Management of Radionuclides from Reprocessing Plant Gaseous Effluents

by Y.V. Zabaluev

INTRODUCTION

In September 1976 the IAEA convened a Technical Committee meeting on Removal Storage and Disposal of Gaseous Radionuclides from Airborne Effluents. This meeting reviewed the present technology and practices for controlling the off-gas emissions from fuel reprocessing operations and a report, IAEA-209, was subsequently issued. The Committee identified a need for co-operation in the field of gaseous waste management and recommended that available technology and techniques for removal and storage of all long-lived isotopes should be thoroughly considered, with emphasis on iodine, noble gases and tritium.

In order to carry out this recommendation, the IAEA has convened meetings of experts to discuss the problems involved This article is based mainly on the results and conclusions arrived at during these deliberations.

PRODUCTION OF RADIONUCLIDES AND THEIR DISCHARGE TO THE ENVIRONMENT

In reprocessing irradiated nuclear fuel, current practice is to release to the environment virtually all the krypton-85, carbon-14 and tritium and a fraction of the iodine-129 which are formed as fission products in the fuel. As nuclear power programmes expand, the global inventory of these long-lived nuclides will increase. It has been estimated that the amounts of the three nuclides, krypton-85, tritium and iodine-129 that arise annually will be 500×10^6, 75×10^6 and 6000 Ci respectively, by the year 2000 and that, if released, their cumulative levels by that year would be 5500×10^6, 400×10^6 and 40 000 Ci respectively. In this context, the release of long-lived gaseous radionuclides may constitiue significant long term sources of radioactivity.

The principal source of krypton-85 and iodine-129 emissions in the nuclear fuel cycle is the fuel reprocessing plant. Carbon-14 and tritium may be emitted in appreciable amounts from both reactors and reprocessing plants.

The release and dilution (and disposal) option now utilized for tritium, krypton-85 and carbon-14 results in exposure to members of the public which are a small fraction of the variation in natural background radiation as well as being within the internationally accepted radiation protection standards.

Mr Zabaluev is in the Waste Management Section, Division of Nuclear Safety and Environmental Protection, IAEA

Table 1. Production Rates by Fission in the Fuel (Ci/GW(e)y)

Reference	Iodine 129					Krypton-85					Tritium				
	LWR	HTGR	FBR	AGR	HWR	LWR	HTGR(b)	FBR	AGR	HWR	LWR	HTGR(b)	FBR	AGR	HWR
Commission of the European Communities(a)	1 2	1 0	1 0	0 95	1 4	3 3 × 10^5	2 7 × 10^5	2 1 × 10^5	2 6 × 10^5	3 8 × 10^5	2 1 × 10^4	1 75 × 10^4	2 5 × 10^4	1 7 × 10^4	2 4 × 10^4
USA	1 2	1 0	0 8	–	–	3 3 × 10^5	5 8 × 10^5	1 6 × 10^5	–	–	2 4 × 10^4	~1,7 × 10^4(c)	2 4 × 10^4(d)	–	–
France	1	–	1 25	–	–	4 × 10^5	–	1 2 × 10^5	–	–	1 7 × 10^4	–	2 7 × 10^4	–	–

(a) Derived from the reactor efficiencies and the Ci/GW(th)y values quoted in KELLY, et al (see Bibliography)
(b) The values cited for Kr 85 are dependent on the different fuel cycles adopted
(c) A value of 2 06 × 10^4 for fission and neutron activation in the fuel (U 235) and core components is given in ANL-8102 (see Bibliography)
(d) A range of 2 4 × 10^4 is given in ANL 8102 (see Bibliography)

Abbreviations

LWR – Light-Water Reactor
HTGR – High-Temperature Gas Reactor
FBR – Fast Breeder Reactor
AGR – Advanced Gas Reactor
HWR – Heavy-Water Reactor

Krypton-85 (half-life: 10.76 years) is a direct fisssion product. Although some (less than 1%) of the krypton-85 leaks from failed fuel elements during irradiation, more than 99% of it is retained until the elements are sectioned and dissolved during reprocessing It is then completely released to the process off-gas system About 330 000 Ci of krypton-85 are released per electrical gigawatt-year (GW(e)y) of nuclear power for LWR fuels and about 580 000 Ci/GW(e)y for HTGR fuels The releases differ because of the different amounts of krypton-85 produced in the fission of uranium-235 and uranium-233 used in the fuel of the two reactor types respectively. About 1.2 to 2.1 X 10^5 Ci/GW(e)y is estimated for LMFBRs. To date, essentially all the krypton-85 from fuel reprocessing has been released to the atmosphere.

