



PROTECTION OF STRATOSPHERIC OZONE: IMPLICATIONS FOR THE OIL AND GAS INDUSTRY

**A Technical Paper by
Standard Alaska Production Company**

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**STANDARD ALASKA PRODUCTION COMPANY
Environmental/Regulatory Affairs
P.O. Box 196612
Anchorage, Alaska 99519-6612**

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PROTECTION OF STRATOSPHERIC OZONE: IMPLICATIONS FOR THE OIL AND GAS INDUSTRY

This paper discusses current theories regarding the origin and chemical processes behind the natural creation/reduction and man-induced reduction of stratospheric ozone. Based on current scientific evidence, a class of artificial gases known as halogenated fluorocarbons (HFC's) is believed to be responsible for this reduction. It is important to note at the outset that the last word has not been written on this subject. The scientific community is not unanimous in its concern for the role of HFC's. Therefore, this paper presents a summary of the current scientific literature on ozone depletion.

Halon 1301 and 1211 are HFC's used in commercial aircraft and industrial fire protection systems throughout the nation because of their effectiveness and their low toxicity to humans. Standard Alaska Production Company, as operator of the western half of the Prudhoe Bay oilfield and the Endicott Development on Alaska's North Slope, uses approximately one percent of the nation's Halon production in fire protection systems. The removal of these fire extinguishing agents from use would greatly threaten the safe production of oil and gas on the North Slope. There is no substitute for Halon that is equal in effectiveness or low toxicity to ensure adequate protection of human life. Production of Halon 1301 and 1211 could be greatly reduced or even halted as a result of regulations proposed by the U.S. Environmental Protection Agency (EPA) for the protection of stratospheric ozone.

STRATOSPHERIC OZONE REDUCTION

The Role of Atmospheric Ozone

Ozone (chemical formula O₃) is found most concentrated in the stratosphere and is the only effective shield of the earth's surface against ultraviolet solar radiation in the range of wavelengths damaging to life on this planet. While the concentration of stratospheric ozone is about 1,000 times that found in the earth's atmosphere at sea level, this stratospheric concentration still amounts to only a trace (10 to 15 parts per million) (Ehrlich et al. 1977). Presently, the ozone layer screens out about 99 percent of the harmful radiation. The small percentage that reaches the earth's surface is known to cause serious food production and health problems such as skin cancer, major eye damage, and crop damage.

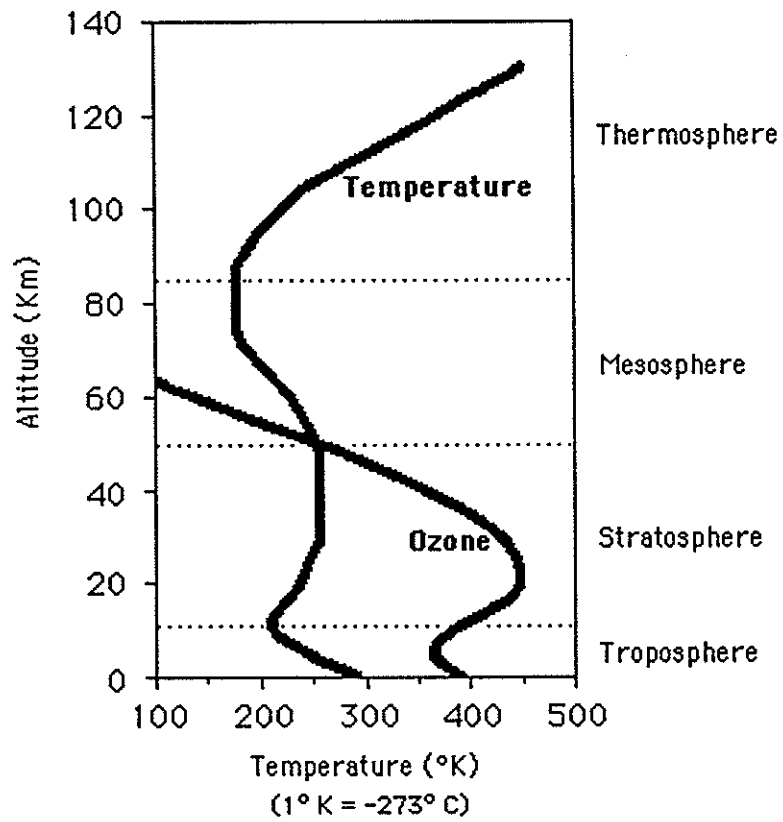
This stratospheric ozone is not to be confused with ozone that originates in the underlying troposphere, which is the layer directly above the Earth's surface. The atmosphere is subdivided into horizontal layers according to measured patterns of temperature variation. The *troposphere* extends from the Earth's surface to approximately 15 kilometers (km) and sustains a temperature decrease of about 6.4°C/km. The overlying *stratosphere* extends from the top of the troposphere to about 50 km in altitude. Temperature increases with altitude in the stratosphere to about 0°C at the top. A profile of ozone in the Earth's atmosphere is provided in Figure 1.

