ENVIRONMENTAL PROTECTION DURING FUEL PROCESSING*

O. O. Yarbrow, J. P. Nichols, W. E. Unger

Oak Ridge National Laboratory
Oak Ridge, Tennessee**MASTER**

INTRODUCTION

In all areas of technical endeavor, the interaction of operating systems with the environment is becoming increasingly important. This increasing interest in protecting and purifying the environment is necessitating reevaluation of systems for effluent control at nuclear facilities. In the past, radioactivity in effluents has been limited to quantities that would yield concentrations of radioactive contaminants at site boundaries well below levels set by national and international agencies for continuous intake by the public. Based on these standards, fission products are removed from plant effluents to a level commensurable with discharge limitations. Such fission products as ^{85}Kr , ^3H , and ^{129}I can be released in total while meeting existing regulations, thus present generation commercial facilities have not made it a practice to remove these materials.

The philosophy of limiting exposure to persons in the vicinity of a nuclear facility to previously acceptable concentrations of activity, as the basis for effluent control, has recently been questioned on at least two fronts. First with the projected future expansion of the nuclear power economy the generation rate of fission product activity will increase many fold over the coming decades. The buildup of a long half-life radionuclides in the world's environment must be considered in addition to the shorter term effects on the immediate local. Second, a general philosophy is developing which requires that, even though activity releases are well below accepted release standards, discharges should be further reduced where technology will permit without undue economic penalties being incurred. Thus new approaches to effluent control from nuclear facilities will probably be required in the future.

Development of highly efficient effluent control systems for future reprocessing plants for fuel from Liquid Metal Fast Breeder Reactors (LMFBR) has been underway at ORNL for a number of years. Due to the higher specific power, higher burnup, and an economic incentive for processing at shorter decay times, future LMFBR fuel reprocessing plants will require fission product retention factors (particularly for volatile fission products) orders of magnitude higher than the capability of existing Light Water Reactor (LWR) fuel reprocessing plants. The technology under development for LMFBR reprocessing plants is directly applicable for effluent control in all types of reprocessing facilities.

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The required removal of particulate activity from gaseous and liquid effluents can probably be obtained by application of existing technology, particularly if the volume of gaseous and liquid effluents are substantially reduced. The most challenging technical problems arise in the development of systems for the removal and control of the volatile fission products, in particular I, Kr-Xe, and ^3H . It is in the area of volatile fission product control that this paper deals in some detail.

EFFECTS OF ROUTINE DISCHARGE OF VOLATILE FISSION PRODUCTS

In an effort to bracket the range of reduction in volatile fission products that might be desirable, the effects of such releases on both local and worldwide environments are summarized.

The effects of long term accumulation of krypton and tritium in the world's environment is presented in Fig. 1. Exposure levels from krypton and tritium assume total release of krypton and tritium from a projected nuclear power economy. Krypton is assumed to mix uniformly with the lower atmosphere and tritium is assumed to mix uniformly with the world's circulating water inventory. The exposure from naturally produced tritium and tritium residue from past thermonuclear bomb tests are included for comparison. Of significance is the observation that krypton exposure in the year 2000 is about 3 mr/year (2% of total natural background). Exposure from tritium in the year 2000 is completely insignificant in comparison with total natural background (~0.002%) but approximately equals the exposure from naturally occurring tritium.

A 3% increase in exposure level in the year 2000 from krypton is small in comparison to incremental exposures from other man made sources (20-200 mr for single chest x-ray, for example) and certainly if krypton were retained by a factor of say 100, the incremental exposure from this source would be insignificant.

Although the exposure from tritium is small in comparison to total background, some concern has been expressed recently over tritium discharges due to the intimate way hydrogen enters into the life process. Experiments to date have shown no measurable effects of tritium activity other than those produced by the accumulated radiation exposure. Even if such a specter proves real in the future, reducing the exposure from tritium produced by nuclear power to a few percent of natural tritium background should be an adequate safeguard. Thus it would appear that from the standpoint of long term effects, reducing the release of both krypton and tritium discharges by factors of ~100 would reduce the already small effects to insignificant values.