All the iodine-129 (half-life. 1.7 X 10^7 years) is produced as a direct fission product. and nearly all of it is retained in the fuel until dissolution Generation rates are about 1.0 Ci/GW(e)y for all reactor types (Table 1). Dissolution of the fuel will release more than 98% of the iodine to the off-gas system and efforts are usually made to remove the iodine from the process off-gas for control of iodine-131 emissions.

Tritium (half-life: 12 3 years) is generated in nuclear fuels chiefly by ternary fission at a rate of 200 000–400 000 Ci/GW(e)y (Table 1). Other sources are neutron activation of a number of light elements present as impurities or components of the fuel, coolant, moderator, cladding and other reactor materials

At fuel reprocessing plants, all the tritium in the zirconium-clad oxide fuels is released at the fuel element sectioning and dissolution stages. From 1 to 2% of the amount present is released to the process off-gas system as the hydrogen-tritium molecule (HT) and discharged in gaseous effluents. Most of the remainder is discharged in aqueous effluents, or these effluents are evaporated and the water vapour discharged to the atmosphere via tall stacks Only a small fraction of the tritium trapped in the Zircaloy cladding of LWRs and HWRs is expected to be released on dissolution of the fuel.

In the case of HTGR fuel elements, 50 to 90% of the tritium present is expected to be released to the off-gas systems during the graphite burning-fuel crushing process that takes place prior to dissolution of the fuel.

Carbon-14 (half-life: 5730 years) is produced during reactor operation as a neutron activation product from carbon, nitrogen and oxygen present as components or impurities in the fuel, moderator, coolant, cladding and structural hardware of the reactor

Some calculations for carbon-14 indicate that for LWR, HTGR and FBR fuel, 10–50, 35–200 and 2–18 Ci/GW(e)y respectively will be released from the fuel at reprocessing plants.

Discharge limits for gaseous radioisotopes are established in most countries in accordance with the recommendations of the International Commission on Radiological Protection (ICRP). These limits differ from one site to another depending on assumptions as to the nature of the effluent and the environment into which the discharges are made. Furthermore, these limits are often dependent upon value judgements such as the significance of very low levels of radiation exposure

Table 2. Comparison of Krypton-85 Separation Process for Nuclear Facilities

Process	Development Status	Advantages	Disadvantages
Cryogenic Distillation	Developed and operated on a significant scale; units located at nuclear reactors, DOE reprocessing plant and Japanese reprocessing plant	– Reasonable capital costs – Separates krypton from xenon – Firm technology base – Potential for high reliability	– Ozone explosion potential – Extensive gas pre-treatment
Fluorocarbon Absorption	Developed and tested in non-radioactive pilot plant	– Low refrigeration costs – Low solvent costs – Low explosion hazards – Minor gas pre-treatment	– High pressure (300–400 PSIG) – High leak potential – Does not separate krypton and xenon – Corrosion hazards - Fluorocarbon releases
Charcoal Adsorption (Ambient and low temperature)	Developed and operated on a significant scale	– Simple operation – Adequate technical background – High reliability – Smaller volume beds for low temperature method	– Fire and explosion hazard – Does not separate krypton and xenon – High refrigeration costs for low temperature method
Selective Permeation (membranes)	Bench-scale tests	– Room temperature operation	– High capital costs – High pressures – Unknown membrane sensitivity

METHODS FOR REMOVAL OF RADIONUCLIDES FROM REPROCESSING PLANT GASEOUS STREAMS

Krypton-85 removal

A number of processes have been proposed for the removal of krypton-85, including cryogenic distillation, fluorocarbon absorption, adsorption, diffusion and selective membrane processes. A comparison of the various separation processes and a brief indication of the development status of each are given in Table 2. Any of these techniques can probably be adapted to the separation of krypton-85 from either LWR or HTGR fuel reprocessing plants.

