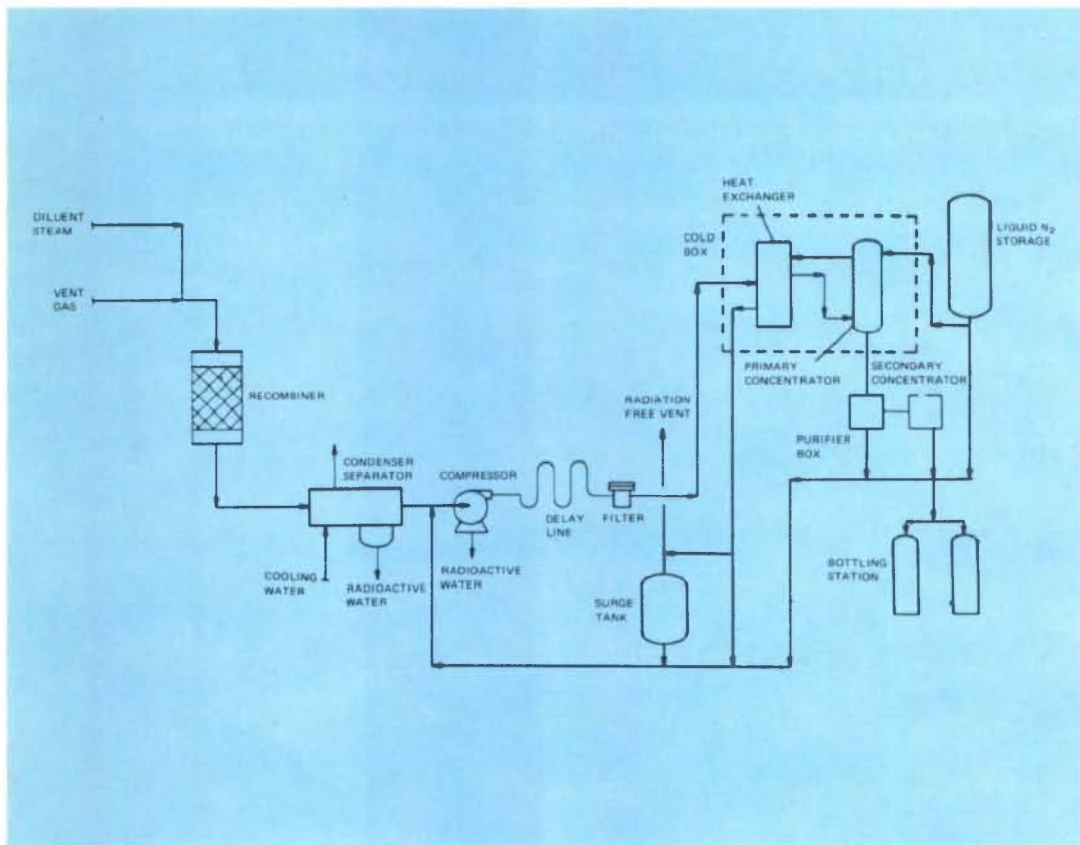




TECHNICAL REPORTS SERIES No. **199**

Separation, Storage and Disposal of Krypton-85



INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1980

**SEPARATION, STORAGE AND DISPOSAL
OF KRYPTON-85**

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SEPARATION, STORAGE AND DISPOSAL OF KRYPTON-85

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SEPARATION, STORAGE AND DISPOSAL
OF KRYPTON-85
ORGANIZED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY

INTERNATIONAL ATOMIC ENERGY AGENCY
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SEPARATION, STORAGE AND DISPOSAL OF KRYPTON-85

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FOREWORD

A Technical Committee Meeting on Separation, Storage and Disposal of Krypton-85 was convened by the Agency on 23–27 October 1978 as a step in an effort to keep a close check and control of this radioisotope in the nuclear fuel cycle. Since a fuel reprocessing plant is a principal source of emission of krypton-85 in the nuclear fuel cycle, the Committee focused its attention on this type of installation. The purpose of the Committee was to:

Identify and quantify the emission sources

Compare available techniques and methods of krypton-85 removal from fuel reprocessing plant off-gases

Consider the necessity for krypton-85 removal from reactor off-gas

Assess the latest developments in krypton-85 storage

Discuss concepts and methods for disposal.

