MASTER

DEVELOPMENTS IN EFFLUENT CONTROL FOR BREEDER REPROCESSING FACILITIES

O. O. Yarbro and M. B. Sears
Consolidated Fuel Reprocessing Program
Oak Ridge National Laboratory*
Oak Ridge, Tennessee 37830

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DEVELOPMENTS OF EFFLUENT CONTROL FOR BREEDER REPROCESSING FACILITIES*

O. O . Yarbro and M. B. Sears

Consolidated Fuel Reprocessing Program
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

1. INTRODUCTION

The trend over the past decade has been toward increasingly stringent
limits on radioactive effluents from nuclear facilities. In the early
1970's the requirement that the releases of radioactive materials should
be "as low as practicable," which was later replaced by "as low as
reasonably achievable," was added to the Code of Federal Regulations,
Title 10, Part 20 (10 CFR 20). This was in addition to the limits on
exposures and off-site concentrations that have been in effect for many
years. More recently (1979) the new Title 40, Part 190 (40 CFR 190)
has imposed tight restrictions on the Light Water Reactor (LWR) fuel
cycle with new limits on the maximum exposure to a member of the general
public and new limits on the quantity of certain isotopes which may be
released.

The trend toward reducing quantity of radioactive materials whiᴄh
may be released from nuclear facilities, the higher burnup and specific
power levels of fast breeder reactor fuels, and the potential economiᴄ
incentive to reduce preprocessing cooling for breeder fuels have placed
stringent demands on the effluent control systems for fast breeder fuel
reprocessing plants. As a result of these trends, a significant part
of the breeder fuel reprocessing development program over the last decade
has been devoted to the development of advanced effluent control systems.

2. SUMMARY OF EXISTING REGULATIONS

Two documents that specifically regulate routine effluents and resulting
off-site exposures from nuclear fuel reprocessing facilities are the
10 CFR 20 and 40 CFR 190. The 10 CFR 20 includes the general requirement
that exposures be kept "as low as is reasonably achievable" and sets
exposure limits in unrestricted areas as follows:

1. Maximum whole body radiation dose of 0.5 rem to any individual
    in one calendar year;

2. Radiation level which if an individual was continuously present
    could result in a dose of 2 millirems in any one hour; and

3. Radiation level which if an individual was continuously present
    could result in a dose of 100 millirems in any seven consecutive
    days.

The 10 CFR 20 also sets maximum concentrations of each significant radioactive isotope in air and water in unrestricted areas as listed in 10 CFR 20, Appendix B, Table II.

The 40 CFR 190 is more restrictive on permissible exposures in unrestricted areas and, in effect, also sets maximum release fractions of some specific isotopes from the total LWR fuel cycle. Specifically, 40 CFR 190 limits the annual dose to a maximum of 25 millirems to the whole body, 75 millirems to the thyroid, and 25 millirems to any other organ for any member of the public from planned discharges of radioactive materials, excluding radon and its daughters.

Limits on the release of specific radioactive isotopes from the entire fuel cycle are set as the maximum permissible release per gigawatt year of electrical energy produced and are as follows:

1. Krypton-85   50,000 curies/gigawatt year

2. Iodine-129   5 millicuries/gigawatt year

3. Plutonium-239 and other   0.5 millicuries/gigawatt year
   transuranics ($t_{1/2} > 1$ yr)

This regulation does not specify or suggest any distribution of these discharge limits among the various parts of the fuel cycle. From past experience, most of the krypton-85 and iodine-129 released from the fuel cycle have resulted from reprocessing. Small releases of plutonium and other transuranics may occur at the various steps of the fuel cycle.

The approximate fuel cycle retention factors needed to meet the 40 CFR 190 release limits are as follows:

		LMFBR fuel cycle	LWR fuel cycle
1.	Krypton-85 retention factor	5	10
2.	Iodine-129 retention factor	200	260
3.	Plutonium-239 retention factor	3×10^{10}	1×10^{10}

The difference in the krypton-85 and iodine-129 retention factor requirements is due primarily to higher proposed electrical efficiencies for fast breeder reactors and slight differences in fission yields. The higher plutonium-239 retention factor for breeder fuels results from the higher plutonium-239 content of breeder fuels and differences in other transuranic element concentrations. The actual retention factor required for any facility will be determined by the types of fuels processed and the way the total release limits are distributed across the various segments of the fuel cycle.

