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**L'ENERGIE ATOMIQUE
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THE PHOTOCHEMICAL METHOD FOR RADIOIODINE ABATEMENT

METHODE PHOTOCHEMIQUE DE REDUCTION DE L'IODE RADIOACTIF

A. C. Vikis

Whiteshell Nuclear Research
Establishment

Etablissement de recherches
nucléaires de Whiteshell

Pinawa, Manitoba R0E 1L0
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RÉSUMÉ

Ce rapport examine la chimie de base de la méthode photochimique d'élimination d'iodes radioactifs de l'air et évalue le concept par rapport à ses diverses applications dans l'industrie nucléaire. La méthode utilise la lumière ultra-violette (200-300 nm) pour convertir les iodures organiques (RI) en iode élémentaire (I_2). On met ensuite le I_2 à réagir avec de l'ozone pour former des oxydes d'iode solides (I_4O_9 ou I_2O_5) qui se déposent à l'intérieur d'un épurateur. On en conclut que cette méthode est applicable à des systèmes à grande échelle et qu'elle aurait plusieurs avantages sur les méthodes classiques de réduction d'iodes radioactifs.

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ABSTRACT

This report reviews the underlying chemistry of the photochemical method for removal of radioiodines from air and evaluates the concept with respect to various applications in the nuclear industry. The method uses ultraviolet light (200-300 nm) to convert organic iodides (RI) to elemental iodine (I_2). The I_2 is then reacted with ozone to form solid iodine oxides (I_4O_9 or I_2O_5), which deposit inside a scrubber. It is concluded that the method is applicable to large-scale systems and would have several advantages over conventional methods of radioiodine abatement.

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1. INTRODUCTION

In the course of energy production by nuclear power reactors, potentially volatile radionuclides of iodine, rare gases, carbon and hydrogen are formed by various nuclear reactions. These radionuclides are normally contained within the reactor system by engineered and other barriers. Any gaseous releases during routine or accident conditions are directed to the off-gas systems of the nuclear facility, where scrubbers are used to reduce radioactive releases to the environment to safe levels [1,2].

The radioactive isotopes of iodine are the most significant radiologically, because, potentially, they can accumulate in the human thyroid gland via the food chain. Thus, a large effort has been expended in developing efficient methods for radioiodine control [1-3]. These efforts are motivated by concerns to reduce to even safer levels the environmental impact of nuclear power, particularly for the future, when nuclear power is forecast to substitute increasingly for conventional hydrocarbon fuels that are presently being depleted.

Several iodine isotopes (^{127}I , ^{129}I , ^{131}I) are produced in reactor fuel by fission and by the decay of fission products. Typical quantities for CANDU* fuel, which has been irradiated to a burnup of 650 GJ/kg U and cooled for one year, are [4]: 6.4×10^{-10} , 4.0×10^{-2} and 1.2×10^{-2} g/kg initial U, for ^{131}I , ^{129}I and ^{127}I , respectively. These isotopes are normally held in the fuel matrix by chemical and physical bonds. The fuel matrix, as well as its cladding, prevent the release of significant quantities of iodine during routine reactor operation. However, significant quantities of iodine could be released from the fuel in some postulated reactor accidents, and in fuel reprocessing the total radioiodine inventory would be released from the fuel during dissolution.

*CANada Deuterium Uranium - Canada's heavy-water moderated and cooled, natural-uranium fuelled reactor.

The long-lived ($t_{1/2} = 17 \text{ Ma}$) ^{129}I isotope is considered to be a long-term radiological risk, which would be important in the case of extensive nuclear fuel reprocessing. The short-lived ($t_{1/2} = 8.05 \text{ d}$) ^{131}I isotope is radiologically significant in the short term, following a reactor accident, or during the reprocessing of short-cooled fuel from fast breeder reactors.

Whether in fuel reprocessing, or following a nuclear reactor accident, only a fraction of the released iodine would become airborne; the rest would remain in solution with the associated liquids. The main airborne species observed in the off-gases are elemental iodine (I_2), organic iodides (mainly CH_3I) and aerosols. Total radioiodine concentrations in the off-gases are estimated to be of the order of a few parts per million, or less. The relative species concentrations would vary significantly, depending on the source and history of the release.

Various methods have been developed for the removal of gaseous radioiodines from air, and these are outlined in Appendix A. In general, solid sorbents or liquid scrubbing solutions are used to effect the removal of small quantities of radioactive iodine from air. There are two intrinsic disadvantages with these approaches. Firstly, mass transfer rates from the gas phase to a surface are slow, which limits the throughput of the air to be decontaminated or requires prohibitively large filters. Secondly, the solid sorbents or liquid scrubbing solutions eventually become poisoned by other air impurities. Although in some cases they can be regenerated, at the expense of complex procedures in radioactive environments, eventually they must be disposed of as large quantities of secondary contaminated waste. Therefore, there is a need for simpler and more efficient methods for radioiodine control.

Research on alternative methods for radioiodine control, based on selective gas-phase chemistry, is being conducted at the Whiteshell Nuclear Research Establishment (WNRE) of Atomic Energy of Canada Limited. Two potential radioiodine removal methods have been identified in the course of this research. These are the Corona Iodine Scrubber method [5] and the Photochemical method [6]. The present report reviews the underlying theory of the photochemical method and evaluates the concept of a photochemical scrubber for radioiodine removal.

2. THE PHOTOCHEMICAL METHOD

The photochemical method uses ultraviolet light (200-300 nm) to convert organic iodides to elemental iodine. The iodine released from the organic iodides, and the rest of the elemental iodine, are then reacted with ozone to form solid iodine oxides, which are captured by deposition on the scrubber surfaces. The above two processes can be carried out simultaneously in a single scrubber, or in two separate scrubbers. Ozone can be produced via a number of conventional techniques, and fed into the scrubber. Alternatively, it can be generated directly in the scrubber via the photolysis of oxygen by ultraviolet light ($\lambda < 220$ nm), in which case an all-photochemical method is realized. The chemistry of these processes and their application are reviewed in the following sections of this report.

2.1 PHOTOCHEMISTRY OF THE ORGANIC IODIDES

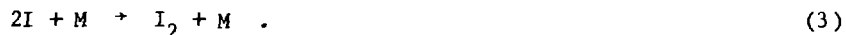
Organic iodides (RI) absorb light in the 200-300-nm wavelength region [7]. Maximum absorption occurs at 260 nm and results in the promotion of electrons, which form the C-I bond, from a bonding to an antibonding state. The photochemistry of the organic iodides in this spectral region is well known [8,9]. Upon absorption of the radiation, the C-I bond decomposes with a quantum yield of one, to form an iodine atom and the corresponding organic free radical (R),



Depending on the conditions, a number of reactions may follow the above primary process. However, for low concentrations of organic iodides in air, as in the present context, the only reactions would be the oxidation of the organic radical to form alcohols and aldehydes [10],



and the recombination of the iodine atoms to form elemental iodine [11],



The recombination of iodine atoms is aided by the presence of the air, which acts as a third body (M). It should be noted that iodine atoms do not react with oxygen. Also, recombination with R to form the initial iodide would be insignificant, because at the oxygen concentrations existing in one atmosphere of air, R would disappear much faster via reaction (2).