Krypton-85 is a fission product with a half-life of 10.76 years arising from the generation of nuclear power. At present nearly all krypton-85 is discharged to the atmosphere where it accumulates to the extent that it is not destroyed by radiodecay. With the growth of the nuclear power industry this accumulation in the atmosphere will increase unless the isotope is separated from the gaseous effluents and retained.

The aim of the present report is to review the technical means available for the retention of krypton-85 and its immobilization, storage and disposal, having regard to the radiological hazards.

The Agency wishes to express its thanks to all the participants who took part in the preparation of the report. The Agency wishes, in particular, to express its gratitude to M. Laser of the Federal Republic of Germany, who served as Chairman of the meeting, and who, as a consultant to the Agency, contributed considerably to the editing of the material. The officer of the IAEA responsible for this work was Yu. Zabaluev of the Waste Management Section.

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1. INTRODUCTION

The fission product krypton-85 is released to the atmosphere from nuclear power plants and reprocessing plants. About 330 000 Ci/GW(e)·a are produced and retained in LWR fuels and about 580 000 Ci/GW(e)·a in HTGR fuels.¹ About 160 000 Ci/GW(e)·a are estimated for LMFBR fuels. Less than 1% of the inventory is released from the nuclear power plant. More than 99% is liberated during reprocessing and discharged at present into the atmosphere where the krypton accumulates. With the growth of the nuclear power industry, the accumulation of krypton-85 will increase if it is not contained. The biological effects of this environmental pollution have been discussed in several papers [1, 2]. Meteorological effects and consequences have also been discussed [2, 3].

In most countries discharge limits have been established in accordance with the ICRP regulations. In the case of krypton-85 these limits are not normally reached. In keeping with the principle of reducing the radiation burden to "as low as practicable", more stringent limits have been established in some countries, particularly in the Federal Republic of Germany and in the United States of America. The FRG's Radiation Safety Commission has recommended limiting the amount of krypton-85 release from a reprocessing plant [4]. In the USA a certain decontamination factor will be the requirement for a reprocessing plant by the year 1983 [5].

Because of the world-wide distribution of krypton, however, international agreement is necessary concerning the expediency and the degree of krypton retention. To meet the technical requirements for krypton-85 separation some developments have been under way for several years. Based on the experience with some of these test facilities, krypton separation plants to reduce krypton-85 emission from reprocessing plants are either under design or at a planning stage. The purpose of this paper is to review technical means for the retention of krypton-85, its encapsulation, storage, transportation and disposal. Safety considerations will be taken into account.

2. METHODS AVAILABLE FOR THE SEPARATION OF KRYPTON FROM OFF-GASES

The fission product noble gas krypton consists of several radioactive and inactive isotopes. It is accompanied by xenon. The radioactivity and the mass of the different isotopes of krypton and xenon are given in Table I. The liberated

¹ 1 Ci = 3.70×10^{10} Bq.

TABLE I. MASS ACTIVITIES AND THERMAL POWER OF THE FISSION NOBLE GASES AS FUNCTIONS OF DISCHARGE TIME (calculated according to ORNL-4628, Rev. March 1975)

Fuel element: 36 000 MW·d/t U burn-up rate; enrichment 3.5%; reactor residence time 1000 d

Decay time			365 d			730 d			1095 d		
	g/t	Ci/t	W/t			g/t	Ci/t	W/t	g/t	Ci/t	W/t
Kr-83	4.34×10^1	1.17×10^4	1.89×10^2			4.34×10^1	1.09×10^4	1.78×10^2	4.34×10^1	1.03×10^4	1.67×10^1
Kr-84	1.22×10^2					1.22×10^2			1.22×10^2		
Kr-85	2.99×10^1					2.81×10^2			2.63×10^1		
Kr-86	2.10×10^2					2.10×10^2			2.10×10^2		
Xe-128	3.51×10^0					3.51×10^0			3.51×10^0		
Xe-130	1.32×10^1					1.32×10^1			1.32×10^1		
Xe-131	4.33×10^2					4.33×10^2			4.33×10^2		
Xe-132	1.27×10^3					1.27×10^3			1.27×10^3		
Xe-134	1.68×10^3					1.68×10^3			1.68×10^3		
Xe-136	2.56×10^3					2.56×10^3			2.56×10^3		

TABLE II. PHYSICAL PROPERTIES OF KRYPTON AND XENON

Property	Unit	Kr	Xe
Critical temperature at 760 torr*	°C	-63.75	16.59
Critical pressure	atm	56.0	60.2
Boiling point	°C	-153.40	-108.12
Melting point	°C	-156	-112
Density at boiling point	kg/ltr	1.5465	1.9959
Density at STP	kg/m ³	3.744	5.896
Heat of vaporization	kcal/kg	25.8	23.7
	kcal/m ³	96.59	139.74
Heat conductivity	W/cm·K	95.1	55.5
Amounts in air	vpm	1	0.08
Ratio in air	—	12.5	1
Ratio in fission product gas	—	1	10

Half-life time of krypton-85: 10.76 a.