To date, there are no specific release limits for tritium and carbon-14 other than their contributions to overall exposure limits.

3. DEVELOPMENT OF ADVANCED EFFLUENT CONTROL TECHNOLOGY

The trend toward more restrictive effluent controls and the potential
economic incentive for reducing decay times prior to reprocessing fast
breeder reactor fuels has lead to an early decision to develop advanced
effluent control systems for breeder fuel reprocessing plants. About
a decade ago, a program was initiated to develop improved effluent
control systems for the volatile fission products iodine-129, iodine-131,
krypton-85 and hydrogen-3. A few years later carbon-14 was added to
the list. Although these volatile fission products contribute a
significant fraction of the total off-site dose from exposure to fuel
reprocessing effluents, little or no retention has been demonstrated
in the past at existing facilities. Improved confinement of other
fission products which, in general, are particulate in nature, appear
to be achievable by reasonable extrapolations of long used and proven
technology.

A good description and the status of the various effluent control
systems for each of the volatile fission products are given in "Alternatives
for Managing Wastes from Reactors and Post-Fission Operations in the
LWR Fuel Cycle," ERDA-76-43. In addition to developing improved effluent
control systems for specific fission products, concepts directed at
simplifying and improving overall effluent control have been developed
over the years. In general, the trend in recently designed facilities
has been directed toward (1) eliminating liquid effluents by evaporating
excess water to the stack after extensive purification and (2) reducing
the volume of off-gases to be treated.

3.1 Iodine Control Technology

Prior to the 1960's, iodine removal systems used at reprocessing
facilities included adsorption on charcoal, scrubbing with caustic, and
adsorption on silver-coated tower packing. Each of these systems has
performed poorly over the long term: (1) charcoal is rapidly poisoned
by trace materials normally found in reprocessing plant off-gases and
is susceptible to ignition in presence of nitrous oxides; (2) caustic
scrubbing effectively removes elemental iodine from pure air but is
ineffective for the normal mix of iodine forms normally found in actual
plant applications; and (3) the silver-coated tower packing has relatively
low active surface areas and long-term performance has been less than
expected.

Two advanced systems for iodine removal which have very high removal
efficiencies for all iodine species normally found in reprocessing
plant off-gas streams, have been developed through engineering scale
demonstration.

One system is based on iodine adsorption on a high surface area
substrate exchanged or coated with silver. Typical of this type of
system is the zeolites chemically exchanged to the silver form. Iodine
retention factors in excess of 10^4 have been demonstrated and should

be maintainable for extended periods of time without bed replacement. This type of adsorbent is fairly insensitive to most trace contaminants, with one exception being the halide elements and sulfur compounds which react with and consume the silver. The system has the advantage of being relatively simple. The major disadvantage is the use of a relatively rare and expensive resource in the form of silver. Various systems for regeneration and recycle of silver have been studied.

A second system uses concentrated nitric acid ($\sim$22 $\underline{M}$) as the scrubbing medium in a bubble cap tower to oxidize and remove all iodine species from the gas streams. Iodine retention factors in excess of 10^4 have been demonstrated. Reconstitution and recycle of the concentrated nitric acid are included in the system, and the removed iodine is in the form of a concentrated solid. The primary disadvantage of the system is the handling of the concentrated nitric acid.

3.2   Krypton-85 Control

In the past, there has been no removal of krypton-85 from reprocessing plant off-gases for effluent control purposes. Existing regulations will require removal of krypton-85 in future commercial reactor fuel reprocessing plants by factors of 5 to 10. Two systems have been demonstrated in engineering scale equipment with capabilities of removing krypton-85 from typical reprocessing plant off-gases by factors of 100. One system absorbs krypton in liquid nitrogen, and then concentrates and purifies the krypton by fractional distillation. All constituents of the off-gas, which could freeze out and cause system plugging, must be removed by a gas pretreatment system. It may be necessary to remove oxygen from the feed gas to prevent ozone formation and concentration for safety reasons. The system uses technology that has been in use for many years in commercial air liquefaction plants.