Organic radioiodides are, in comparison with elemental radioiodine, very difficult to remove from off-gas streams. For instance, in power reactor applications, ordinary charcoal filters do not retain organic radioiodines unless they are thick and impregnated with special complexing agents, such as triethylene diamine (TEDA) and/or KI [3]. Such charcoal filters are known to degrade with time, due to accumulation of poisoning impurities and, in the case of TEDA, volatilization of the impregnant [12]. There is also concern [3] that these charcoals may not function effectively under conditions of high-temperature, high-humidity and high-radiation fields, which may exist following some postulated reactor accidents. Organic iodide removal is also a problem in fuel reprocessing applications [3]. In such cases, to remove organic iodides from off-gases, highly oxidizing solutions or expensive silver-loaded sorbents are used. Thus, a simple method for converting organic iodides to elemental iodine is needed.

Photochemical pretreatment of off-gases, to convert organic iodides to elemental iodine, appears promising. The above photochemistry applies to all organic iodides, including the aromatic ones. Intense and efficient light sources of the mercury/rare-gas type, as well as lasers, are available for this wavelength region. Also, within the wavelength range of maximum absorption by the organic iodides, normal components of air and other expected impurities (with the exception of NO_x) do not absorb light. The effect of NO_x , which is present at significant concentrations (up to 2%) in Purex-type reprocessing off-gases, is discussed in Appendix B, where it is shown that NO_x concentrations in excess of about 0.2% by volume are undesirable, because too high light intensities would be required.

2.2 A PHOTOCHEMICAL CONVERTER

Two types of photochemical converter are envisaged, depending on geometry and mode of illumination: (a) a long tubular converter illuminated with a beam of light (Figure 1), and (b) a cylindrical converter illuminated concentrically with a tubular light source (Figure 2). The rate of photochemical conversion for these two cases is examined below.

The rate of photochemical conversion in a tubular flow reactor illuminated end-on and uniformly with a parallel beam of monochromatic* light is given by

$$-\frac{dc}{dl} = \alpha I_0 c f^{-1} A \exp(-\alpha c l) \quad (4)$$

where c = concentration of absorbing species (i.e. RI)
 α = absorption cross-section of species
 I_0 = incident radiation flux
 l = radiation path length
 f = volumetric flow
 A = reactor cross-section.

An approximate solution of Equation (4), which holds well for optically thin systems ($\alpha c l \leq 0.1$), like the present one, is given by

$$\ln \frac{c_0}{c_f} \approx \alpha I_0 A l f^{-1} \quad (5)$$

where c_0 and c_f are the initial and final concentrations, respectively.

An equation similar to Equation (5) can also be derived for coaxial illumination of a cylindrical reactor of radius R , which is illuminated radially with a tubular light source of radius r ($r \ll R$),

*For the case of polychromatic radiation, the product $\alpha(\nu)I_0(\nu)$ would have to be integrated over the applicable frequency (ν) range.

$$\ln(c_o/c_f) \leq \alpha I_o' f^{-1} R \quad (6)$$

In Equation (6), I_o' is equivalent to the total radiation coupled into the reaction vessel.

The ratio c_o/c_f is defined as the photochemical conversion factor, and is plotted as a function of light intensity and optical path length in Figure 3. A reference flow of $200 \text{ m}^3 \cdot \text{h}^{-1}$, containing CH_3I at concentrations of $10 \text{ } \mu\text{m}^3 \cdot \text{m}^{-3}$ or less, was assumed in these calculations. Illumination with monochromatic radiation at 260 nm was also assumed. The absorption cross-section of the CH_3I molecule at 260 nm is $1.4 \times 10^{-18} \text{ cm}^2$ [7]. Other organic iodides have higher absorption cross-sections [7], and thus would require lower light intensities for the same conversion factor.

Typical designs for the two types of photochemical converter are shown in Figures 1 and 2. For end-on illumination (Figure 1), a tubular steel vessel, e.g. 5 m long and 0.3 m in diameter, is envisaged. Quartz windows used to couple the light into the vessel from an external source are supported by O-ring flanges. External reflectors at either end could also be employed to achieve higher effective path lengths and thus higher organic iodide conversions for a given light intensity. High-pressure mercury-xenon arc lamps (e.g. Hanovia Model 929B-90/Xe-Hy, 2.5 kW) are particularly suitable for end-on illumination.

For coaxial illumination (Figure 2), a cylindrical scrubber made of steel, e.g. 3 m to 4 m long and 1 m to 2 m in diameter, is envisaged. Light from one or more tubular light sources is coupled into the scrubber via a coaxial quartz tube. Medium-pressure mercury/rare-gas arc lamps (e.g. Canrad Hanovia Model 6577A431, 15 kW) are suitable in this case.

Other photochemical converter arrangements may also be used, depending on the particular situation. For example, to treat large flows ($10\,000 \text{ m}^3 \cdot \text{h}^{-1}$) of reactor or reprocessing vessel off-gases, a cubical enclosure (e.g. 5 m x 5 m x 5 m) containing several lamps, arranged in banks (see Figure 4), may be used. The lamps can be in direct contact with the off-gas stream or they can be inserted into the enclosure from the

outside via tubular slots made of quartz tubing. If 20 tubular lamps (Hanovia Model 6577A431, 15 kW) were used, organic iodide conversion factors of about 10^3 would be achieved.

In conclusion, efficient organic iodide photochemical converters can be designed for a variety of applications, particularly for reactor and reprocessing vessel off-gases. The photochemical converters are simple vessels, with no internal components, safe and easy to operate remotely in radioactive environments.

2.3 FIXATION OF ELEMENTAL IODINE BY REACTION WITH OZONE

Elemental radioiodine, present in the off-gas streams or generated by photochemical conversion of organic radioiodides, must be removed from the off-gases before the latter are vented to the atmosphere. Conventional methods for elemental iodine removal could be used at this stage. However, earlier research at WNRE showed that, under certain conditions, iodine removal could be achieved using selective gas-phase chemistry. We showed [13] that iodine (I_2) reacts with ozone, in the gas phase, to form I_4O_9 at room temperature and I_2O_5 at elevated temperatures (> 370 K). Both I_4O_9 and I_2O_5 are low vapour-pressure solids and sufficiently stable to allow efficient removal of low concentrations of radioactive iodine from off-gases.