Turning now to the local exposures resulting from routine discharge of volatile fission products, Table 1 summarizes the input, and discharges from a typical, present generation plant reprocessing one metric ton/day of fuel decayed 150 days. As indicated the maximum exposure rate of a person spending full time at the downwind site boundary is ~155 mrem/year, comparable to natural background. Recently imposed regulations on reactor installations have limited total exposure

LONG TERM EXPOSURES TO WORLD POPULATIONS FROM KRYPTON AND TRITIUM

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Table 1. Relative Insult to Local Environment From Release of Volatile Fission Products From Reprocessing Plants

	Input ^a (Ci/ton)	Plant Retention Factor	Environmental Concentration Factor	Exposure ^b At Site Boundary mrem/year	Percent of Total Volatiles
¹²⁹ I	0.04	10	700 ^c	60	39
¹³¹ I	2	100	700	60	39
⁸⁵ Kr	10 ⁴	1	1	30	19
³ H	700	1	1	<u>5</u>	<u>3</u>
Total Volatile				155	100

^aTypical LWR fuel decayed 150 days.

^bAnnual average aeolian dilution of 2.2×10^{-7} sec/m³ assumed for 100 M stack and 1.5 km distance to site boundary.

^cAssumed value to demonstrate relative effect.

at site boundaries to a maximum of 5 mrem/year. As a single reprocessing plant handles the fuel from about 15 reactors and reprocessing plants are usually more remotely located, a similar limit on reprocessing plants is at least an order of magnitude more conservative on a benefit-effect basis. Assigning 2 of the 5 mrem/year to the volatile fission products, with 0.5 mrem/year going to each of the four isotopes listed in Table 1, yields retention factor of 1.2×10^3 for ^{129}I , 1.2×10^4 for ^{131}I , 65 for Kr and 10 for ^3H .

From this rather simple analysis it would appear that the desired retention factor for fuel reprocessing plants are: of the order of 100 for ^3H , 10^2 - 10^3 for ^{85}Kr , 10^4 - 10^5 for ^{131}I , and 10^3 - 10^4 for ^{129}I . If they could be practically attained, they should reduce both the local and long-term effects to insignificant values. If decay time of the fuel is reduced below the 150 day value assumed, the ^{131}I retention factor should be increased a factor of 10 for each 28 day reduction in decay time prior to processing.

OFF-GAS FLOWSHEET FOR VOLATILE FISSION PRODUCT CONTROL

In order to attain significant improvements in the retention of the volatile fission products, greater attention must be given to containment and to the reduction of both gaseous and liquid effluent volumes. Reduction of net effluent volumes, by two to three orders of magnitude below current practice, is desirable and possibly mandatory for the economic operation of high efficiency removal systems.

One approach to the control of the volatile fission products in a fuel reprocessing plant is depicted in flowsheet form in Fig. 2. Tritium must be evolved from the fuel and trapped prior to contacting the fuel with aqueous solutions in the dissolver, to avoid hopeless dilution of the tritium by the plant water inventory. Krypton is released during dissolution and can be trapped from the relatively small volume of dissolver off-gas. Most of the iodine can be vaporized from the dissolver solution and recovered from the dissolver off-gas by the primary iodine removal system. This is desirable as it prevents the bulk of the iodine from contacting organics in the solvent extraction systems and thus forming organic iodide complexes that are much more difficult to remove than elemental iodine.

The primary iodine removal equipment on the dissolver off-gas stream should provide decontamination capabilities in excess of 10^3 , so that iodine remaining in the effluent is less than that evolved from downstream equipment. The effluent from the primary system is combined with the off-gas from the remainder of the process equipment, and the off-gas from the high-level analytical cells, and passes through a secondary iodine removal system with a DF capability in excess of 10^3 . The effluent from the secondary system is combined with the cell off-gas and is passed through a final iodine removal system where a DF of 10^3 - 10^4 is desirable. This final system should have some excess capability for iodine removal to protect against abnormal conditions such as temporary malfunction of one of the preceding systems or a significant release of iodine to the cell atmosphere.

Processes for the control and removal of each of the volatile fission products from process streams have been under development at ORNL for a number of years. Some of the more attractive systems applicable to the process steps illustrated in the flowsheet (Fig. 2) are described in some detail here.

OFF GAS TREATMENT FLOWSHEET -

FUEL REPROCESSING PLANT

VOLATILE FISSION PRODUCT CONTROL SYSTEMS

Tritium Evolution and Removal

The control of tritium in a fuel reprocessing plant depends on the evolution of tritium from the fuel, prior to contacting the fuel with aqueous systems, and then effectively trapping the evolved tritium from a relatively small off-gas stream. Tritium escaping from failed fuel pins during mechanical handling and disassembly operations may be significant in comparison to tritium retention requirements, and thus require the off-gas from the mechanical handling cell to be treated for tritium removal. Shearing of the fuel elements will most certainly release tritium in significant quantities and necessitate treatment of the shear off-gas.