Decay product of krypton-85: stable Rb-85.

* 1 torr = 1.333×10^2 Pa.

krypton is diluted to a greater or lesser extent by air and/or other gaseous components depending on the carrier gas used in the krypton absorption process. The physical properties of krypton and xenon are given in Table II. For the enrichment and separation of krypton from the off-gas, several processes are available or under development. The following are of special interest:

The cryogenic distillation process

The liquid absorption process

The charcoal adsorption process.

Finally, special processes of minor importance have been proposed.

During the enrichment step xenon also is enriched. A separation of krypton and xenon may be of interest with regard to the storage of the radioactive gas. In all cases reliable operation of the process requires a more or less extensive pre-purification of the off-gas. In the following sub-sections principles, advantages and disadvantages of the above-mentioned processes are described. Details and the necessary pre-purification steps can be found in the special sections 3 and 4.

2.1. CRYOGENIC DISTILLATION PROCESSES

Cryogenic processes for the separation of krypton and xenon from the diluting gases are favoured in most countries because the cryogenic technology is a well-proven one. They are, therefore, discussed in more detail.

Although cryogenic distillation is generally considered to be available for commercial application, its adaptation to the special conditions and problems of the nuclear power industry needs further development.

Special problems encountered in this respect are:

- (a) Formation of ozone from oxygen at cryogenic temperature caused by radiation of krypton-85.
- (b) Sudden ozone decomposition and undesired reactions of oxygen and ozone with nitrogen oxides or hydrocarbons or other components in the cryogenic units which can occur in an explosive way.
- (c) Plugging of the cryogenic unit due to a freezing-out of off-gas contaminants such as nitrogen oxide, carbon dioxide and water.
- (d) Formation of solid xenon in the cryogenic rectification column due to the high xenon/krypton ratio.

To prevent the undesirable effects mentioned above in (a), (b), and (c), the different contaminants must be kept at an acceptably safe concentration level.

Normally the removal of nitrogen oxides, oxygen and hydrocarbons is facilitated in catalytic reactors. Experience has shown that minor quantities of these undesired reactants are not converted by the catalytic reactors and thus follow the fluid stream to the cryogenic unit where they might be retained and concentrated. The concentration levels of these impurities which are acceptable for safe operation of the cryogenic unit are still uncertain in some cases. Further investigation in this field is obviously needed.

As far as iodine, carbon dioxide and water are concerned these compounds can be reduced to an acceptably low level with currently available technology.

Another problem is the formation of solid xenon during cryogenic distillation; this is caused by the different krypton/xenon ratio from that of the usual cryogenic technology. In air the krypton/xenon ratio is about 12.5 : 1, but in the case of fission product gases it is almost the reverse. Solid xenon is formed either from the gaseous or the liquid phase depending on temperature, pressure and xenon concentration in the cryogenic unit.

To overcome these problems pre-treatment steps have been proposed and/or methods of achieving conditions very similar to those of known air-rectification systems.

In the AZUR plant in the FRG pure krypton will be recycled to reverse the krypton/xenon ratio. Another approach is to increase the operating pressure of

the cryogenic columns. In the krypton pilot plant in Japan xenon is removed from the off-gas stream by low temperature adsorption on silica gel.

In the technical presentation of different krypton gas removal systems given in sub-section 4.1, the FRG's AZUR plant, the Japanese krypton pilot plant and the French CEA pilot plant are described in particular detail. Cryogenic processes are favoured by several countries because they are the most advanced and will be realized on a technical scale in the near future.

2.2. LIQUID ABSORPTION PROCESSES

Liquid absorption processes are also well known in chemical technology. Several solutions have been considered for the removal of noble gases from the off-gas. However only one process using Freon is presently under development.