Tropospheric ozone is linked to a number of air quality problems in the continental United States and is one of the gases linked to the "greenhouse effect". Production of tropospheric ozone is not a problem for oilfield operations on Alaska's North Slope and will not be discussed in this paper.

Data collected by the National Aeronautics and Space Administration's (NASA's) Nimbus 7 satellite show that total global ozone declined about 3 percent between the end of 1978 and 1984, while current atmospheric models predicted a decline of only 1 percent (Pearce 1988). The United Nations Environmental Program Montreal Protocol estimates that a 1 percent decrease in the ozone layer would cause a 6 percent increase in skin cancers (Glenny 1987). The EPA predicts that given the current rate of ozone depletion, 40 million additional cases of skin cancer will develop between now and the year 2075 (Ember et al. 1986). The absorption of ultraviolet radiation in the stratosphere by ozone and the resulting heat production also influence world climate.

Mechanisms of Ozone Depletion

Ozone is naturally produced in the stratosphere when molecular oxygen (O₂) is split by ultraviolet solar radiation and the resulting oxygen atoms attach themselves to other O₂ molecules ($O + O_2 = O_3$). Destruction of O₃ has been found to occur by several reactions but proceeds very rapidly in the presence of specific catalysts which are normally very scarce in the stratosphere: the hydroxyl radical (OH, which originates from water vapor in the stratosphere), nitric oxide (NO), and atomic halogens such as fluorine, iodine, chlorine, and bromine. A summary of basic ozone destructive reactions is provided in Figures 2 and 3. Nitric oxide is emitted into the atmosphere in the largest percentage, with the sources being primarily biological activity. Human activity accounts for emission of only one-fifteenth of the total. However, the majority of the nitric oxide is rapidly oxidized in the troposphere to nitrogen dioxide and is not transported to the stratosphere (Moore et al. 1976).



Adapted from: Ember et al. 1986

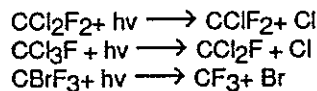
FIGURE 1
OZONE AND TEMPERATURE PROFILES IN EARTH'S ATMOSPHERE

The chemistry influencing atmospheric ozone concentrations varies with altitude because of the role played by high-energy solar radiation. It is believed that the reactions accounting for the equilibrium concentration of ozone are as follows:

- 1)
$$\text{O}_2 \xrightarrow{\text{uv light}} \text{O} + \text{O}$$
- 2)
$$\text{O}_2 + \text{O} + \text{other gas molecules} \longrightarrow \text{O}_3 + \text{excited gas molecules that heat upper atmosphere.}$$
- 3)
$$\text{O}_2 + \text{O} \longleftarrow \text{O}_3$$
- 4) This equilibrium is interrupted by the following combination:

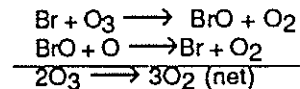
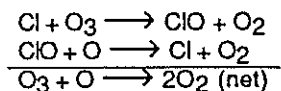
$$\text{O}_3 + \text{O} \longrightarrow 2\text{O}_2$$

Free atomic chlorine and bromine is produced by photodissociation of compounds with long atmospheric lifetimes such as man-made halogenated fluorocarbons:

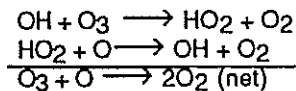


The odd nitrogen and hydrogen radicals and atomic chlorine and bromine participate in catalytic cycles that destroy ozone, such as in the following:

Freons and Halon



Water Vapor



Biological Action (majority) and Industry

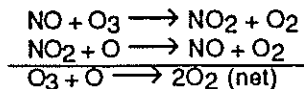


FIGURE 2
STRATOSPHERIC OZONE CREATION/REDUCTION REACTIONS

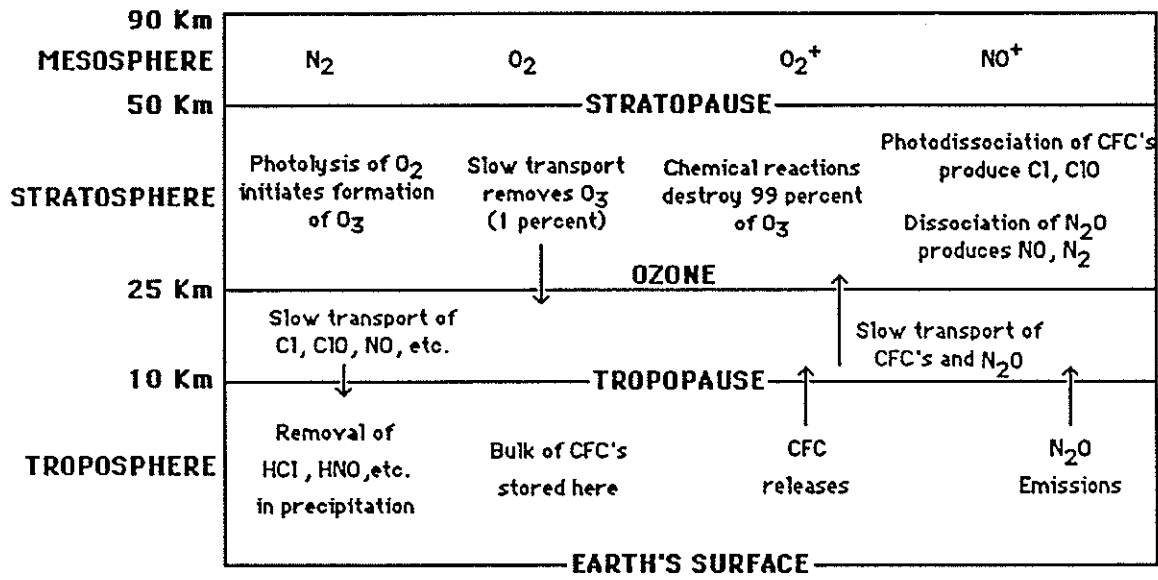
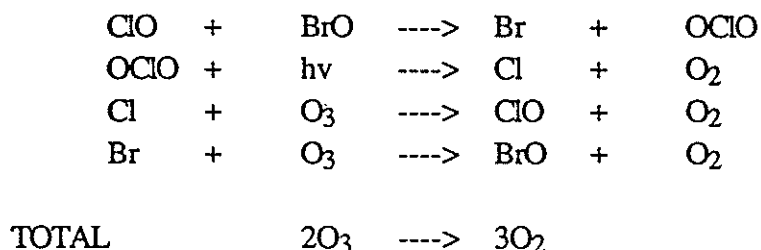


FIGURE 3
OZONE-RELATED REACTIONS IN THE ATMOSPHERE

The concern for ozone depletion in the stratosphere arose in the 1970's and was directed at releases of water vapor and nitric oxide by the proposed operation of supersonic transport aircraft. The potential problem was well researched and the proposed use of these transports prohibited in the United States.

It was then recognized that halogenated fluorocarbons (HFC's) could be dissociated by wavelengths of sunlight present only in the stratosphere and thus release free halogens, the most effective catalyst known for destroying ozone. The majority of these gaseous compounds are essentially inert to chemical reaction and relatively insoluble in water. Because of these properties, HFC compounds put into the atmosphere stay there until they reach the stratosphere. The properties of these compounds, including their relatively low toxicity, have made them very attractive for use as refrigerants, fire extinguishing agents (Halon systems), and aerosol spray propellents.