Cryogenic processes are favoured in most countries because the technology is a well-proven one used in the air products industry. It can be readily adapted to commercial krypton-85 removal but needs some further development to adjust it to the special conditions and problems of the nuclear industry.

Experience with industrial air separation plants has shown that in the presence of oxygen, nitrogen oxides in the parts per million range can cause explosions. Therefore, special attention must be paid to this hazard which is enhanced by radiolysis Also, hydrocarbons (mainly methane) which are present to a small extent in the effluents of a catalytic hydrocarbon converter, can result in destructive explosions in the presence of oxygen. To avoid the possibility of explosions, nitrogen oxides and hydrocarbons must be removed to a very high degree and the formation of ozone prevented.

Other contaminants such as iodine, carbon dioxide and water should be removed in a preliminary separation in order to prevent freezing and plugging of the system. This same removal process may be used to trap carbon-14 if necessary.

Liquid absorption processes are also well-known chemical technology. Several solutes have been considered for the removal of noble gases from the off-gas. One process, using Freon, is presently under development.

These techniques have the advantage of high tolerance to impurities in the inlet gas mixture. It should be pointed out, however, that they require an extra follow-on process for separation of the more abundant xenon from krypton, since both are absorbed in the solvent.

Processes involving charcoal adsorption, selective membrane permeation and gas diffusion have also been considered for this application but they have not been developed beyond the laboratory stage at the present time

Radioiodine removal

Different iodine removal techniques are being developed to meet different requirements and criteria, such as iodine species removal efficiencies, maintainability, waste management considerations, compatibility with upstream and downstream off-gas treatment components, and installation and operating costs. In off-gas streams where high radioiodine removal efficiencies are required, it is assumed that primary and secondary removal systems may be necessary. In some cases, the primary and secondary removal components might be the same.

There are two alternative methods for trapping radioiodine from the off-gas, viz. liquid scrubbing and sorption on solid materials.

Caustic scrubbing technology has been applied at some of the operating reprocessing plants in dissolver off-gas treatment for iodine Packed columns are usually recommended to give good contact times. A caustic solution of potassium hydroxide rather than sodium hydroxide is also recommended because with the latter the low solubility of the reaction product can lead to plugging of the columns and discharge lines. Reductants such as sodium thiosulphate can also be added to improve the removal efficiency, but this may present operating problems because of the potential radiolytic formation of free sulphur which could also cause plugging.

The recovery of iodine by the caustic scrubbing method is limited by the relatively low removal efficiency for organic iodine compounds The overall decontamination factor is usually much less than 100. Another disadvantage is the relatively large volume of waste produced

For scrubbing with acid-mercuric nitrate solution, a packed column may be used in which the scrubbing solution is recirculated. The mercuric nitrate in the nitric acid will react with the iodine to form mercuric iodide (HgI_2) which may be dissolved in the scrubber solution as complex ions such as $(HgI_3)^-$ and $(HgI_4)^{2-}$.

To reach higher decontamination factors for organic iodine compounds, the concentration of the nitric acid, which acts as a strong oxidizing agent, should be as high as 8 to 12 molar, whereas the mercury concentration will be in the range of 0.2 to 0.4 molar. Decontamination factors of around 100 may be reached with a well designed scrubber system of this type. Here again however the efficiency of mercuric nitrate/nitric acid scrubbing is limited by the content in the off-gas of higher organic iodine compounds and by the removal rate of radioiodine from the recirculating solution

The development of concentrated nitric acid scrubbing techniques (Iodox process) has been carried out for application in the reprocessing of FBR fuel This technique employs the use of hyperazeotropic nitric acid, 20 to 22 molar as the scrubbing solution in bubble-cap columns. The technique removes both elemental and organic iodine with removal efficiencies of greater than 99.99% (decontamination factor: 10 000) when the equipment is carefully operated. The acid concentration should not be reduced below 20 molar nor the solubility of the HI_3O_8 iodine product exceeded The major disadvantages of the concentrated nitric acid scrubbing technique are complicated design, potential operating problems associated with the highly corrosive nature of the scrubbing solution, the explosion hazard of the scrubbing solution, and high capital and operating costs

Silver-impregnated amorphous silicic acid materials have been developed in several countries for radioiodine removal from reprocessing plant off-gas streams These materials have been demonstrated to be effective for both elemental and organic iodine removal provided the off-gas is heated to about 150°C. The main disadvantage of this technique is a relatively high cost associated with the use of silver

Several metal-exchanged zeolites have been investigated for the removal of radioiodine but this technique is at present in the development stage

Iodine precipitation techniques have been designed to obtain the iodine in a concentrated form suitable for final conditioning (glass or metallic matrix).