The main advantage of this process is its versatility. Efficient operation is possible over a wide range of conditions, with different feed-gas compositions. In addition the process is not very sensitive to impurities as far as is known. The disadvantage however is that radiolysis of the solute takes place leading to corrosion of the construction material by the radiolysis products and expensive make-up of the solute. An appreciable secondary waste stream results from the corrosion and make-up. Furthermore no krypton/xenon separation will be possible in the columns, so that the necessary storage volume for the product gas will be increased by a factor of 10.

Another aspect that needs clarification before the process is available for industrial application is its integration into the total off-gas system of the plant. Initially, the Freon process was developed for the separation of krypton from reactor off-gas, especially the blanket off-gas of LMFBRs. Presently, however, the process has more importance for reprocessing off-gas decontamination. In a new development (USA) of this process the absorber has been integrated in a single combination column.

In the United Kingdom a liquid absorption process using carbon tetrachloride was developed on a laboratory scale very early in the mid-fifties [6, 7]. However, the work was terminated because no necessity for krypton retention was seen at that time.

2.3. CHARCOAL ADSORPTION PROCESSES

Charcoal adsorption processes are widely used in reactor technology. For the most part, the charcoal beds are used as delay beds. The short-lived isotopes decay, whereas krypton-85 breaks through and is discharged into the atmosphere. However, it is also possible to isolate krypton-85 and xenon by a cyclic sorption/desorption operation of parallel charcoal beds.

Cyclic operation can be achieved by adsorption at either ambient or reduced temperature and desorption at a higher temperature, or by the so-called pressure-swing method. The advantage of the charcoal method is its very simple operation, so that most modern nuclear power reactors use charcoal beds.

2.4. SPECIAL PROCESSES

The different solubilities of the components of the off-gas in a homogenous organic polymer membrane can be used for the isolation of krypton and xenon [8, 9]. The small differences require a multi-stage process but the equipment is relatively compact. Consequently this method has been proposed for the separation of krypton from a post-accident atmosphere inside the reactor building by means of a mobile plant. However, the radiological importance of the krypton isotopes after a big reactor accident can be considered of minor concern compared with that of other isotopes present inside the reactor building after such an accident. A fundamental disadvantage of the process is the low mechanical and radiation stability of the membrane. In addition porous membranes, 200 Å in pore diameter and $10^7/\text{cm}^2$ in pore number,² and hollow fibres or metallic membranes have been considered for the separation of noble gases from reactor off-gas.

2.5. SEPARATION OF KRYPTON AND XENON

The separation of krypton and xenon may be advisable when considering the following aspects:

The volume of radioactive gas to be stored can be reduced remarkably.

If ozone is formed even at very low concentrations it will be separated with the xenon and will not increase corrosion of krypton-85 metal containers.

If the gas is stored in pressurized containers, the pressure at a given content of krypton-85 is reduced.

If the xenon can be decontaminated to a very high degree, it may be used for commercial purposes, which, however, seems to be of minor interest.

The separation of krypton and xenon can be achieved by one of the above-mentioned processes or by a combination of them. In addition to these, adsorption processes using inorganic materials such as molecular sieves have also been considered.

² 1 Å = 1.00×10^{-10} m.

3. SEPARATION OF KRYPTON FROM REACTOR OFF-GAS

During normal operation the reactor off-gas is delayed to permit the decay of short-lived krypton and xenon isotopes. The separation of krypton-85 from the reactor off-gas is considered unnecessary because of the relatively small amount (a few thousand curies of krypton-85 annually per reactor) and the low radio-toxicity of krypton-85. Nevertheless, processes for separating krypton from BWR and PWR off-gases have been developed.

3.1. SEPARATION FROM BWR OFF-GAS

For the separation of krypton from BWR reactor off-gas the US company Air Products and Chemicals, Inc. has developed a cryogenic process [10]. The first plant has been installed at Brunswick and will operate in the near future. The flowsheet is shown in Fig.1. The off-gas from the nuclear power plant is expelled from the main condenser steam jet air rejectors and is mixed with a diluent stream to produce a mixture which has a hydrogen concentration of 4% by volume. This stream enters the catalytic recombiner where $\geq 99.99\%$ of the hydrogen reacts with oxygen to form water. The water is subsequently removed in the cooler condenser.

