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GENERAL SURVEY OF TECHNIQUES FOR SEPARATION AND CONTAINMENT
OF NOBLE GASES FROM NUCLEAR FACILITIES

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Radioactive noble gases produced during uranium fission constitute a waste material requiring special treatment and handling techniques if releases to the environment are to be reduced or minimized. To date, treatment has been confined to short-term holdup of nuclear reactor off-gases, to allow short half-life fission products to radiolytically decay. Although the required degree or efficiency of noble gas separation and containment is not yet determined, considerable development effort has been expended on a variety of separation processes. With some separation processes, the technology is advanced sufficiently that commercial separation units are now being offered for sale. Early installations of these will be mainly at reactors where their prime advantage is a reduction in size of the holdup system required and an increase in the holdup time for radiolytic decay. Eventually, separation processes may have to be installed at nuclear fuel reprocessing facilities to collect the long-lived krypton-85.

NOBLE GAS SEPARATION

The separation processes⁽¹⁻⁶⁾ potentially applicable to removing fission-product noble gases from the off-gas streams include absorption in liquids (liquid air, carbon dioxide, or fluorocarbons), adsorption on charcoal or other solids, and diffusion through a selective membrane. These processes are at a variety of technological levels and each has its own particular advantage or disadvantage (summarized in Table I) with respect to the recovery efficiency,

129

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Page 2

purity, and ultimate containment requirements of the noble gases. The technological level, advantages, and disadvantages of each process are discussed individually as follows:

Cryogenic Distillation

The major advantage of the cryogenic distillation process for absorption of noble gases is its present high technological level. Liquid air plants have been in existence for decades and thus considerable knowledge has been assembled on materials of construction, valves, compressors, distillation column design, modes of operation, and reliability. Specific cryogenic processes recovering natural krypton from air have also been operated for some time. Because of this the projected capital and operating costs for a fission-product noble-gas removal system are well defined. In addition, the cryogenic distillation process is the only process to have operated on a significant scale at a fuel reprocessing facility for the recovery of production quantities of krypton-85⁽⁷⁻¹⁰⁾. A number of U. S. companies are offering similar units for use at nuclear facilities and have projected krypton-85 recovery efficiencies typically in excess of 99 percent. A significant disadvantage of the cryogenic process is explosion hazards associated with the radiolytic formation and concentration of ozone. Methods to minimize this specific explosion hazard include either total removal of oxygen from the process gas⁽¹¹⁾ or dilution of an ozone-bearing stream through periodic flushing or dilution⁽¹⁰⁾ using appropriate operating parameters. Adequate control of krypton-85 leakage rates to achieve high recovery efficiencies has not been demonstrated yet, but appears achievable. A high degree of process gas cleanup is required, and product purity is relatively high.

Absorption in Fluorocarbons

A significant decrease in refrigeration costs can be achieved by using a fluorocarbon⁽¹²⁾, such as Freon-11 or 12, to absorb the fission-product noble gases at temperatures of -30 to -90°F and at pressures up to 400 psig. Process system size, mode of operation, and capital costs are comparable to the cryogenic distillation process, although the quantity of mechanical cooling equipment is higher. The high pressure required for the process increases the possibility of gas leaks and product losses. The fluorocarbon process has been extensively pilot-plant tested at ORNL, but additional information on the effect of process gas contaminants is desirable. The solvent cost is relatively low, but solvent losses through volatilization and radiation degradation need more definition. Explosion hazards with ozone or xenon-tetrafluoride are estimated to be very low. No plant-scale tests at a power reactor or a reprocessing facility have been performed.

Absorption in Carbon Dioxide

Absorption of the noble gases in distillation processes using liquid carbon dioxide appears possible for gas streams rich in carbon dioxide, such as those coming from reprocessing of graphite fuels⁽¹⁵⁻¹⁷⁾. Scoping tests of the process have occurred at ORNL and are continuing in order to obtain basic carbon dioxide absorption data of the noble gases. Refrigeration needs, operating pressures, process equipment, mode of operation, and temperatures are similar to the fluorocarbon process. No explosion hazards from ozone or other radiolytic products have been identified, and a ready supply of solvent is available in the process gases. The process is specific for gas streams with high carbon dioxide concentration and is not applicable to other gas streams.

Ambient-Temperature Charcoal Adsorption

Adsorption of fission-product noble gases on charcoal beds at ambient temperatures has been used for delaying release of radioactive gases in off-gases of nuclear power reactors^(2,14). No attempt has been made to use the ambient-temperature adsorption process specifically as a recovery system for fission-product noble gases. The quantity of charcoal required for a typical nuclear facility is in the tens-of-tons range; thus, process equipment would be large and bulky, although operation could be relatively simple. A distinct fire hazard exists, although fires are easily extinguished by shutting off the flow of oxygen containing gases. Use of adsorbent material other than charcoal cannot be considered because of increased bed volume and higher unit costs. Due to the quantities of charcoal required, such a recovery process may be limited to small scale, batch processes.