We studied the kinetics of the gas-phase I_2/O_3 reaction in the temperature range 293-370 K, using a flow system [13]. Nitrogen and oxygen at atmospheric pressure were used as carrier gases for I_2 and O_3 , respectively. Iodine concentrations in the range $1-5 \mu\text{mol}\cdot\text{dm}^{-3}$ and O_3 concentrations in the range $2-20 \mu\text{mol}\cdot\text{dm}^{-3}$ were used. The ozone was generated on-line, in oxygen carrier gas, by a corona discharge.

The reaction rate, in the temperature range 293-370 K, obeyed the differential rate law

$$-d[I_2]/dt = -R^{-1}d[O_3]/dt = k[I_2][O_3] \quad (7)$$

In Equation (7) the reaction stoichiometric factor, R, is equal to the ratio of O_3 molecules consumed per I_2 molecule reacted. The value of R, determined by gas-phase titration, was 3.9 ± 0.2 . We also determined the value of the rate constant, k, in the temperature range 293-370 K (see Figure 5). The relationship obtained is given by

$$\ln k = (14.7 \pm 0.6) - (2050 \pm 230)T^{-1} \quad (8)$$

where k is in units of $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$.

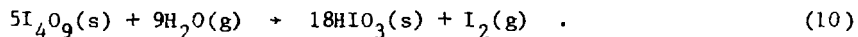
The iodine-oxide product of the room-temperature reaction of I_2 with O_3 was identified as I_4O_9 . Thermogravimetric (TGA), differential thermal (DTA) and elemental analyses were used for this purpose. The DTA and TGA data showed that the product decomposed at ≈ 370 K to form I_2O_5 according to



The I_2O_5 solid is known [14] to decompose to I_2 and O_2 above 600 K.

Kinetic considerations (Equation (8)) show that the reaction of I_2 with O_3 is faster at higher temperatures. This higher reaction rate can be exploited for more efficient fixation of the radioiodine. At temperatures greater than about 370 K, I_2O_5 will be formed. Therefore, chemical information on I_4O_9 and I_2O_5 is needed, particularly on the reactions of these oxides with the water vapour present in humid atmospheres.

Chemical information on the various iodine oxides (I_4O_9 , I_2O_4 and I_2O_5) is available in a number of publications [14-19]. The I_4O_9 formed by the reaction of I_2 with O_3 is an amorphous solid. In the presence of water vapour, it forms the oxyacid HIO_3 , releasing I_2 according to



In the presence of O_3 , the I_2 released according to Equation (10) would, of course, react further to form I_4O_9 , and eventually HIO_3 .

I_2O_5 is a commercially available crystalline solid, which is also hygroscopic, absorbing water to form HIO_3 , as follows:



We have verified experimentally that, in the presence of water vapour, the oxyacid (HIO_3) is the final solid at ambient and higher temperatures. HIO_3 is a stable crystalline solid, which is also available commercially. It dehydrates to $HI_3O_8(s)$ at 373-403 K, and subsequently to I_2O_5 in the range 468-488 K [14].

A proposed radioiodine scrubber, based on the I_2/O_3 reaction, is shown in Figure 6. It would consist of a steel vessel, 5 m³ to 10 m³ in volume, packed with a material such as steel mesh to provide sufficient surface area for the deposition of the iodine oxide. The necessary ozone would be generated on-line, as required. Several types of commercial ozone generators, used mostly for industrial sterilization, are available for this purpose [20,21].

The performance of the scrubber can be modelled on the basis of the kinetics discussed above. Equation (7) can be integrated for conditions of excess ozone ($[O_3] \geq 10[I_2]$) to give

$$\ln \frac{[I_2]_i}{[I_2]_f} = k[O_3]_i t \quad (12)$$

where the subscripts i and f refer to initial (inlet) and final (outlet) concentrations. The reaction time, t, is the residence time of the off-gases in the scrubber, defined by V/F, where V is the scrubber volume and F is the volumetric flow.

The calculated decontamination factor ($[I_2]_i/[I_2]_f$) of this scrubber is plotted in Figure 7, as a function of ozone concentration and temperature, for scrubber volumes of 5 m³ and 10 m³. A reference flow of 200 m³·h⁻¹, containing $\leq 10 \mu\text{m}^3 \cdot \text{m}^{-3}$ of I_2 , was assumed in the calculations. High decontamination factors (10^2 - 10^3) can be achieved, particularly at the

higher temperatures, with relatively compact scrubbers. Most importantly, the ozone concentrations required are well within safe limits*.

Removal of radioactive iodine oxides or HIO_3 from the scrubber can be accomplished by washing with water, or by heating. With washing, the iodine would be recovered as IO_3^- (aq), which can then be precipitated as an insoluble iodate (e.g. BaIO_3) for permanent disposal. With heating, the iodine would be recovered as elemental iodine in an inert carrier and sorbed on solid sorbents for permanent disposal. Either method would require essentially stoichiometric quantities of scrubbing liquids or solid sorbents, but much smaller than the quantities required by the conventional methods used to remove traces of iodine from air.

Nitrogen oxides (NO_x) present in the off-gases of Purex-type reprocessing facilities, due to fuel dissolution in nitric acid, would interfere with the iodine fixation step. The NO_x are known [22] to catalyze the decomposition of ozone by the following rapid reactions:



We have shown that NO_2 concentrations of the order of a few hundred parts per million can be tolerated at the expense of excess ozone. However, NO_x concentrations of 2-3%, normally present in such off-gases, are unacceptably high. It should be noted that nitrogen oxides are also a problem in conventional off-gas treatment methods, particularly in the removal of ^{85}Kr , which ordinarily follows the ^{129}I removal. Methods have been developed [23] for NO_x abatement prior to ^{85}Kr removal. Thus, in principle, the present problem can be solved if NO_x abatement methods are adapted for application ahead of the iodine recovery system.

*Ozone is potentially explosive when used in high gas-phase concentrations (> 9%) or in the liquid phase, in the presence of hydrocarbons or other oxidizable substances. Low concentrations of ozone in air are used safely in industry for sterilization purposes [20,21].

In conclusion, the rate of I_2/O_3 reaction is sufficiently fast and the solid product(s) sufficiently stable to be used for the removal of radioactive I_2 from air. Also, simple radioactive iodine scrubbers can be constructed. Nitrogen oxides (NO_x) present in Purex-type reprocessing off-gas streams can interfere and must be removed upstream of the iodine scrubber.