A process step, given the name "voloxidization," in which the sheared fuel is heated in air to $\sim 450^{\circ}\text{F}$ for two to four hours effectively evolves tritium from the fuel. In rather extensive laboratory and hot cell experiments¹ with the voloxidization systems, residual tritium has ranged from < 0.1 to $\sim 0.5\%$ of that produced in the fuel. If the combined off-gas from the mechanical handling cell, the shear, and the voloxidization step can be limited to a few tens of cfm, removal of tritium as tritiated water is a straightforward process using common desiccants such as molecular sieves. Keeping the off-gas rate low is important both from the standpoint of equipment size and complexity and to limit the volume of tritiated water that must be permanently stored. For example, the water content of a 10 cfm air stream saturated at 70°F is approximately two gallons a day.

Evolution and Removal of Krypton-85

As was the case with tritium, a significant fraction of the krypton may escape from ruptured fuel pins during mechanical handling and disassembly, thus requiring krypton removal from the mechanical handling cell off-gas. Krypton and xenon are evolved during shearing and voloxidization to the extent of 30 to 90% with the remainder being evolved when the fuel is dissolved. Thus, as indicated in Fig. 2, the logical location for krypton removal equipment is on the combined off-gas streams from the dissolver and tritium removal equipment. Effective krypton removal can be accomplished at any point downstream of the dissolver but effective and economic control of krypton-xenon is closely related to relatively low off-gas rates.

A number of systems for removing krypton from off-gas streams have been demonstrated and three of the most promising include cryogenic adsorption on charcoal or other solid sorbents, cryogenic adsorption in liquid nitrogen followed by fractional distillation, and selective adsorption in fluorocarbons. A brief description of each of these systems with reference to more detailed reports follows.

Cryogenic Adsorption on Charcoal

Adsorption on charcoal at liquid nitrogen temperatures is an effective system for removing krypton and xenon from pure off-gas streams and was demonstrated on

a large scale on the dissolver off-gas at the Idaho Chemical Processing Plant about 15 years ago. Although the removal system is relatively simple, effective and safe operation is totally dependent on elaborate gas pretreatment systems to remove essentially all contaminants such as CO_2 , nitrous oxides, hydrocarbons, water, and oxygen. ~~The disadvantages of such a system limit its applicability to the off-gas from a reprocessing plant.~~ *This elaborate pretreatment limit*

Cryogenic Absorption in Liquid Nitrogen

Absorption of krypton and xenon in liquid nitrogen, followed by fractional distillation to concentrate the krypton-xenon fraction, is an effective method of removing and concentrating the krypton for storage. The systems, like cryogenic adsorption on charcoal, ^{are} dependent on a pure feed gas free of all contaminants such as water, CO_2 , nitrous oxides, and organics. A potential explosive hazard exists from the buildup of trace organics or radiation-produced ozone in the system. It is felt that these problems can be satisfactorily dealt with and cryogenic distillation is considered to be one of the two most promising processes for krypton-xenon recovery. Such a system has been in operation for a number of years at the Idaho Chemical Processing Plant and systems are presently being marketed commercially for removal of krypton-xenon from reactor off-gas streams.

Selective Absorption in Fluorocarbons

Absorption and separation of krypton and xenon from air streams by contacting with fluorocarbons has been demonstrated on a pilot plant scale at the Oak Ridge Gaseous Diffusion Plant. This system operates in the temperature range of -50 to $+25^\circ\text{F}$ and thus avoids the potential hazards associated with operating at liquid nitrogen temperatures. The system is also much less sensitive to contaminants in the feed gas such as trace organics, CO_2 , and nitrous oxides. Water must be effectively removed, however, to prevent icing up of the system. The system is shown schematically in Fig. 3.

IODINE CONTROL SYSTEMS

Overall containment of iodine in a reprocessing plant requires an understanding and control of iodine in each of the process steps as well as the ability to effectively remove iodine from liquid and gaseous effluent streams. This total control becomes increasingly important as retention factor requirements increase. The approach to iodine control illustrated in Fig. 2 includes the evolution of the bulk of the iodine from the dissolver solution and subsequent trapping of the iodine from the dissolver off-gas. All plant effluent streams, both liquid and gaseous are further treated to remove trace quantities of iodine which escape or bypass the primary system. A number of systems for evolution and trapping of iodine are in various stages of development.