Low-Temperature Charcoal Adsorption

By reducing the temperature of the charcoal bed, the adsorption capacity is increased, thus reducing the bed volume required^(2,14) by 50 to 80%. Although a slightly more concentrated product then is possible, the other disadvantages with charcoal beds remain relatively unchanged. A cryogenic temperature adsorption system was used extensively at ICPP at one time, but proved to be unreliable and refrigeration costs were prohibitive. Use of dual adsorptive beds of relatively small capacity in conjunction with a small cryogenic distillation system to achieve high purity product has been suggested.

Perm-Selective Membranes

Differences in permeability of gases through a special membrane is the bases of a perm-selective membrane separation process. Using this difference at high pressures (150 psi) with a silicon rubber membrane, krypton and xenon gases

can be separated from the bulk off-gases, as shown in tests at ORNL^(18,19).

Large membrane surface areas and high pressures are required, and this results directly in high capital and power costs with a high mechanical ratio. Long-term radiation and chemical effects on the membrane are not known, and the membranes are particularly sensitive to ozone and NO_x damage. The system also can be damaged by thermal and pressure shock. The concentration factors are in the range of 10-500 at the reported decontamination factor of 10⁴. The system appears economical for low decontamination factors only.

NOBLE GAS CONTAINMENT

High pressure storage of the recovered noble gases in steel cylinders presently appears to be the leading means for practical ultimate disposal. However, inclusion or encapsulation of the krypton-85 into glasses, resins, clathrates, molecular sieves, and metal offer ways of reducing the effective vapor pressure in a cylinder and may provide primary containment for the radioactive gases. Long-term disposal means that have been considered include placement of the cylinders into an engineered storage facility, dumping of cylinders into the sea, and direct discharge of the krypton-85 into an appropriate geologic formation. Commercial uses^(20,22) will not utilize significant quantities of the recovered krypton-85. However, a demanding market for the recovered xenon is envisioned. A comparison of the various containment techniques is given in Table II.

Low Pressure Storage

Storage of recovered krypton-85 within steel cylinders at ambient pressure and temperature conditions has been studied. The storage volume required has been studied. The storage volume required has been predicted to be similar to the volume of medium-level liquid wastes presently stored at nuclear facilities. With

such storage conditions, rupture of a single tank is considered to be controllable and very improbable. Ozone removal is considered necessary and the stored gas must be free of either oxygen, nitrogen, or both to prevent formation of corrosive products through radiolysis. Although storage at ambient conditions appears possible, considerable economic evaluation appears necessary before considering use at reprocessing facilities.

High Pressure Storage

High pressure storage⁽²³⁾ appears to be practical and economical, and has extensive technical development obtained during many decades of use in a wide variety of systems. In addition, some experience with high-pressure storage and shipping has been obtained at ICFP during shipment of their product to ORNL. A well-engineered facility could provide a double containment design and minimize such things as leak probability, actual krypton-85 release if a leak occurs, and corrosive radiolytic products. The double-containment concept is deemed necessary because an instantaneous release of one high-pressure storage cylinder may produce unacceptable radiation doses. Further study into overall costs of the complex facility and the long-term effect of possible corrosion of storage cylinder walls by radiolytic products is required. High-pressure storage may require high-purity noble gases, to prevent formation of corrosive, oxidizing products through radiolysis.

Storage Through Adsorption or Encapsulation

Inclusion or encapsulation^(5,24-28) of the krypton-85 into molecular sieves, clathrates, resins, glasses, and metals may offer a means to provide primary containment within a steel cylinder and also reduce the effective vapor pressure within the cylinders. Cost, safety, and environmental adequacy of any of these

inclusion methods are dependent upon storage capacity, temperature restrictions, and radiation damage of the material. Present information is available only on a lab-scale basis. Storage capabilities of molecular sieves are fairly well-known, but are limited at ambient or elevated temperatures. Use of molecular sieves at low or cryogenic temperatures is not desirable since any loss-of-cooling accident would cause high storage-cylinder pressures and increase the probability of massive, uncontrollable leaks. All of the encapsulation materials require extensive investigation to determine the storage capacity and the long-term effect of radiation, possible radiolytic corrosion products, and elevated temperatures. Possible engineering difficulties in constructing a truly effective (and efficient) inclusion facility need considerable study. The proposed encapsulation methods are technically difficult, require very high pressures to achieve significant storage capacity, and require complicated and expensive equipment. At best, encapsulation is presently a laboratory possibility and requires lengthy investigation.

