apparently "about the same as the exposure in the listed incidents."

Page 7: 4th paragraph: beginning line 2,

"an exposure of $\sim 10^6$ r has existed in the known incidents."

TABLE I

Known Instances of Explosions

No.	Place	Experimenter	Irradiation Source	Cryogenic Equipment	Exposure (rad)
1 ⁽⁴⁾	ORNL	Coltman, Blewitt, Noggle	Graphite Reactor	Open Dewar of Liquid N ₂	$\sim 5 \times 10^8$
2 ⁽⁴⁾	ORNL	Coltman, Blewitt, Noggle	Graphite Reactor	Air Froze on He Re- frigeration Loop	$\sim 1.4 \times 10^8$
3 ⁽⁵⁾	ORNL	Coltman, Blewitt, Noggle	Graphite Reactor	Open Dewar of Liquid N ₂	$\sim 4 \times 10^7$
4 ⁽⁶⁾	UND	Milton Burton	Van de Graaf	Open N ₂ Trap	
5 ⁽⁶⁾	UND	Milton Burton	Van de Graaf	Open N ₂ Trap	

time it had received a total exposure of approximately 5×10^8 r (i.e., 0.7×10^5 r/hr $\times$ 72 hr). The explosion occurred without apparent provocation.

In the second incident listed, air was normally excluded from the exterior of the cold portion of the closed helium loop in the reactor. However, a leak developed which permitted air to condense on the in-pile section. Although this leak was repaired after 4 or 5 hours the oxygen which had already condensed on the outer surfaces of the loop was not removed. About one day later when the temperature of this loop was raised approximately 60°F the explosion occurred. In view of the extenuating circumstances it is suspected that the increase in temperature may have caused the reduction of ozone to oxygen (a lower energy state) with the consequent release of energy.

In the third incident the Dewar of the type first employed was equipped with a sampling tube. After about six hours' exposure in the reactor a sample was withdrawn. As this sample passed through a piece of rubber tubing connecting the Dewar to a sample container an explosion occurred at the tubing. It is apparent that the tubing provided the

necessary reducible materials to initiate the release of energy in the ozone.

In the two incidents which occurred at the University of Notre Dame an open N_2 trap was employed to cool equipment being irradiated by the Van de Graaf. In both instances the resulting explosion shattered the liquid nitrogen container and the window of the Van de Graaf.

Discussion

As may be seen from an examination of the following table the liquefaction temperature for oxygen is higher than that of helium or nitrogen. Consequently when ozone, oxygen, or air has access to these low-temperature regions it will be liquefied and over a period of time will be thus concentrated.

TABLE II

Physical Properties of Gases Used in Cryogenic Apparatus⁽⁷⁾

	<u>He</u>	<u>N₂</u>	<u>O₂</u>	<u>O₃</u>
Melting point, °C	- 272.2	- 210	- 227	- 250
Specific gravity (liq/H ₂ O)	-	0.804	1.105	1.6
Liquid color	-	colorless	bluish	blue
Boiling point, °C	- 210	- 195.5	- 183	- 112
Specific gravity (gas/air)	0.138	0.967	1.105	2.144 g/l ⁽⁸⁾
Gas color	colorless	colorless	colorless	colorless
Gas odor	odorless	odorless	odorless	odorless

Ozone is an allotropic form of oxygen which is produced in nature and commercially by high-voltage discharge in air,^(7,8) the ionization processing being such as to cause oxygen atoms to regroup into a molecule consisting of three atoms.⁽⁹⁾ In this condition the molecule has one of the highest oxidation potentials known ($E^0 = - 2.07$), being second only to fluorine.⁽¹⁰⁾ Irradiation of oxygen in neutron and gamma fields is likewise capable of producing ozone.

Ozone when formed in cryogenic apparatus tends to remain concentrated because of its relatively high boiling point compared to liquid N_2 or O_2 . In fact, it has been suggested⁽⁶⁾ that the ozone may be formed by the ionization of the oxygen in air and then concentrated in the cryogenic equipment as it condenses therein. Dissolved in liquid oxygen, ozone has a vapor pressure of less than 1 mm.⁽²⁾

In all incidents listed in Table I the oxygen and/or ozone was able to collect in a portion of the system in the high radiation field. In four of these instances static liquid N_2 was the coolant and the oxygen and ozone upon liquefying in the N_2 would collect in the bottom of the Dewar because of the lower density of the N_2 . In the second incident listed in Table I the cold part of the He refrigeration loop, upon which the ozone condensed, was in the radiation field.