2.4 SIMULTANEOUS PHOTOCHEMICAL ABATEMENT OF ORGANIC AND ELEMENTAL RADIOIODINES

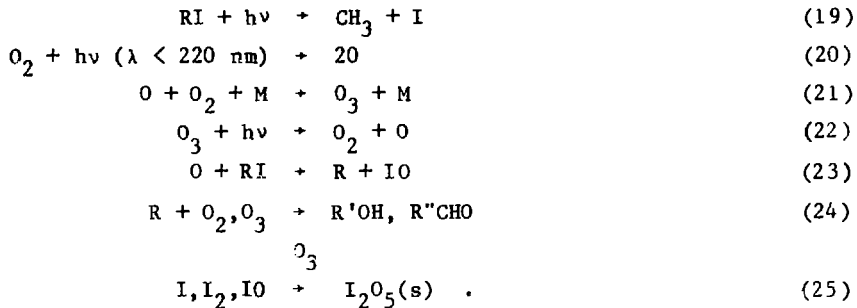
Ultraviolet light sources of the mercury/rare-gas type, constructed with suprasil-quartz envelopes, emit a significant amount of light at wavelengths less than 220 nm. Wavelengths shorter than about 220 nm are absorbed by oxygen to produce ozone via the following reactions [20,24]:



The photochemical generation of O_3 makes it possible to achieve the simultaneous conversion of organic radioiodides and fixation of the iodine, using a single all-photochemical scrubber.

A laboratory-scale photochemical scrubber, based on the above principle, has been tested. The scrubber consisted of two concentric suprasil-grade quartz tubes 85 cm long; the inner one was 2.2 cm O.D. and 2.0 cm I.D., and the outer one was 8.0 cm O.D. and 7.5 cm I.D. A tubular (1.6 cm O.D. and 79 cm long) low-pressure mercury lamp (Westinghouse Model G37T6VH, 39 W) was fitted inside the inner tube. The lamp emitted radiation at 254 nm, needed for the decomposition of CH_3I , and radiation at 185 nm, needed for the generation of ozone. Air containing CH_3I , I_2 , or both species, at concentrations of 2 to 40 $\mu\text{m}^3 \cdot \text{m}^{-3}$, was passed through the annulus formed by the two quartz tubes. The scrubber was operated at 390-410 K, at 100 kPa and a flow rate of 42 $\text{cm}^3 \cdot \text{s}^{-1}$. Decontamination factors in the range 30-500 were achieved for the above conditions, even though the radial optical path length was only 5.3 cm.

The chemistry of the combined system was more complex than the sum of the two separate processes discussed in Sections 2.2 and 2.3. In this case, the main reactions were



For optically thin ($ac\ell < 0.1$) conditions, which would hold in this application, and particularly for the above experiment ($ac\ell < 0.01$), most of the UV light would escape unabsorbed. However, reaction (22) in combination with reaction (23) resulted in more efficient use of the UV light. Thus, shorter optical paths (more compact scrubbers) could be used for the combined system.

Another advantage of a combined all-photochemical scrubber is that the rate of reaction between iodine atoms and ozone is several orders of magnitude faster than that between iodine molecules and ozone [25]. Thus, for the same iodine decontamination factor, lower ozone concentrations would be required if the iodine were in the atomic form. Iodine, which is already present in the molecular form (I_2), can be converted to the atomic form by the absorption of radiation components below 190 nm and in the range 450-550 nm, and thereby react faster with the ozone.

A disadvantage of the combined all-photochemical scrubber is the deposition of iodine oxides on light-transmitting surfaces. This was a problem in the laboratory experiments. However, this problem can be dealt with by heating the light-transmitting surfaces to a sufficiently high temperature ($\sim 600 \text{ K}$) to sublime or decompose the interfering deposits.

3. CONCLUSIONS

The chemistry underlying the photochemical method for removing radioactive iodines from air has been reviewed and the concept of a photochemical radioiodine scrubber evaluated. The main conclusions arising from this work are as follows:

- A two-step process can be devised, consisting of (a) conversion of organic radioiodides to elemental iodine using ultraviolet radiation, and (b) fixation of elemental iodine to solid iodine oxides by reaction with ozone. These steps can be carried out separately or simultaneously, as the situation may require.
- Photochemical conversion of organic iodides alone merits special consideration, because organic iodides are most difficult to remove by conventional methods. The photochemical method can be easily adapted to reactor off-gas streams, allowing the replacement of TEDA-impregnated charcoal filters with lesser quantities of the more reliable KI-impregnated charcoal filters. It can also be adapted to fuel reprocessing off-gas streams, permitting the use of less rigorous and inexpensive scrubbing techniques for the subsequent removal of elemental radioiodine.
- Efficient fixation of radioactive iodine by ozone can be achieved at room temperature. However, the reaction rate is faster and the iodine oxide produced (I_2O_5) is more stable when the reaction temperature is higher than about 370 K.
- The solid iodine oxides (I_4O_9 and I_2O_5) and their oxyacid (HIO_3) are sufficiently stable for removing radioactive iodine from air and can be converted easily to compact and stable forms suitable for permanent disposal.
- The low levels of ozone ($\sim 0.02\%$) required for the fixation of elemental iodine are safe and can be generated conveniently by well-established procedures.

- Nitrogen oxides (NO_x), at concentrations present in Purex-type reprocessing off-gas streams, interfere with the iodine fixation step and must be reduced to less than $\sim 0.01\%$ upstream of the iodine scrubber. The photochemical method can tolerate higher NO_x concentrations, but practical considerations dictate that the NO_x should be less than $\sim 0.2\%$.

- The photochemical scrubber is inherently simple and thus can be adapted easily to operation in radioactive environments. The main advantage, compared with existing methods, is the absence of large volumes of solid sorbents or liquid scrubbing solutions, which require frequent replacement and result in large quantities of contaminated waste.

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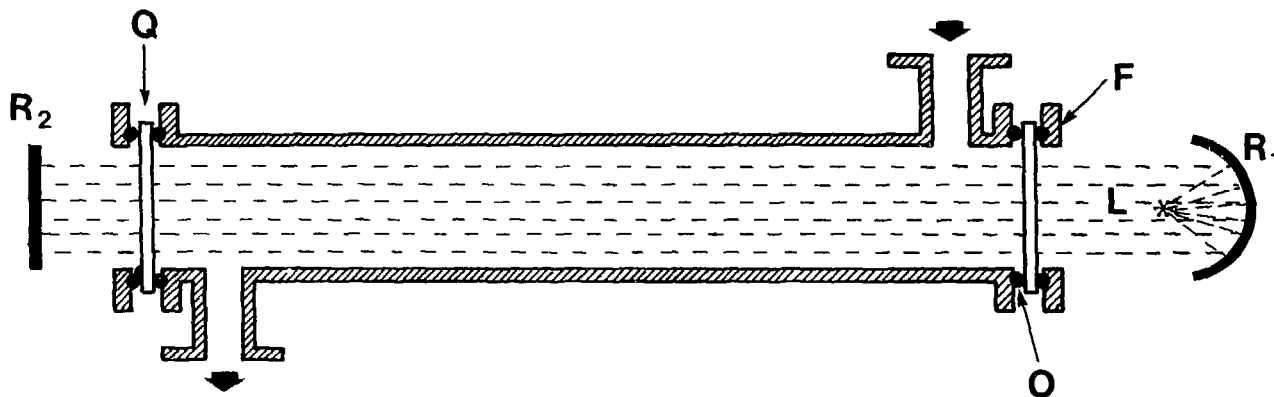