Tritium removal

Three principal options are being developed for the recovery of tritium form oxide fuels They are.

- Volatilization and collection of tritium from the chopped fuel before dissolution,
- Isotopic enrichment and collection from the liquid effluents,
- Aqueous recycle with removal and solidification of a small side stream

At present, none of the techniques is sufficiently developed for application

The "Voloxidation" process depends on oxidation of UO_2 to U_3O_8 in order to break down the crystal lattice and release gases from it. Tritium release efficiencies of greater than 90% are expected from the fuel with this process which exposes the fuel to 450 to 500°C for several hours (4 to 6) in a rotary kiln. The evolved gas is passed through a catalytic converter to ensure that all the tritium has been converted to HTO before it is removed as water in solid absorbents A large fraction of the tritium left in LWR fuel elements is probably bonded in the Zircaloy cladding and will remain with the cladding during fuel dissolution. This process would probably not work for ThO_2 fuels since there is no higher oxide of thorium Metal fuels may also be difficult to treat in this way because heat generation rates may be difficult to control during oxidation.

Several isotopic enrichment processes are being investigated for removal of tritium from the waste water which is presently released or evaporated

Catalytic exchange techniques similar to the one now being used to remove tritium from the Celestin reactor (from the heavy water moderator) in Marcoule, France, are under investigation in the United States. A hydrophobic catalyst developed at Chalk River Nuclear Laboratories (Canada) and which promotes the chemical exchange reaction between liquid water and gaseous hydrogen (or tritium) in direct contact is being evaluated. This approach should minimize the problems of catalyst deactivation and simplify (and reduce the cost of) reactor design. The process is in an early stage of development, and a number of problems must be solved before it can be considered practical for use in reprocessing plants. Water distillation and hydrogen distillation are also being considered for tritium enrichment. Isotopic enrichment by reversible electrolysis is also being investigated in the United States.

Recycle of all the water and nitric acid as a means of containing tritium in reprocessing facilities has received considerable attention, but the study conclusions are generally the same: a large amount of expensive pilot-scale development work would be necessary to prove the feasibility of the technique

TECHNIQUES FOR THE STORAGE OF RADIONUCLIDES

Storage of krypton-85

For storage and transportation the separated gas should be encapsulated Filling pressurized containers is the simplest method. This is a well-proven technology with non-radioactive gases, however as the risk of leakage cannot be excluded, it has been proposed to use adsorbents to reduce the pressure inside a container and to allow only a slow release of the contents in case of a leak. A pressure reduction to nearly zero can be achieved by embedding the krypton in a metal matrix.

Pressurized cylinders containing krypton-85 could probably be stored at the reprocessing site for several months or years before being shipped to a final disposal site. Obviously, the longer this interim storage period, the less activity will be involved in handling and shipping because of radioactive decay.

As krypton-85 has a half-life of 10.76 years concentrated forms of it must be isolated from the environment for about 150 to 200 years. For this length of time, storage of pressurized steel cylinders in engineered facilities might be feasible Such an engineered storage facility should have means for the safe removal of decay heat, the detection of leaking containers and a containment shell for limiting an accidental release of krypton into the environment.

Other methods for disposing of krypton-85 are also being considered in some nations. For example, injection into porous underground formations either as gas or in water or cement solution is being studied in the Soviet Union and in the United States Deep sea dumping of specially constructed, pressurized steel cylinders has also been proposed as a disposal alternative. However, this method needs further investigation and would require international approval.

Storage of iodine-129

The different techniques under consideration for removing iodine produce a variety of materials requiring further treatment or storage. Briefly, these are:

- iodine precipitates from scrubbing liquids,
- silver molecular sieves and other solid absorbents;
- charcoal filters impregnated with various doping agents.