In a number of experiments at ORNL⁽¹⁾ involving liquid N_2 Dewars in a 2.4×10^4 r/hr Co^{60} source, the apparent conditions for an explosion existed. Furthermore, ozone is known to have been created as the N_2 had a bluish cast and the ozone odor was prevalent. However, no explosion occurred after a month's exposure during which time the N_2 was replenished every 16 hours. The exposure of approximately 1.7×10^7 r was apparently somewhat less than the exposure in the listed incidents.

In yet another⁽¹¹⁾ series of experiments with cryogenic equipment at ORNL a closed liquid nitrogen loop has been operated in the LITR. The gamma and neutron flux in this experiment is not known accurately but is believed to be some factor from 5 to 10 times less than that in the incidents listed in Table I which occurred in the Graphite Reactor. The initial oxygen content of the nitrogen was $< 1/2$ wt%. Although most of the tests have lasted from 8 to 12 hours at least one test extended for a three-day period. While the nitrogen is replaced for each test there has been no indication of the formation of ozone.

The limiting conditions for an ozone explosion are not well defined nor is it known if the explosion can be spontaneous or whether it must be triggered by some external agency. It is variously reported that "ozone is explosive above 25% by weight in gas;"⁽²⁾ "concentrations of liquid ozone in excess of 30% by weight are very explosive even with very

minute amounts of organic material;"⁽²⁾ "liquid ozone is easily exploded, as are concentrated ozone-oxygen mixtures (above about 3% ozone) in either the liquid or the vapor state."⁽⁷⁾

Ozone explosions in irradiated liquid nitrogen traps may be avoided by the simple expedient of placing a diffusion barrier (cotton gauze) at the open end of the trap,⁽⁶⁾ but whether this prevents an explosion by excluding oxygen (which is subsequently ozonized) from the trap or by excluding ozone is not known. In any event, the amount of oxygen which is initially in the nitrogen as an impurity is apparently incapable of generating sufficient ozone to be of concern, even when the ozone concentration is increased several times by replenishing the evaporated N_2 . In particular, the oxygen concentration of the carload lots of liquid N_2 runs < 10 ppm oxygen although the purchase contract requires only less than 1 volume %. Nitrogen bottled from the tank cars generally has about 10 times the oxygen concentration of the bulk quantity. Similarly, commercially available cylinder nitrogen generally has an oxygen content of approximately 200 ppm.

The known ozone explosions in cryogenic apparatus have not released much total energy as in all cases the resulting damage has been limited to the immediate equipment. In the Van de Graaf irradiations (Table I, 4 & 5) the liquid N_2 container and the Van de Graaf window were broken,⁽⁶⁾ and in the Graphite Reactor irradiations the bottom of the Dewar container was blown out in one instance (Table I, 1),⁽⁵⁾ and the cryostat exploded in another (Table I, 2), but not to the extent that some parts could not be salvaged and reused.⁽⁴⁾

Application to the N.S. Savannah

If the gaseous waste disposal system on the N.S. Savannah were to incorporate a liquid nitrogen-cooled charcoal trap,⁽¹²⁾ through which the gases generated in the primary system would be removed, the possibility of an ozone explosion exists. Furthermore, potential sources of oxygen exist both in the liquid nitrogen itself and in the gas system. (In the latter case ozone and/or oxygen would collect where the gas is cooled to low temperatures as it passes over the charcoal.) In either

case the sources of radiation would be that from the primary shield and piping⁽¹³⁾ of approximately 100 r/hr as well as that which might originate within the charcoal trap itself due to the adsorption of radioactive gases and radioactive particulates.

Although oxygen may exist in the primary system due to the dissociation of the water, the presence of the hydrogen ambient over the water and the hydrogen recombiners in the gaseous waste disposal system⁽¹²⁾ should remove oxygen from the system before it reached the trap. Even if this were not so the hydrogen ambient would certainly react with the ozone in the trap as the latter were formed and would therefore prevent the accumulation of ozone on the gas side of the trap.

On the other hand, the liquid N_2 in the B&W refrigeration loop is circulated so that there can be no opportunity for the liquid ozone (or oxygen) to collect in a part of the system. Furthermore, the use of a closed loop would limit the oxygen concentration of the loop to that initially in the nitrogen as an impurity. This in itself should be adequate to prevent an ozone incident assuming, of course, that the oxygen concentration of the liquid nitrogen was less than around 200 ppm.

It is also pertinent that, in addition to high oxygen concentration, an exposure of $> 10^7$ r has existed in the known incidents.