The remaining uncondensed stream, consisting of air in-leakage, trace fission gases and about 200 vpm residual hydrogen, is compressed to 8 atm. The compressor discharge is cooled in an aftercooler, which condenses additional water, and subsequently passed through a short delay line to permit the decay of most of the short-lived isotopes. The compressed air stream enters the cryogenic section via a reversing heat exchanger. At a temperature of about -170°C water and carbon dioxide are frozen out. Subsequently the gas is further cooled by expansion and fed into the distillation column. More than 99.99% of the krypton and practically 100% of the xenon entering the column are accumulated in the bottom of the column.

The build-up of hydrocarbons is readily prevented by continuously withdrawing a small stream of liquid from the column bottom, passing it through a hydrocarbon oxidation chamber, and recycling it to the suction of the feed compressor. This continuous hydrocarbon removal system has the additional capability of thermally decomposing any ozone which might be formed by irradiation of the liquid oxygen.

The liquid oxygen containing the krypton and xenon is periodically removed and the noble gases are further concentrated on a batch basis by removing the

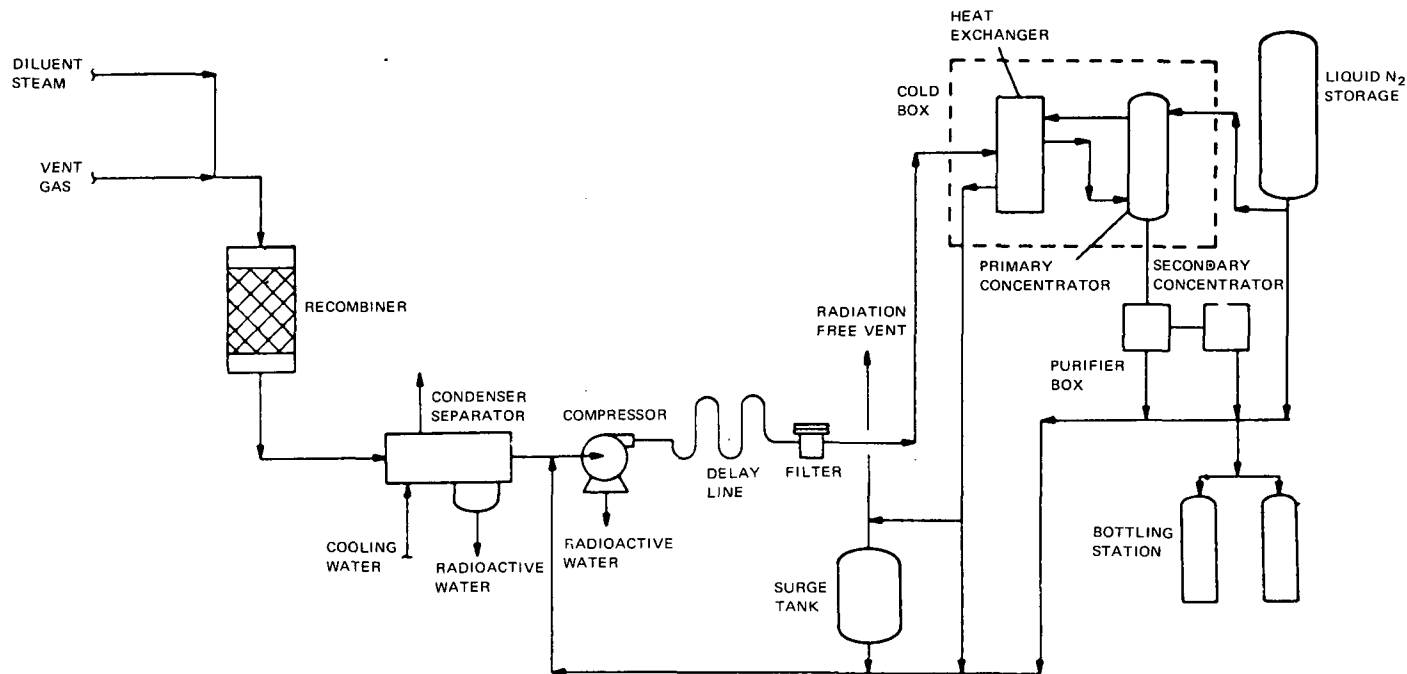


FIG.1. Krypton separation from BWR off-gas (Air Products and Chemicals Inc.).