Figure 2
KRYPTON-XENON ABSORPTION PROCESS PILOT PLANT
SCHEMATIC FLOW DIAGRAM

Iodine Evolution from Aqueous Streams

In general, 95-99% of the iodine can be evolved from dilute (< 6 molar) nitric acid solutions by gas sparging or by evaporation of 5-10% of the liquid. For reasons not completely understood, further removal of iodine activity is difficult, even if stable iodine carrier is added to restore the initial ($\sim 10^{-5}$ molar) iodine concentration. A number of methods for promoting isotopic exchange between the added carrier and the residual activity have been investigated. These include refluxing at the boiling point for 24 hr, autoclaving at elevated temperatures, and sparging the solution with an excess of ozone. Although each of these techniques is capable of producing the desired isotopic exchange, many practical problems must be solved before these techniques are applicable to actual dissolver solution on a plant site.

Off-Gas Scrubbing With Concentrated Nitric Acid

An aqueous scrubbing system employing nitric acid at concentrations in the range of 16 to 19 molar is very effective in removing both elemental iodine as well as organic iodides from gas streams. All iodine forms are oxidized to the I^{+5} valence state by the concentrated nitric acid and can be removed from the bottoms of an evaporator as dense I_2O_5 solids. Laboratory data indicate that iodine retention factors in excess of 10^4 are attainable in scrubbing equipment operating at normal liquid and gaseous throughputs. This system is particularly attractive for the primary iodine removal systems where kilogram quantities of iodine must be removed in a form suitable for permanent storage.

Off-Gas Scrubbing with Mercuric Nitrate-Nitric Acid

With the addition of 0.2 to 0.4 molar mercuric nitrate to nitric acid in the concentration range of 10 to 14 molar, efficient scrubbing of both elemental and organic iodides can be obtained. The iodine is removed as mercuric iodate and can either be disposed of in this form or converted to sodium iodide and the mercury recycled to the scrub system. The mercuric nitrate scrub system has similar advantages and applications to the concentrated nitric acid system and the choice between the two may be one of choosing between working with mercury or above-azeotropic nitric acid.

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Solid Sorbents for Iodine Removal

In considering some of the more promising solid sorbents for removing iodine from plant off-gas streams, we must include charcoal which has long been used to effectively remove both elemental and methyl iodide from clean, dry gas streams. Applications of charcoal beds for removal of iodine from actual processing plant off-gas streams have often proven ineffective due to the sensitivity of charcoal to poisoning by trace organic vapors and other contaminants. The efficiency and useful life of charcoal beds can be greatly improved by preceding the charcoal by a catalytic oxidation step to convert all iodine to the more effectively adsorbed elemental form and to completely oxidize all organic vapors in the gas stream.

Other solid sorbents for removal of iodine compounds from gas streams have been investigated and one of the most attractive is Linde 13X Molecular Sieve, in which the normal sodium zeolite matrix has been partially converted to silver zeolite. This material has removal capability equal to, and possibly better than, charcoal for most iodine forms, with the additional advantages that it is noncombustible and appears to be less affected by organic contaminants in the off-gas stream. Methyl iodide decontamination factors approaching 10^4 can be obtained at gas velocities of 20-50 ft/min for 2-in.-thick beds of silver zeolite. The most favorable operating temperature for silver zeolite beds is in the range of 200°C.

Although much superior to charcoal with respect to poisoning by organics, other contaminants, specifically halides and sulfur compounds, quickly poison silver containing beds if present in significant quantities.

SUMMARY

The trend toward tightened restrictions on the radioactivity of effluents from nuclear facilities is evident. Recent revisions to ^{10 CFR} part 50 of the Federal Register have reduced the permissible discharge limits from reactors, by approximately a factor of 100 and part 20 has been revised to require discharges to be reduced "as far below the limits specified in this part as practicable." In response to these requirements for improved effluent control, new methods for removing the volatile fission products are under development. Efficient methods for controlling tritium, krypton-xenon, and iodine in fuel reprocessing plants have been demonstrated on a laboratory and small engineering scale. Full-scale demonstrations have not been carried out as yet and many scale-up questions as well as the engineering problems associated with an actual plant applications are yet to be answered. In the direction of answering some of these questions, study contracts have been arranged with commercial fuel reprocessors to determine if and how this recent technology can be applied to existing plants. Continuing research and development is directed toward further improving systems for effluent control and obtaining a better understanding of basic reactions of the important fission products in the many chemical steps found in a fuel reprocessing plant.