HFC's include artificial gases such as chlorofluorocarbons (CFC's), Halon 1301 (bromotrifluoromethane, CBrF_3) and Halon 1211 (bromochlorodifluoromethane, CF_2ClBr). These gases contain bromine as their reactive halogen, and the ozone-destructive reaction is as follows:



The extent to which a halogenated fluorocarbon will contribute to ozone depletion depends on its chlorine and bromine content and its atmospheric lifetime. Considerable speculation exists concerning the ozone depletion potential of Halon versus other HFC gases. Referring to Table 1 of this paper, it should be noted that based on production volumes and percent emissions, Halon 1211 and 1301 are released in much lower quantities than three of the major Freon gases of concern and methyl chloroform.

The steady increase in the use of HFC products since World War II has correspondingly increased their concentration in the atmosphere. Because concentrations of other contributors to ozone depletion (OH and NO) have remained relatively stable, further concern has arisen regarding HFC products. The compounds that have received the most attention and are being looked at for eventual phase-out include the Freons CFC 11, CFC 12, and CFC 113, and Halon 1211 and 1301. Historically, the CFC 11 and CFC 12 contained in aerosol sprays have been cited as the most dangerous com-

TABLE 1
1985 U.S. PRODUCTION OF FULLY HALOGENATED SUBSTANCES
AND METHYL CHLOROFORM

SUBSTANCE	PRODUCTION (Metric Tons)	PERCENT EMITTED	WEIGHTED PERCENT
CFC-11*	96,000	100%	27.8%
CFC-12*	153,000	100%	44.2%
CFC-113*	68,000	100%	15.7%
Halon 1211	2,800	16%	0.4%
Halon 1301	3,600	29%	3.0%
Methyl chloroform	307,000	100%	<u>8.9%</u>
			100.0%

*Freons

Source: Great Lakes Chemical Company

pounds; however, Halon 1211 and 1301, according to a study by Rand, have a greater ozone-depleting potential (Crawford 1986). In terms of production volumes and percent emissions thereof, information compiled from 1985 indicates that CFC 11, CFC 12, and CFC 113 are of greater concern (Table 1).

Global reduction of ozone from these catalytic reactants in the stratosphere is difficult to measure, and thus predictions are supported primarily through modeling. In the winter of 1985, a British antarctic survey team measured a substantial seasonal decrease (as much as 50 percent) of the ozone layer over Antarctica. This ozone depletion was not predicted and could not be verified by the accepted ozone-depletion predictive models. This has led to a heightened concern that an "ozone hole" has developed over Antarctica and that the global ozone layer is threatened. A number of theories concerning the antarctic observations have arisen. Some claim that natural conditions have caused the seasonal depletion, while others claim that an increase of HFC's and other pollutants in the stratosphere is causing the depletion.

NASA and the National Oceanic and Atmospheric Administration (NOAA) have conducted research on the ozone layer through satellite studies and contend that ozone reductions are occurring and that they may be cyclical based on solar activity. Based on this information, a panel of scientists from NASA and NOAA formed an ozone trend panel with the objective of re-analyzing the data collected over the past 20 years from various ozone monitoring stations located on the ground. In March 1988 the panel released a report of its findings in Washington. This review found evidence of previously undiscovered seasonal trends in ozone levels, especially in higher latitudes. The processes they theorized as causing the antarctic hole, however, do not apply to the Arctic or anywhere else on the globe (Pearce 1988). The panel believes HFC's are primarily responsible for the ozone trends in the Northern Hemisphere.

The study of the stratospheric ozone layer is complex and surprising at times. Stations for monitoring ambient air quality at the Prudhoe Bay oilfield detected two dramatic increases in ozone concentration during the 1979-1980 monitoring program. The data suggested that stratospheric ozone was actually transported into the troposphere during unique climatic conditions (Evans 1981).