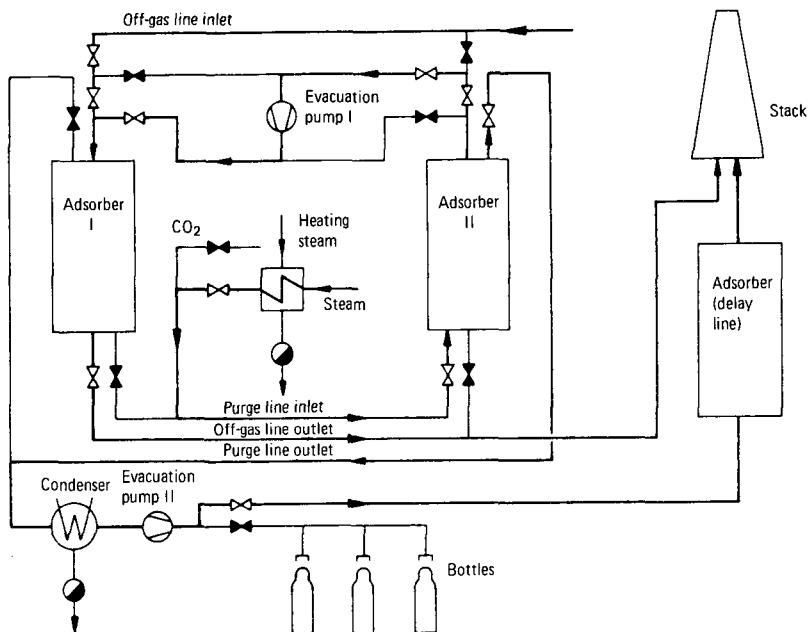


FIG.2. Charcoal adsorption process for BWR off-gas.

oxygen. At 1% fuel leakage and 70 m³ STP/air in-leakage, this operation is usually carried out four times a year. This infrequent batch operation for secondary concentration of the fission gases is accomplished in about 24 hours.

3.2. THE KWU CHARCOAL ADSORPTION PROCESS

In the Federal Republic of Germany, the reactor company Kraftwerke Union (KWU) has developed a charcoal adsorption process for use with a boiling water reactor [11]. The main objective of the development was to reduce the volume of the delay beds by substantially reducing the quantity of off-gas to be delayed.

In another variant, however, the isolation of krypton also is possible. Both variants are shown in the flowsheet (Fig.2).

The equipment consists of two parallel adsorbers with associated purge gas cycle and one charcoal delay bed. The off-gas passes adsorber I until krypton breaks through. At this moment the off-gas line is connected to the parallel adsorber, II. During loading of the parallel adsorber, II, adsorber I is evacuated. The gas is combined with the off-gas stream. Adsorber I is connected with the purge cycle and pump II pumps a condensable gas, i.e. carbon dioxide or steam,

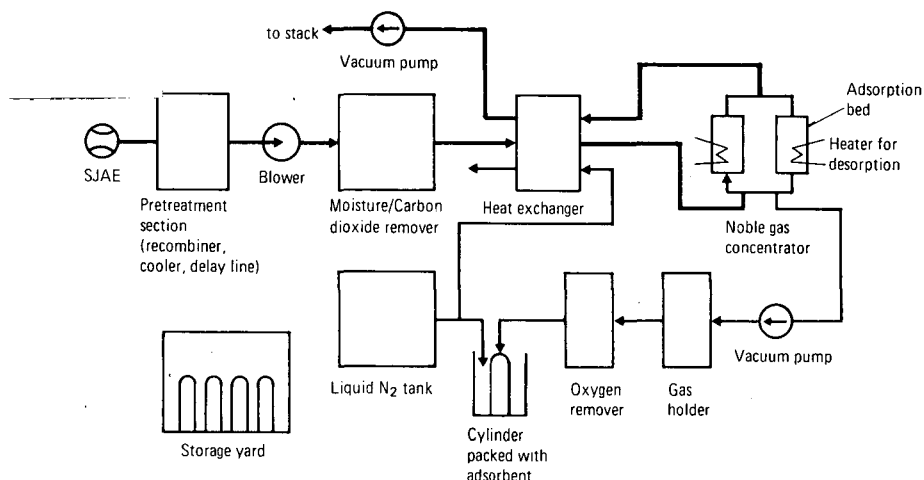


FIG.3. Schematic flow diagram of the proposed off-gas clean-up system for nuclear power plants in Japan.

through the bed. After a few minutes the krypton has been desorbed completely, whereas only a small part of the xenon has been desorbed. After separation of the condensable purge gas in the condenser, krypton can be withdrawn from the system. Xenon can be desorbed and withdrawn in the same manner by further purging. The desorbed noble gases can be bottled for final storage, or delay in a concentrated form for further decay, prior to release to the atmosphere. After the conclusion of extensive laboratory tests it has been found that compared with a normal charcoal-delay system the process is much more complicated and no economic advantage could be found because of the more difficult equipment. But in case noble gas removal from the off-gas stream, with the possibility of subsequent bottling of the noble gases, is required, the process described is suitable.