The extremely long half-life of iodine-129 and its high mobility in water combine to make permanent disposal of this waste product an especially difficult problem. No chemical form or secondary container is likely to retain it for any appreciable portion of the more than 100 million years which it will take to decay away substantially.

Interim storage and transportation of iodine-129 waste should pose little problem since its external radiation emission is quite low.

As it might take some time to determine and decide on safe long-term storage and disposal conditions for iodine-129, it might be reasonable to organize a temporary retrievable storage for this radioisotope for 100—200 years. Several alternative iodine-129 disposal techniques have been proposed, they are not considered to be within existing technology but are expected to be available in future. These are transmutation and extraterrestrial disposal

Storage of tritium

Waste water which contains a substantial quantity of tritium, may be stored in sealed containers prior to disposal. Low concentrations can be disposed of safely in deep wells in certain areas and under engineered conditions which preclude contamination of fresh water aquifers. More concentrated tritium in either the gaseous or liquid phase should be immobilized in a durable solid suitable for long-term geologic or engineered storage.

Low concentrations of tritium in waste water may possibly be disposed of safely in the ocean.

In the storage of highly concentrated tritiated water, special care is required due to the possible build-up of explosive quantities of hydrogen (HT) from radiolysis To avoid this problem, forced ventilation is usually provided in the tritiated water tank using special equipment such as circulation pumps, heaters, regenerative heaters, and water-cooled heat exchangers.

The storage requirements for concentrated tritiated wastes will be different from those for the more diluted forms. Either geologic disposal or engineered storage of the concentrated wastes may be acceptable, but in either case immobilization and secure containment of the tritium should be ensured. The most promising technique for the storage of this type of waste is a combination of fixation within concrete together with secure secondary containment or fixation in a concrete-polymer combination material, recently demonstrated in the United States.

Storage of carbon-14

Collection and storage of compounds containing carbon-14 does not appear necessary in the immediate future. Nevertheless, storage in geologic formations appears to be an acceptable technique for carbon-14. Calcium carbonate seems to be the most likely form for storing this radioisotope.

CONCLUSION

Current practice at operating reprocessing plants is to discharge most of the gaseous radionuclides to the environment. As nuclear programmes expand and mature it is expected that this procedure will no longer be acceptable.

Methods exist for removing these nuclides from gaseous discharges, and they could be applied to present day reprocessing plants with varying amounts of development work being required. Newer, more promising methods have been proposed but many of these would require extensive development.

Storage methods for the separated radionuclides will probably follow standard or modified practices now used industrially. In most cases, disposal will likely be in geologic formations with different sequestering or fixation methods being envisaged for different nuclides.

Bibliography

1 INTERNATIONAL ATOMIC ENERGY AGENCY, Removal, Storage and Disposal of Gaseous Radionuclides from Airborne Effluents, IAEA-209, IAEA, Vienna (1978)

2 KELLY, G N , et al., The Predicted Radiation Exposure of the Population of the European Community Resulting from Discharges of Krypton-85, Tritium, Carbon-14 and Iodine-129 from the Nuclear Power Industry to the Year 2000, Document V/2676/75, Commission of the European Communities, Luxembourg (September 1975)

3 PENCE, D T , STAPLES, B.A., "Solid Adsorbents for Collection and Storage of Iodine-129 from Reprocessing Plants", Proc 13th Air Cleaning Conference, 12 August 1974, San Francisco, Calif. (1974) 758–64

4 NAKHUTIN, I E , et al , "Removal of Radioiodine from Gases", Peaceful Uses of Atomic Energy (Proc. 4th Int Conf , Geneva, 6–12 September 1971) Vol 11, UN, N Y , and IAEA, Vienna (1972), 399–413

5 COMMISSION OF THE EUROPEAN COMMUNITIES, Proc Seminar on Radioactive Effluents from Nuclear Fuel Reprocessing Plants, Document V/2266/78, Commission of the European Communities, Luxembourg (November 1977)

6. TREVORROW, L E , et al., *Tritium and* Noble-Gas Fission Products *in* the Nuclear Fuel Cycle, ANL-8102, Argonne National Laboratory (October 1974).