FIGURE 1: Tubular Photochemical Converter (Schematic). The body of the converter is constructed from steel. Estimated dimensions: length, 5 m; diameter, 0.3 m. UV light from the light source (L) is coupled into the converter with the aid of a parabolic reflector (R_1). A second reflector (R_2) may be added to increase light utilization efficiency. Quartz windows (Q) are used to transmit the UV light into the converter, and are supported using O-rings (O) and flanges (F).

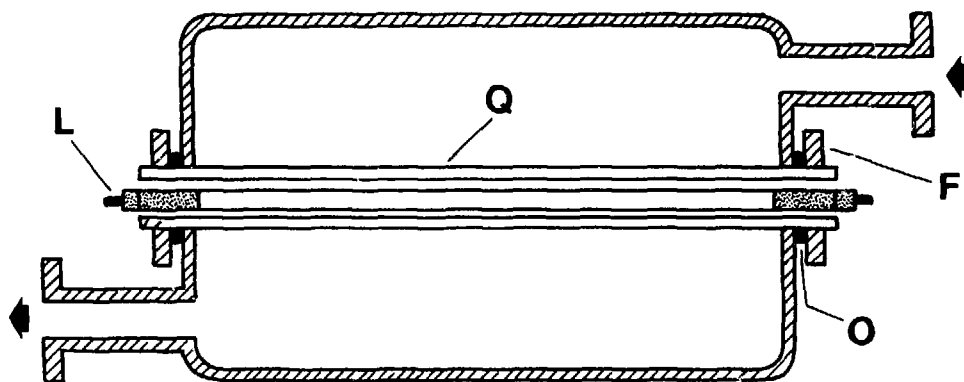


FIGURE 2: Cylindrical Photochemical Converter (Schematic). The body of the converter is constructed from steel. Estimated dimensions are: length, 3-4 m; diameter, 1-2 m. UV light from a tubular light source (L) is coupled into the converter through a cylindrical quartz tube (Q). The latter is fitted along the axis of the converter using O-rings (O) and flanges (F).

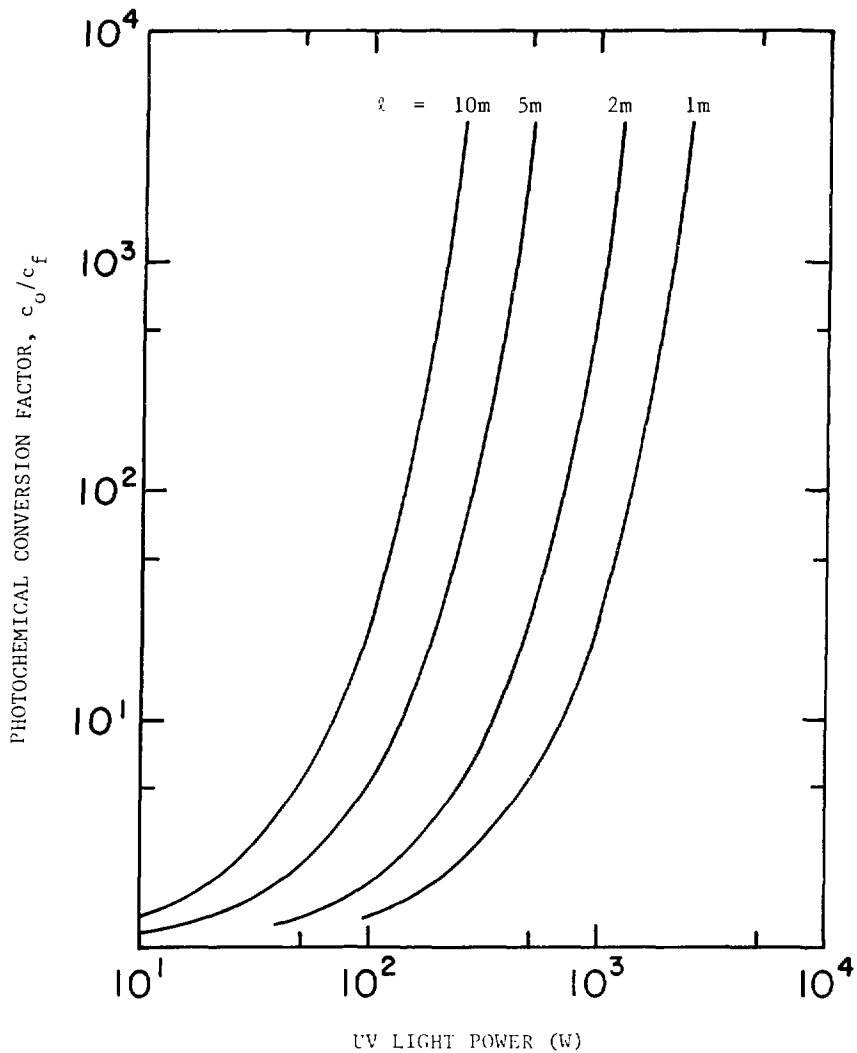


FIGURE 3: Calculated Photochemical Conversion Factor Vs UV Light Power. A reference flow of $200 \text{ m}^3 \cdot \text{h}^{-1}$ of CH_3I , irradiated with 260 nm radiation, was assumed. Conversion factors are plotted as a function of the optical path length (l).