Regulatory Reactions

The United States and Canada adopted a ban on the nonessential use of CFC's in 1978. The European community in the early 1980's pledged to reduce CFC aerosol production by 30 percent. In March of 1985, under the auspices of the United Nations Environment Program (UNEP), 28 nations including the Soviet Union met to form the

Vienna Convention for the Protection of the Ozone Layer. The Vienna Convention delegates have developed a document called the Montreal Protocol to address the ozone concerns. The Protocol has three major components:

- (1) Reduction of production and consumption of ozone-depleting substances over the next decade (50 percent reduction by 1999),
- (2) Revision of reduction requirements based on assessments of scientific information, and
- (3) Prevention of trade in ozone-depleting products with countries that do not take part in the agreement.

The Protocol had been signed by 29 nations as of May 1988, but only the United States and Mexico had ratified it. The Protocol will become effective on January 1, 1989 if "11 nations or regional economic integration organizations representing at least two-thirds of estimated 1986 global consumption of the controlled chemicals have ratified it" and when other conditions are met (EPA 1987a).

In the December 14, 1987, *Federal Register*, the U.S. Environmental Protection Agency published proposed regulations for the protection of stratospheric ozone (EPA 1987b). These proposed regulations are modeled after the UNEP Montreal Protocol and call for limiting the production of CFC's and other HFC's such as Halon 1301 and 1211 at 1986 levels. The regulations contain other phase-out restrictions. In addition, a final rule was published in the same issue of the *Federal Register* requiring that businesses involved in the production, import, or export of specified ozone-depleting chemicals in 1986 provide certain information to EPA within 30 days. This information is to be used as a baseline for setting CFC production restrictions. The finalization of the EPA ruling is dependent on the success of the Montreal Protocol.

HFC CONTROLS: IMPACT ON OILFIELD SAFETY

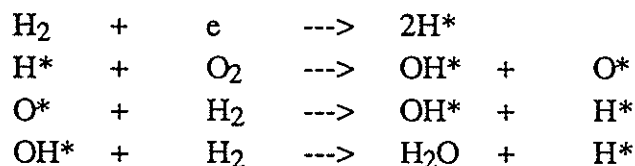
The EPA-proposed regulations to limit and/or ban the production and use of various HFC's as part of EPA's plan for the protection of stratospheric ozone could have a major effect on the safe production of oil and gas in the United States. Standard Alaska Production Company, operator of the western half of Alaska's Prudhoe Bay oilfield and the Endicott field, uses Halon 1301 and 1211 as fire extinguishing agents. Halon 1301 (bromotrifluoromethane, CBrF_3) is the primary product used in all production facility flood systems on the North Slope, while Halon 1211 (bromochlorodifluoromethane, CF_2ClBr) is contained in individual portable extin-

guishing units. Halon 1301 and 1211 are colorless, odorless gases that have low toxicity and are extremely effective as fire extinguishing agents.

Physical Properties of Halon

Halon is defined as a halogenated extinguishing agent. These agents are hydrocarbons in which one or more hydrogen atoms have been replaced by a halogen atom. The common halogen elements used are fluorine, chlorine, bromine, and iodine. Halon is a member of a unique class of extinguishing agents which actually extinguish flames by chemically reacting with the flame. It is believed that Halon actually breaks the "chain" of the combustion process, rather than cooling or smothering it. Although empirical information supports the observation that flame inhibition occurs, the actual chemical reactions are only partially understood and are the subject of continuing research. The outstanding effect of this method is the extreme rapidity and high efficiency with which flames can be extinguished. Additionally, when properly executed, this method is the only means by which an explosion can be prevented in a flammable gas/air (or even a gas/oxygen) mixture after ignition has occurred (McKinnon 1981).

To understand the flame inhibition process, a discussion of a basic combustion chain reaction is needed. The branched-chain combustion reaction of the hydrogen-oxygen system is the simplest and most rapid type of combustion:



Following the initial splitting of the hydrogen molecule, the individual hydrogen atoms (active H species) interreact with oxygen molecules to produce active OH* and O* species. Research has shown that the flame velocity is dependent on the concentration of the active OH* species and on the pressure at which the reaction proceeds. For fuels not containing hydrogen, the active species O* becomes the determinant of flame velocity. Extinguishment by flame inhibition is possible only when the active species (also referred to as chain carriers) OH*, H*, and O* are not allowed to fulfill their role in sustaining the flame (McKinnon 1981).