Long-Term Disposal/Containment

Eventually, all recovered cylinders containing krypton-85 must be transported to an AEC facility for long-term disposal or containment. Long-term disposal methods may include placement of the cylinders into an engineered storage facility, dumping of cylinders into the sea, and even direct discharge of the krypton-85 into deep or shallow wells leading into a geologic formation⁽²⁸⁻³⁷⁾. An engineered facility could be specifically designed to monitor and protect the storage cylinders from the environment (storm, earthquake, etc.) and also provide secondary containment or recovery of gases should initial releases occur. Dumping of storage cylinders into a deep-sea trench might be technically feasible and acceptable, but public acceptance would be difficult to predict. Disposal into deep geological

formations^(28,29) is in the same category. Very high pressures are required (i.e., high leak potential) and the required detailed knowledge of the deep geologic formation is difficult and expensive to obtain. In the public's eye, there is always the fear of the "undiscovered crack" which could release the radioactive gases into one's backyard. Some investigation and testing has been done on shallow-well disposal of krypton-85⁽³⁰⁻³²⁾. Such a disposal means does not involve high pressures and does not depend on impermeable geologic formation, but assumes the soil will adsorb the noble gases and release them slowly over a period of decades. Such a method would require large volumes of loosely packed rock and relatively large ground surface areas. However, the concept suffers from the disadvantage of a constant, highly visible-to-the-public, release of krypton-85 to the atmosphere, however small. Well-engineered facilities for high-pressure storage of the radioactive gases still appear to have an important technological and experience advantage over other methods.

TABLE I

COMPARISON OF KRYPTON-85 SEPARATION PROCESSES FOR NUCLEAR FACILITIES.

Process	Development Status	Advantages	Disadvantages
Cryogenic Distillation	Developed and operated on a significant scale; commercial units for nuclear reactors have been sold.	Low capital costs well defined; product purity relatively high; high technical background gives high reliability.	Ozone explosion potential must be controlled, high-efficiency gas cleanup required.
Fluorocarbon Absorption	Developed and tested in pilot plant; no demonstration or operating experience at nuclear facility.	Low refrigeration costs; low solvent costs; very low explosion hazards; reduced process gas pretreatment.	High pressure (300-400 psig) with high leak potential; low product purity with corrosion hazards.
Absorption in Liquid Carbon Dioxide	Pilot-plant scoping tests performed and continuing; feasibility studies completed.	Zero solvent costs; low refrigeration costs; no explosion hazards identified.	High pressure with high leak potential; low product purity; restricted to HTGR nuclear fuels.
Ambient Temperature Charcoal Adsorption	Laboratory tests completed; presently used in delayed release facilities.	Simple operation; adequate technical background to assure reliability.	Large-volume beds; fire and explosion hazard.
Low Temperature Charcoal Adsorption	Developed and operated on a significant scale.	Smaller volume beds.	Fire and explosion hazard; high refrigeration costs; reliability unproven.
Perm-Selective Membranes	Bench scale tests; no pilot-plant tests.	Room temperature operation.	High capital costs; high pressures; high power costs; membranes sensitive to oxidizing chemicals.

TABLE II
COMPARISON OF KRYPTON-85 CONTAINMENT TECHNIQUES

Technique	Development Status	Advantages	Disadvantages
Low-Pressure Tanks	Feasibility studies performed; no field tests.	Low pressures with low leak probability.	Very large storage volume; ozone removal required; radiolytic product corrosion unknown.
High-Pressure Cylinders	Used for shipment at ICPP; no long-term tests.	Low storage volumes; long technical background.	Long-term corrosion unknown; high-pressures increase probability of massive release; secondary containment required.
Adsorption on Charcoal	Development data completed; short-term operation.	Reduces vapor pressures of containers.	Large storage volume; fire and explosion hazard.
Encapsulation	Laboratory studies only partly completed.	Reduces vapor pressures of containers; provides primary containment.	Effects of radiation, temperature, and corrosion need extensive study; process technically difficult.
Engineered Storage Facility	Cost and feasibility studies continuing; no field experience.	Protection from environment, earthquakes, and gas leaks; secondary containment and recovery of leaked gases.	High capital cost; perhaps high operating cost.
Deep Sea Disposal	Feasibility studies limited; field experience on related chemicals.	Long storage time; isolated from public; simple concept.	Public opinion; reliability not 100% assured.
Deep Geologic Formation	Feasibility studies performed.	Long-term storage.	Public opinion; very high pressure; complicated site investigation required.
Shallow Geologic Formation	Field tests performed.	Unaffected by earthquake; long-term reliability; low cost.	Public opinion.

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