3.3. SEPARATION FROM PWR OFF-GAS

For the separation of noble gases from PWR off-gas, KWU has proposed a combined charcoal adsorption/cryogenic distillation process [12].

This process opens up the possibility of breaking up the off-gas stream into its different components. The noble gas can be removed and bottled, while the nitrogen and hydrogen, which had been added for the adjustment of the primary water, can be separated and recycled for further use. By continuous out-gassing of the coolant the release of radioactive gases can be reduced by 75% at a purification rate of 10%.

3.4. SEPARATION FROM NUCLEAR POWER PLANT OFF-GAS IN JAPAN

A group of Japanese companies has proposed a low temperature adsorption process [13], which is described schematically in Fig.3, for the separation of noble gases from nuclear power plant off-gas.

After passage through a conventional pre-treatment section, the effluent enters a moisture/carbon dioxide removal unit. The concentrations of these species are a few parts per million.

The off-gas is cooled in a heat exchanger almost to the temperature of liquid nitrogen.

The noble gas concentrator consists of two adsorption columns filled with charcoal or molecular sieves. The off-gas from the exchanger enters one of these two columns. After break-through the noble gases are desorbed by heating and combined with the fresh off-gas.

The noble gases in this combined stream are removed by another adsorption column.

After the correct number of repetitions of this switching, considerable enrichment on the adsorbent is achieved.

A higher concentration of noble gases can be obtained by using selective desorption just before the transfer to the next processing step.

To prevent ozone formation and explosion during storage, oxygen is removed from the concentrate by contact with a metal.

The concentrated gas is filled into a cylinder which has been cooled with nitrogen and is packed with adsorbent. By using this method the filling operation can be carried out under sub-atmospheric pressure. The internal pressure of the cylinders during storage at room temperature is also lower in cases where an adsorbent is packed into the cylinders than in cases where it is not.

3.5. SEPARATION OF NOBLE GASES FROM A PWR HYDROGEN PURGE GAS STREAM

In Japan a new off-gas treatment system has been tested on a laboratory scale using a palladium alloy film for the separation of the noble gases from the hydrogen purge gas stream of a PWR [14]. The flowsheet of the process is shown in Fig.4.

The system consists of gas compressors, purifiers, gas separation cells, the Pd-alloy film and gas decay tanks. The hydrogen which penetrates the membrane is stored in a tank for re-use, while the fission gases which do not pass through the membrane can be collected in a small volume.

The Pd-cell is operated at a temperature of 350 to 470°C and a pressure³ of 2 to 10 atm with a feed gas containing 60 to 100% H₂.

³ 1 atm = 1.013 25 × 10⁵ Pa.

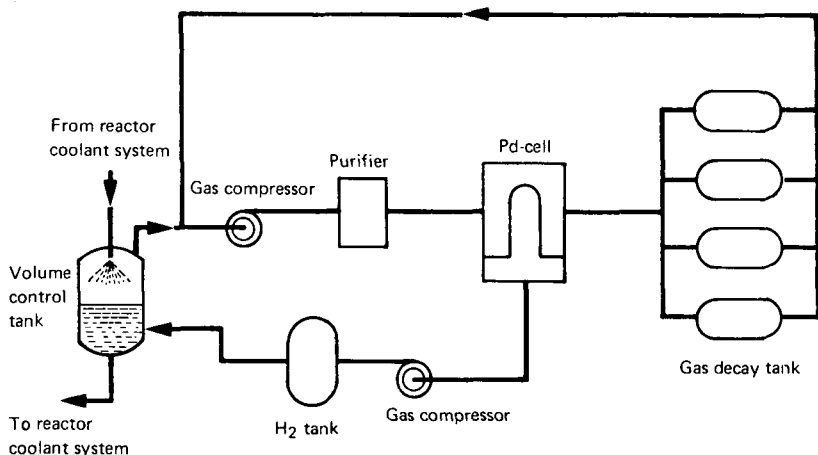


FIG.4. Schematic diagram of the separation system by Pd-cell.