When Halon is injected into a flame, the gas thermally dissociates into its anionic and cationic free radicals and catalyzes the union of the OH* and H* combustion reaction chain carriers, thereby mitigating their influence upon the continuation of the flame.

As an example, Halon 1301 (CBrF₃) when released into a fire produces hydrogen bromide (HBr) and hydrogen fluoride (HF). Extinguishing agents like Halon which accomplish this flame inhibition do so without other extinguishing methods such as cooling, oxygen dilution, fuel removal, or covering. However, they do not efficiently extinguish glowing fires except under certain conditions.

Advantages of Halon

The low toxicity of Halon 1301 allows it to be discharged safely from total-flood systems in occupied spaces, an advantage which no other gaseous agent has. When a fire is being extinguished by Halon, only 5 percent of the oxygen by volume is tied up. Halon 1301 is the only gaseous extinguishing agent accepted for use in occupied areas by the National Fire Protection Association. Additionally, Underwriters Laboratories, Inc. classifies Halon 1301 in toxicity group 6, the lowest of the six groups defined. Halon is also considered the most effective gaseous extinguishing agent. Halon 1301 is approximately 2.5 times more effective than carbon dioxide (CO₂) in combating a fire.

Figure 4 provides a comparison of the toxicity versus effectiveness of four major extinguishing agents. A safe human exposure of 15 minutes is allowed for Halon 1301, while the same exposure to CO₂ could be lethal. In a gas or liquid fire, the fire spreads very rapidly, often too rapidly to allow for evacuation of people prior to the initiation of extinguishing actions. When carbon dioxide extinguishers are used, people must be evacuated before CO₂ can be safely discharged. With Halon, the fire can be extinguished with people present, so that by the time personnel are evacuated, the fire is out.

North Slope Halon Usage

Halon 1301 and 1211 are used as fire extinguishing agents throughout oilfield facilities on Alaska's North Slope. Because nearly all of the North Slope equipment is housed within heated, enclosed modules, the processing of hydrocarbons within these modules makes fire protection essential. The fire suppression system in these confined spaces must be non-hazardous to personnel and non-destructive to hydrocarbon-processing equipment.

Approximately 9,000,000 pounds of Halon 1301 were produced last year in the United States. The safety systems for Standard Alaska Production Company facilities at Prudhoe Bay and Endicott contain a total of about 900,000 pounds of Halon. Last year, less than one tenth of the Halon in these systems was discharged -- an amount