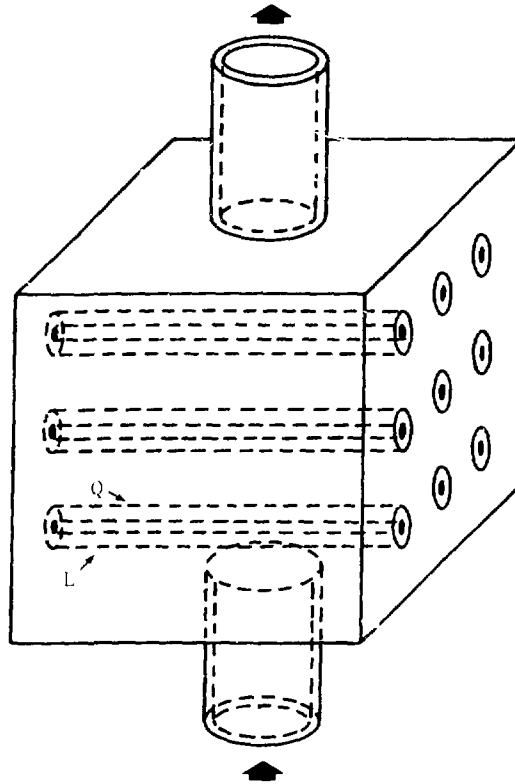


FIGURE 4: Large-Scale Photochemical Converter (Schematic). The body of the converter is constructed from steel. Estimated dimensions: 5 m x 5 m x 5 m. UV light from several tubular light sources (L) is coupled into the converter through cylindrical quartz tubes (Q) hermetically sealed into the body of the converter. This converter would be suitable for flows of $\sim 10^4 \text{ m}^3 \cdot \text{h}^{-1}$, for reactor and reprocessing vessel off-gas streams.