The second system is based on selective absorption of krypton in a fluorocarbon solvent with subsequent fractionation to concentrate the krypton. This system is relatively insensitive to the constituents of reprocessing off-gases. Some pretreatment of the feed gases may be desirable for economic reasons, but failure of a pretreatment system does not result in system shutdown.

Both of the krypton-removal systems can be tailored by minor additions to remove carbon-14 as CO_2 from the feed gas. In the cyrogenic system, CO_2 must be removed in the gas pretreatment system whereas the fluorocarbon system will remove CO_2 along with the krypton for subsequent separation.

3.3   Tritium Control Technology

In the past, tritium has been released from fuel reprocessing plants primarily in the effluent water or water vapor stream. There are currently no regulations specifically limiting the release of tritium except as a contributor to maximum off-site exposure limits.

Two approaches to tritium control are being developed. One is based on the evolution and subsequent trapping of tritium from the sheared fuel prior to dissolution thus preventing the mixing of the tritium with the plant water inventory. The second minimizes the volume of excess water leaving the plant and applies some type of isotopic separation system to remove and concentrate the tritium from the effluent water.

4. APPLICATION OF ADVANCED EFFLUENT CONTROL SYSTEMS

The demonstration of advanced effluent control systems is a major objective of the Hot Experimental Facility (HEF), a pilot plant currently in conceptual design for reprocessing fuels from early demonstration fast breeder reactors. Improved effluent control results from a combination of reduced off-gas volumes, the use of advanced effluent control systems, and careful attention to the elimination of bypasses around treatment systems. A simplified effluent control system proposed for the HEF is shown in Fig. 1 to illustrate this approach. Off-gas volumes are kept as low as practical and contaminants are removed near their source to minimize dilution and mixing throughout the plant off-gas systems. The process cell is designed for very low gas inleakage, and all cell off-gas is routed to and treated by the process vessel off-gas system.
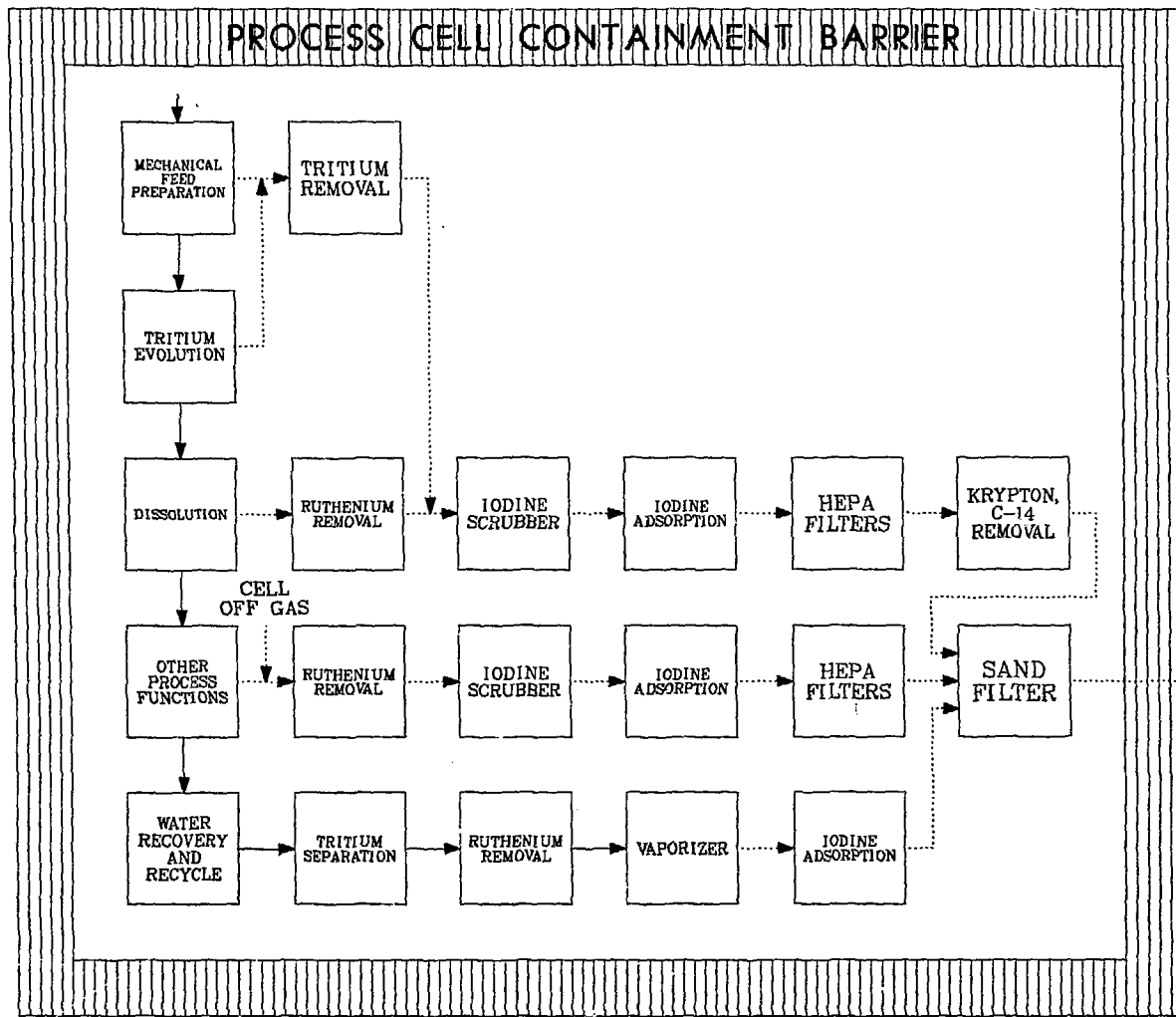
Tritium is evolved from the fuel prior to dissolution into a small off-gas stream and subsequently trapped. Greater than 95% of the iodine is evolved from the dissolver solution into the dissolver off-gas system and removed by a concentrated nitric acid scrubbing system backed by silver zeolite sorbent beds. Krypton-85 and carbon-14 (as CO_2) are also released during the dissolution step and are removed from the dissolver off-gas by a fluorocarbon absorption system. The dissolver off-gas is also treated to remove ruthenium and is extensively filtered for particulate removal.