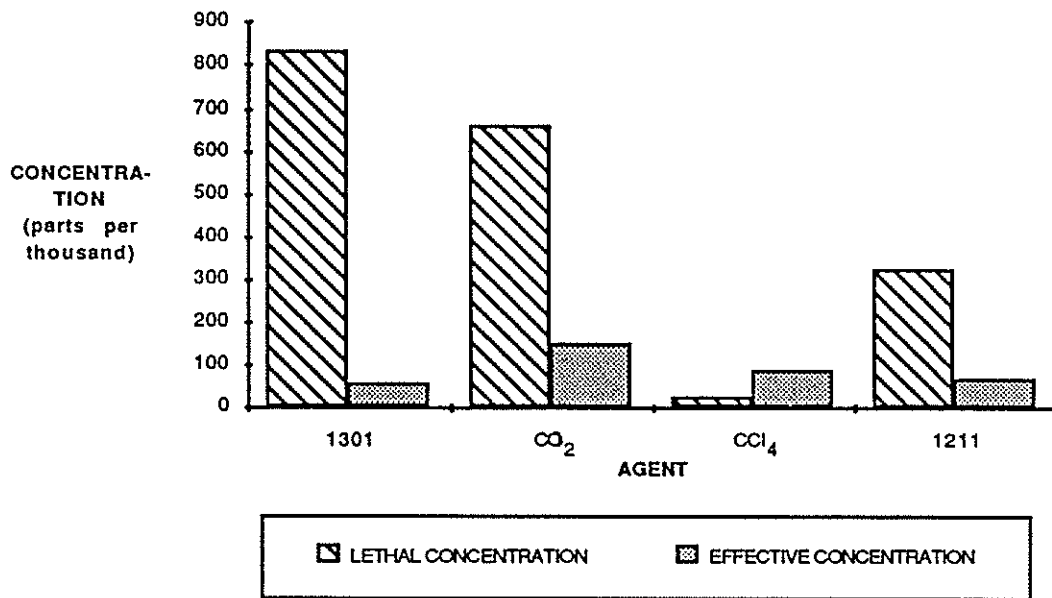


FIGURE 4
LETHAL AND EFFECTIVE CONCENTRATIONS
FOR VARIOUS FIRE-EXTINGUISHING AGENTS

equal to about one percent of the annual U.S. production. System discharges occur when the safety detection systems sense a gas release or detect a flame or spark. Halon can also be discharged accidentally by human or equipment error. Improvements in SAPC's maintenance procedures have greatly reduced the discharges by human error, while still maintaining maximum human safety (Figure 5). Because Halon is extremely expensive (\$1,200 per 200-pound bottle), steps to prevent accidental releases on the North Slope were taken prior to the concern for Halon's role in ozone depletion. A company study board is in place to review the circumstances of all Halon releases at SAPC facilities and to make recommendations to reduce future releases.

The low toxicity of Halon 1301 allows it to be discharged safely from a total-flood fire-suppression system in occupied spaces -- an advantage which no other gaseous agent has. Chemical manufacturers such as Du Pont and Great Lakes Chemical Corporation (the largest manufacturer of Halon) have committed to stopping the production of many artificial gas products which contain CFC's; however, they are still strongly committed to the business of Halon production.

Alaska's North Slope safely contributes 25 percent of the nation's domestic oil production. After more than 10 years of operation, there has never been a fire-related fatality or injury. Of all uses of halogenated fluorocarbons, the use of Halon for fire suppression is the most justifiable. Other available extinguishing agents, such as carbon dioxide, do not satisfy the effectiveness or low toxicity requirements for the protection of facilities and more importantly, the protection of human life.

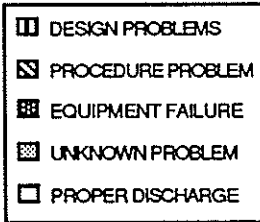
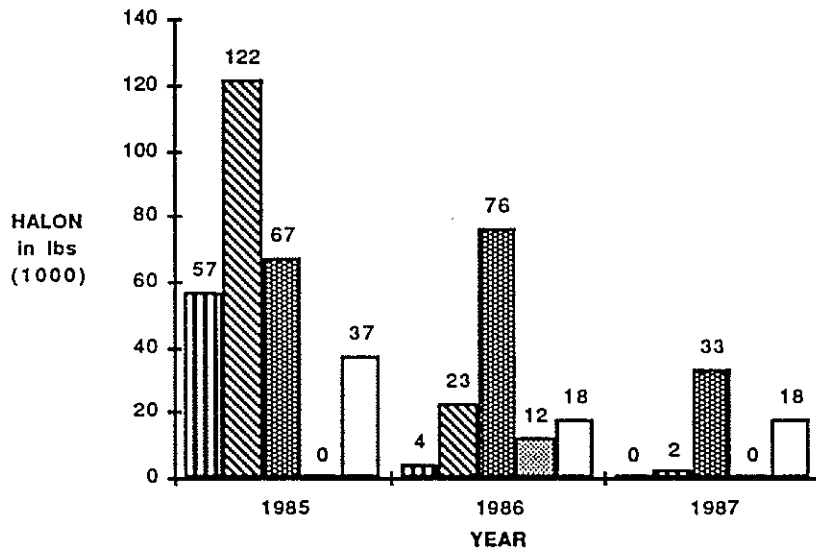


FIGURE 5
HALON DISCHARGED BY STANDARD ALASKA PRODUCTION COMPANY

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