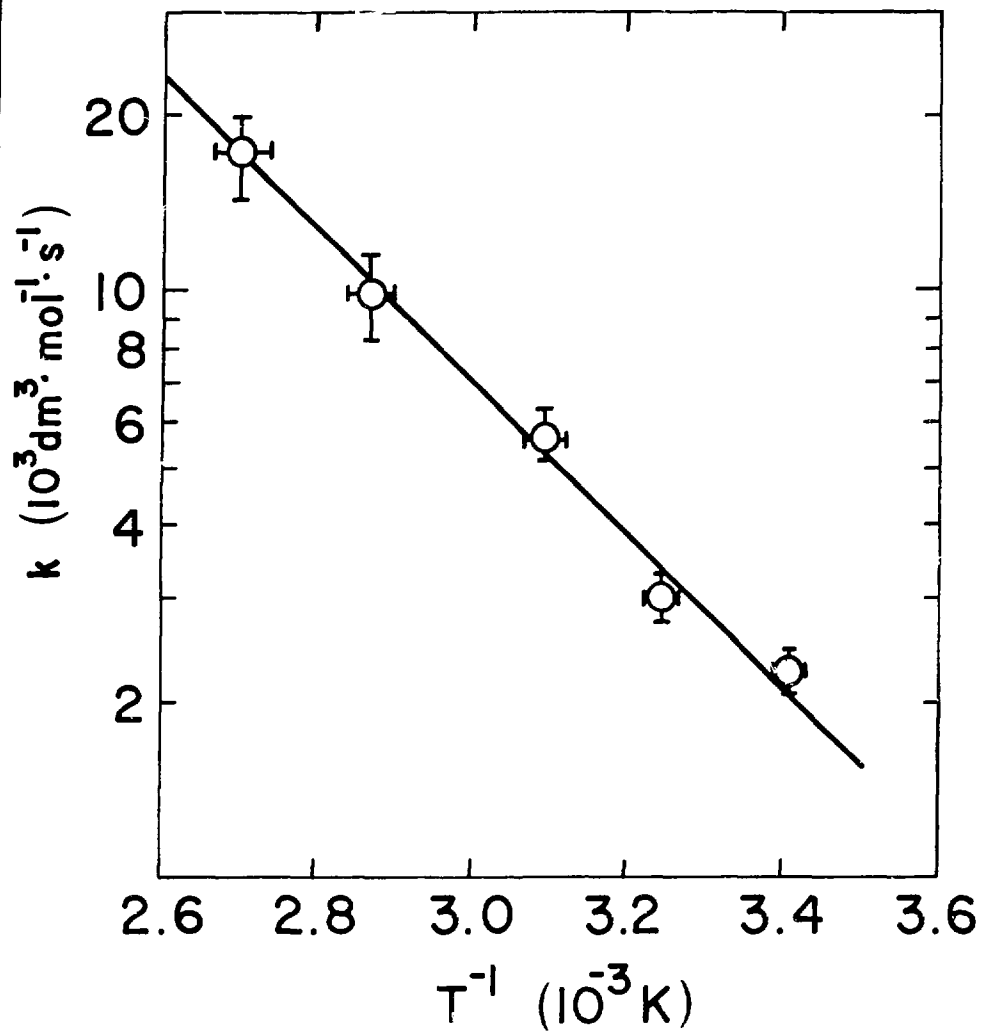


FIGURE 5: An Arrhenius Plot of the I_2/O_3 Reaction Rate Constant Vs Temperature

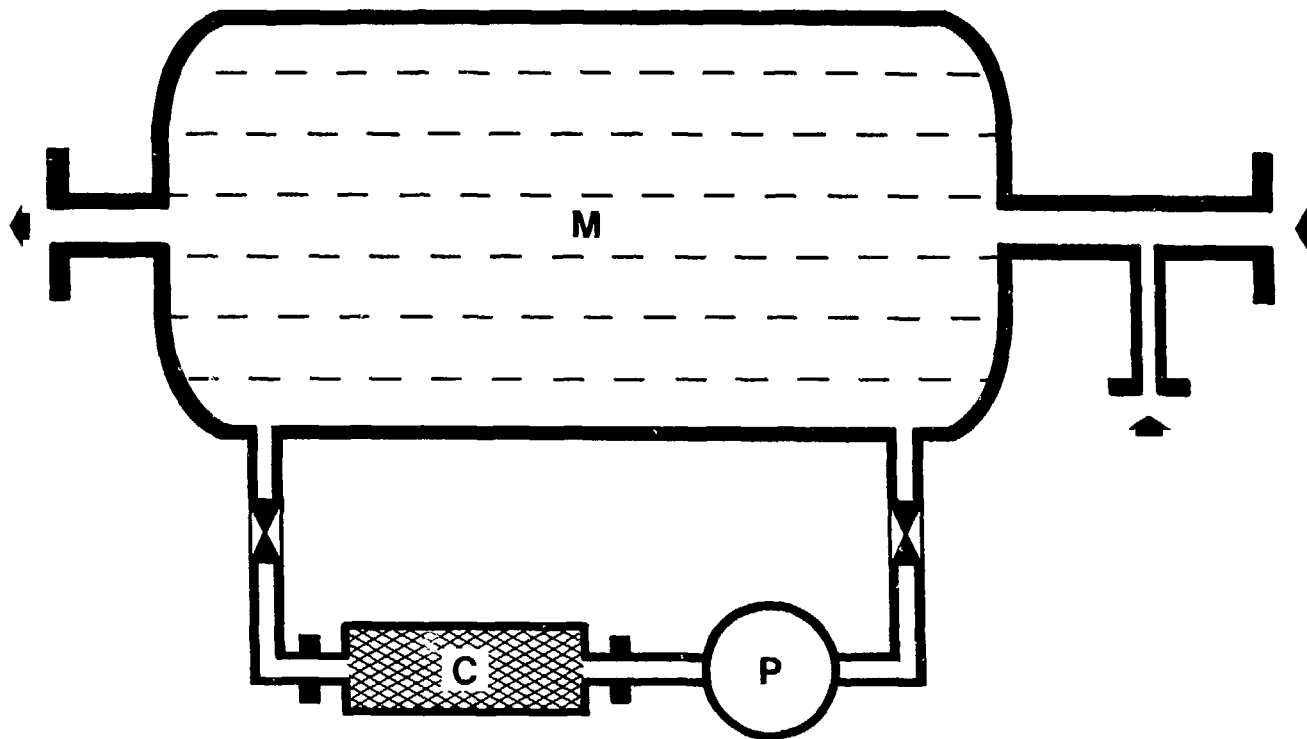


FIGURE 6: Radioiodine (I_2) Scrubber (Schematic). The scrubber is constructed from steel. Estimated dimensions: length, 3-4 m; diameter, 1-2 m. A steel mesh (M) is included in the scrubber to provide sufficient surface area for the entrainment/deposition of iodine oxides. A system for removal of the deposited iodine oxides is also included. The latter consists of a circulating pump (P) and a canister (C) for final storage of the radioiodines.

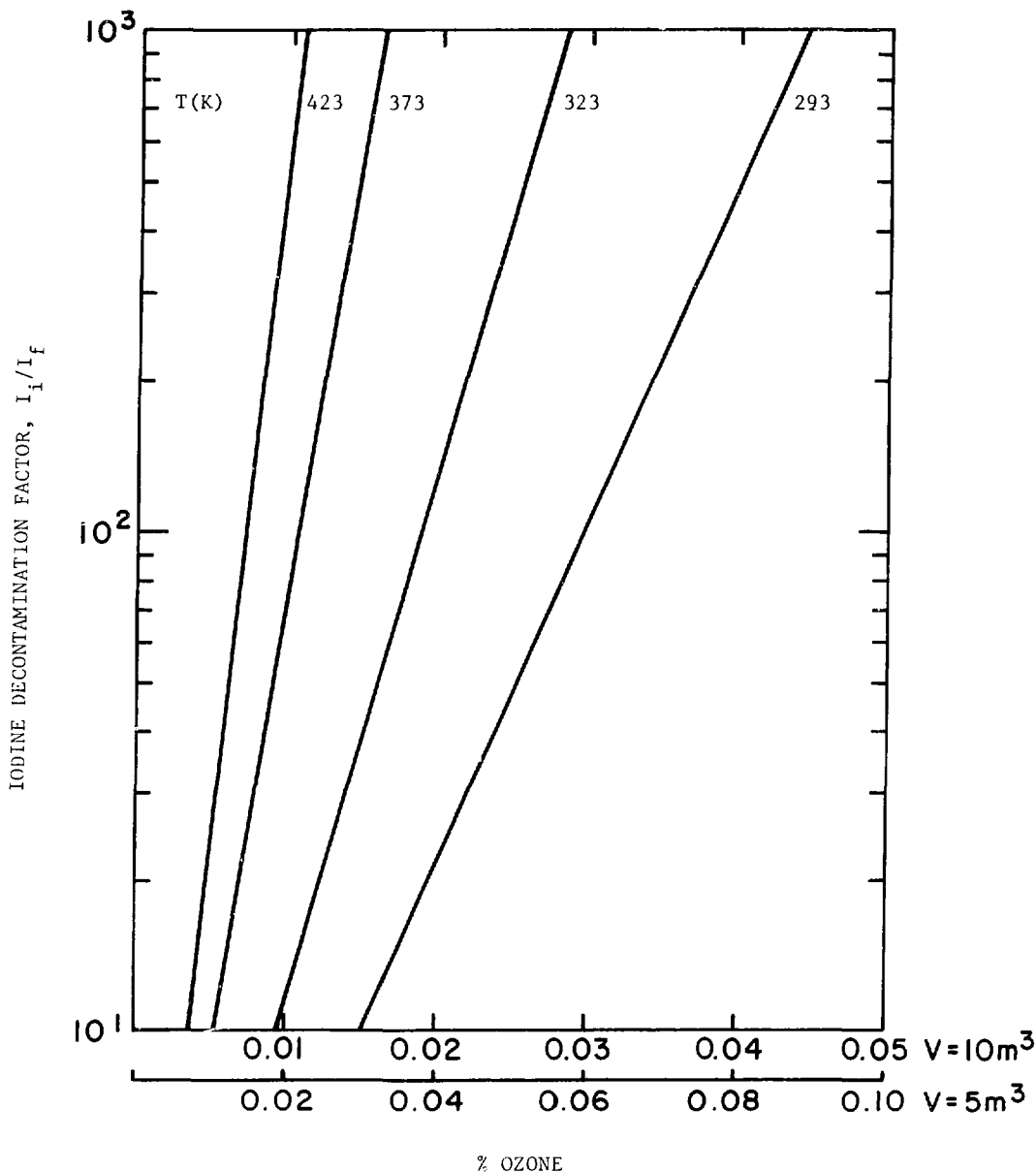


FIGURE 7: Calculated Iodine Decontamination Factor Vs Ozone Concentration. A reference flow of $200 m^3 \cdot h^{-1}$, containing $\leq 10 \mu m^3$ of I_2 , was assumed. Decontamination factors are shown as a function of scrubber volume and temperature.

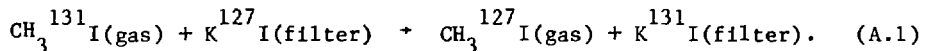
APPENDIX A

CONVENTIONAL METHODS FOR RADIOIODINE ABATEMENT

Conventional methods for the removal of radioactive iodines from nuclear reactor and fuel-reprocessing facility off-gases are briefly described below.

Charcoal Filters

Charcoal filters are used routinely in the nuclear industry for removing radioactive iodine from reactor off-gases [A.1-A.3]. For plain charcoal filters, the iodine removal mechanism is physical adsorption, which is not sufficient for the retention of organic iodides. To increase the decontamination efficiency for organic iodides, triethylene diamine (TEDA) is used as an impregnant. Charcoal impregnation with KI is also used to reduce any iodine release, via the following isotope-exchange process:



Some of the most common problems with charcoal filters are due to aging. Humidity and co-adsorbed vapours of acids and organic materials tend to passivate the charcoal. Therefore, because of the high concentrations of acids in fuel-reprocessing off-gases and the potential fire hazard, charcoal filters are not recommended for filtering reprocessing off-gases. TEDA-impregnated charcoals tend to degrade with time, primarily due to volatilization of the TEDA. There is also a concern regarding the ability of TEDA-impregnated charcoals to function effectively following a severe accident, when conditions of high temperature, humidity and radiation fields would exist.