Although there is a lot yet to be learned with regard to ozone explosions, the existing information does support the contentions that the proposed nitrogen refrigeration loop may be employed on the N.S. Savannah without undue concern for an ozone explosion, providing the following precautions are observed:

1. The off-gas is principally hydrogen and passes through an oxygen recombiner ahead of the charcoal trap.
2. The oxygen content of the nitrogen in the refrigeration loop is less than approximately 200 ppm. Continuous circulation of the nitrogen in this loop also reduces the ozone hazard.

List of References

1. Personal communication from Ellison Taylor, ORNL.
2. N. Irving Sax, Handbook of Dangerous Materials, Reinhold Publishing Corporation, 1951.
3. D. M. Richardson, "Calorimetric Measurement of Radiation Energy Dissipated by Various Materials Placed in the Oak Ridge Pile", ORNL-129, December 23, 1948.
4. R. R. Coltman, T. H. Blewitt, and T. S. Noggle, "Techniques and Equipment Utilized in Low Temperature Reactor Irradiation", Rev. of Sci. Inst., Vol 28, No. 5, 375-380, May 1957.
5. Personal communication from W. E. Browning, ORNL.
6. Personal communication from Milton Burton, University of Notre Dame.
7. Unless otherwise indicated all data in this table were taken from the Condensed Chemical Dictionary, edited by Arthur and Elizabeth Rose, Reinhold Publishing Corporation, 5th edition, 1956.
8. Ralph K. Strong, Editor, Kingzetta's Chemical Encyclopedia, D. Van Nostrand Co. Inc., 1952.
9. John L. Magee and Milton Burton, "Elementary Processes in Radiation Chemistry", J. of the Am. Chem. Soc., Vol 73, 523-536, 1951.
10. Wendell M. Latimer, "Oxidation Potentials", Prentice Hall, 1952.
11. Personal communication from Devaughn Nelson.
12. Such a system is not implied by the preliminary information on the gaseous waste disposal system outlined in "Status Report on the Reactor Safeguards Analyses", BAW-1044, May 9, 1958, but was proposed by B&W representatives at the N.S. Savannah Design Review Meeting in Washington on July 1-2, 1958.
13. BAW-1101, "Design of the NMSR Primary Shield", April 1958.

APPENDIX A

Dose to N_2 Due to Neutron Irradiation⁽¹⁾

The dose would be due to the 0.57-mev protons liberated in the (n,p) reaction with nitrogen.

Dose from Fast Neutrons

$$\alpha = \left(\frac{14 - 1}{14 + 1} \right)^2 = \left(\frac{13}{15} \right)^2 = 0.752$$

$1 - \alpha$ = maximum fractional energy loss per collision

0.25 maximum possible fractional energy loss per collision

0.125 average

$$\text{Proton energy from collision} = \frac{1}{8} N\phi E$$

$$\left(\frac{1}{8} \frac{N\phi E}{6.2 \times 10^7} \right) = r/\text{sec}$$

$$r/\text{hr} = \left(\frac{1}{8} \frac{N\phi E}{6.2 \times 10^7} \right) 3600$$

$$E = 2 \text{ mev}$$

$$N = \text{No. of N nuclei/gram}$$

$$N = \frac{N_0}{A} = \frac{6.02 \times 10^{23}}{14} = 4.3 \times 10^{22}$$

$$\phi = 7 \times 10^{11}$$

$$\sigma = 1 \times 10^{-24}$$

$$r/\text{hr} = \frac{(4.3 \times 10^{22})(10^{-24})(7 \times 10^{11})(2)(3600)}{(6.2 \times 10^7)} = 4.36 \times 10^5 \text{ r/hr}$$

Dose from Thermal Neutrons

$$\frac{1}{8} \frac{N\phi E}{6.2 \times 10^7}$$

$$N = 4.3 \times 10^{22}$$

$$\phi = 7 \times 10^{11}$$

$$\sigma = 1.75 \times 10^{-24}$$

$$E = 0.025 \text{ ev} = 2.5 \times 10^{-8} \text{ mev}$$

$$\therefore r/\text{hr} = \frac{1}{8} \frac{(4.3 \times 10^{22})(1.75 \times 10^{-24})(7 \times 10^{11})(2.5 \times 10^{-8})(3600)}{(6.2 \times 10^7)}$$

$$= 9.5 \times 10^{-3}$$

(1) Glasstone, "Principles of Reactor Engineering", pp 550-552.