The vessel off-gas system handles the process off-gas from the remainder of the process and the cell off-gas. Vessel off-gas is treated for iodine removal by a concentrated nitric acid scrubbing system backed by a silver zeolite sorbent bed. The vessel off-gas is treated for ruthenium removal and extensively filtered for particulate removal.

Excess water from the process operation is minimized by limiting water input to the extent practical. Process liquid wastes are treated to recover and purify water and acid for recycle. Excess water is to be treated to remove tritium by isotopic separation, passed through a ruthenium removal system, and then vaporized. The water vapor is treated for iodine removal, filtered, and released to the stack.

This concept is intended to demonstrate the feasibility of the various advanced effluent treatment systems and is based on the reprocessing of fast breeder fuels decayed as little as 90 d. Off-site exposures from routine releases are projected to be more than an order of magnitude below current regulations. Two tritium removal systems have been included

in an effort to demonstrate the feasibility and capability of each, and one or the other will be used. With a less stringent set of design objectives, some of the treatment systems illustrated here could be eliminated. One of the objectives of the HEF concept is to determine feasibility and provide information relative to cost/benefit for advanced effluent control systems.

PROCESS CELL CONTAINMENT BARRIER

MECHANICAL FEED PREPARATION → TRITIUM REMOVAL

TRITIUM EVOLUTION

DISSOLUTION → RUTHENIUM REMOVAL → IODINE SCRUBBER → IODINE ADSORPTION → HEPA FILTERS → KRYPTON, C-14 REMOVAL

CELL OFF GAS

OTHER PROCESS FUNCTIONS → RUTHENIUM REMOVAL → IODINE SCRUBBER → IODINE ADSORPTION → HEPA FILTERS → SAND FILTER

WATER RECOVERY AND RECYCLE → TRITIUM SEPARATION → RUTHENIUM REMOVAL → VAPORIZER → IODINE ADSORPTION

TO STACK

HEPA FILTER

HIGH EFFICIENCY EFFLUENT CONTROL SYSTEM FOR
BREEDER FUEL REPROCESSING PLANT

ornl