Caustic Scrubbing

Caustic (NaOH, KOH) scrubbing is being considered for elemental iodine removal following the dissolver off-gas system of fuel-reprocessing facilities [A.1]. The I_2 is retained in the scrubbing solution as iodide (I^-). The main disadvantages of this method are the inability to retain the organic iodides and the large volumes of contaminated solutions generated.

The Mercurex Process

This process was developed in Belgium [A.4]. It uses $Hg(NO_3)_2$ - HNO_3 scrubbing solutions. The iodine is retained as insoluble HgI_2 . It is effective for elemental iodine removal and also for organic iodides, provided high concentrations (3 to 12 mol/L) of HNO_3 are used. The chief disadvantages of the process are its complexity and the large volumes of contaminated solutions generated.

The Iodex Process

The Iodex process [A.5,A.6] uses hyperazeotropic nitric acid (20-22 mol/L) as the scrubbing solution. Both elemental and organic iodines are precipitated, as HI_3O_8 . Like the Mercurex process, it is complex and generates large volumes of contaminated solutions. The use of highly concentrated nitric acid is an additional disadvantage because of its corrosive properties and explosion hazard.

The Faster Process

This process, normally used for the removal of ^{85}Kr , can also be used for the simultaneous removal of elemental and organic radioiodines [A.7]. It uses freon as an absorbent. The method has been sufficiently studied for removing ^{85}Kr , but not for iodine. The subsequent removal of the iodines from the freon solvent and the corrosive properties of the mixture have yet to be addressed.

Solid Adsorbents

Various solid adsorbents containing silver have been shown to be successful in removing both elemental and organic radioiodines from air [A.8,A.9]. These include AgNO_3 heated to 420-470 K, silica which has been impregnated with AgNO_3 (AC6120), and silver-exchanged faujasite and mordenite. These materials are by far the most promising ones for removing radioiodines from reprocessing off-gas streams. Some of the disadvantages are the high cost of silver and the high operating temperature (420-470 K). The options of regenerating the adsorbents or substituting other metals for silver are being explored.

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APPENDIX B

THE EFFECT OF NO_x ON THE PHOTOCHEMICAL CONVERSION
OF ORGANIC IODIDES

Nitrogen oxides (NO_x) are known to be present, at concentrations of up to 2% by volume, in the off-gas streams of Purex-type reprocessing facilities [B.1]. They arise from the nitric acid that is used to dissolve the fuel. The NO_x interfere with the conventional methods of radioiodine abatement, and particularly the removal of ⁸⁵Kr [B.2]. They are also atmospheric pollutants. Aqueous scrubbing techniques can be used to reduce NO_x to about 0.3% by volume [B.3]. Reduction to less than 0.05% can also be accomplished by selective reaction with NH₃, using hydrogen mordenite as a catalyst [B.1]. The effect of NO_x on the efficiency of photochemical conversion of organic radioiodides to elemental radioiodine is discussed below.

The main components of NO_x are NO₂, N₂O₄, NO and N₂O. Only NO₂ and N₂O₄ absorb light in the wavelength range (240-280 nm) that is most useful for the photolysis of the organic iodides. The absorption coefficients for NO₂ and N₂O₄ [B.4] are $\approx 7 \times 10^{-20} \text{ cm}^2$ and $\approx 7 \times 10^{-19} \text{ cm}^2$, respectively. Although absorption of light would result in oxygen atom formation, which may contribute to the decomposition of the organic iodides, as discussed in Section 2.4, this favourable effect is discounted in order to determine the maximum NO_x impact. The NO_x are also known to be good scavengers of organic radicals and thus would react with the organic radicals formed by the photolysis of RI; however, this has no adverse bearing on the process at hand. Also, no stable compounds of NO_x with iodine are known to exist; thus the recombination of iodine atoms to elemental iodine will not be affected.

The N₂O₄ is produced by the dimerization of NO₂, as follows:



Equilibrium considerations [B.5] show that the N_2O_4 concentration decreases with decreasing NO_2 concentration and increasing temperature. Thus, N_2O_4 is unimportant at NO_2 partial pressures less than about 0.001 atm, achievable by NO_x scrubbing techniques. At higher NO_2 partial pressures, N_2O_4 can be reduced to insignificant levels by raising the temperature of the off-gases to more than 330 K.

Therefore, the only NO_x effect to be considered is light absorption by NO_2 .

The effect of NO_2 on the photolysis of organic iodides amounts to that of an "inert absorber", and can be predicted by including in Equation (4) (Section 2.2) a term for light intensity attenuation due to absorption by NO_2 . This term is given by $e^{-\alpha'c'\ell}$, where α' and c' are the absorption coefficient and concentration of NO_2 , respectively. On integration of the modified Equation (4), we obtain

$$\ln(c_0/c) = \alpha I_0 f^{-1} A \left(\frac{1 - e^{-\alpha'c'\ell}}{\alpha'c'} \right) \quad (B.2)$$

Equation (B.2) is identical to Equation (5) except for the factor in parenthesis, which replaces the optical path length, ℓ . This factor corresponds to the effective optical path length in the presence of NO_2 .

To achieve the same organic iodide conversion factor as without NO_2 , the light intensity would need to be increased by a factor of $\alpha'c'\ell / (1 - e^{-\alpha'c'\ell})$. Numerical values of this factor are given in Table B-1, as a function of NO_2 concentration and ℓ . Table B-1 shows that for NO_2 concentrations up to 0.1% by volume, achievable by NO_2 scrubbing, only a moderate increase in light intensity is required. In the absence of NO_2 scrubbing, with NO_2 concentrations of up to 2% by volume, the intensity would need to be increased by a factor of 4 ($\ell = 1$ m) to 40 ($\ell = 10$ m) to achieve conversion factors comparable to those in the absence of NO_2 . Light intensity requirements for the latter case can be achieved only with coaxial illumination ($\ell = 1$ m).

In conclusion, NO_x concentrations in excess of about 0.2% by volume are undesirable in the photochemical conversion of organic iodides, even though the NO_x effect can be mitigated at the expense of higher light intensities.

TABLE B-1

INTENSITY ENHANCEMENT FACTORS REQUIRED TO ACHIEVE
THE SAME ORGANIC IODIDE CONVERSION AS IN THE ABSENCE OF NO_2

Path length z (m)	NO_2 (% by vol)			
	0.1	0.2	1	2
1	1.1	1.2	2.1	3.6
2	1.2	1.4	3.6	7.0
5	1.5	2.1	8.8	18
10	2.1	3.6	18	35

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