3.6. SEPARATION OF NOBLE GASES FROM REACTOR OFF-GAS USING HOMOGENEOUS AND POROUS MEMBRANES

Homogeneous and porous membranes are used for the separation of krypton and xenon from air in a 1 m³/h experimental plant in Japan [14]. The plant operates at a temperature of 25 to 80°C. The pressure difference is 0.8 kg/cm². For a 99% krypton recovery five units are necessary. The power input is 60 kW. The cooling water consumption amounts to 2.5 t/h.

3.7. SEPARATION FROM FBR OFF-GAS

At the Grenoble NRC the CEA is designing a pilot plant to purify FBR off-gases, using argon as the carrier gas.

The system, based on a cryogenic process, consists of concentrating the rare gases in a liquid argon bath in the column boiler.

The excess purified argon is removed at the condenser head and recycled to the reactor.

In principle, the rare gases are only drawn off in the boiler when a concentration of 1 to 2% is reached, thus allowing many months of operation without removal in view of the low concentration in the feed gas.

This concentrate can be stored in compressed gas cylinders and then sent to the rare gas recovery unit of the fuel reprocessing plant.

This installation is essentially intended to ensure the operating safety of the reactor in case of accidental failure of several fuel elements.

4. SEPARATION OF KRYPTON FROM REPROCESSING OFF-GAS

In the reprocessing plant the cladding material of the spent fuel elements is destroyed and the nuclear material is dissolved. The noble gas inventory is liberated and, according to the present state of technology, discharged through a chimney stack into the atmosphere so that about 10 000 Ci of krypton-85 per tonne of spent fuel, with a burn-up of about 3%, are emitted. To reduce the krypton-85 release several krypton retention plants are either under construction, design or at an experimental stage. To achieve an effective krypton retention at reasonable cost it is essential to prevent unnecessary dilution of the off-gas containing the krypton by proper design of the cells and equipment. A back-fitting of existing plants would probably be very difficult and expensive.

Design data for the volume and the composition of the off-gas are summarized in Table III. Components not given in the table are iodine, iodine-containing compounds, organics, water vapour, tritium etc.

4.1. LWR AND FBR DISSOLVER OFF-GAS DECONTAMINATION

In LWR and FBR reprocessing plants krypton is liberated during chopping of the fuel elements and during the dissolution of the fuel. For a highly efficient krypton separation the purge gas from the chopper is routed through the dissolver. At less restrictive release limits it may be desirable to treat only the dissolver off-gas during the first hours of a dissolution batch when krypton-85 is liberated.

Most plants apply a cryogenic process with the exception of the Oak Ridge Freon plant which is a liquid absorption plant.

In all cases efficient aerosol and iodine removal from the off-gas is also necessary.

4.1.1. Industrial plants

4.1.1.1. *The Idaho cryogenic plant (USA) (operating plant)*

The first cryogenic process for the separation of krypton was developed in the Idaho Chemical Processing Plant. However, no attempt has been made to optimize this process and to minimize the release of krypton because there has been no real incentive to do so. Krypton has only been recovered to supply a demand for the isotope, not for environmental protection. Presently a modernization of the cryogenic unit is planned to make it comparable with other processes [15].

The capacity of the plant is about 35 – 50 m³ STP/h. A flowsheet is shown in Fig.5. The dissolver off-gas is pumped first into combination surge and scrubbing

TABLE III. DESIGN OFF-GAS VOLUMES AND COMPOSITIONS OF A TYPICAL COMMERCIAL PLANT

	Volume (m ³ STP/h)	Compositions					
		N ₂ (%)	O ₂ (%)	NO _x (%)	CO ₂ + CO (%)	Kr (vpm)	Xe (vpm)
LWR – DOG	100 – 500	70	0 – 20	0 – 20	–	60 – 300	500 – 2500
HTGR – BOG	1500 – 2000	–	< 10	–	> 90	1 – 20	6 – 100
HTGR – DOG	~ 10	–	~ 97	0.6	–	~ 2800	~ 15 000

DOG = Dissolver off-gas after passing the scrubber.

BOG = Burner off-gas.



FIG. 5. Rare gas plant of the Idaho Chemical Processing Plant.

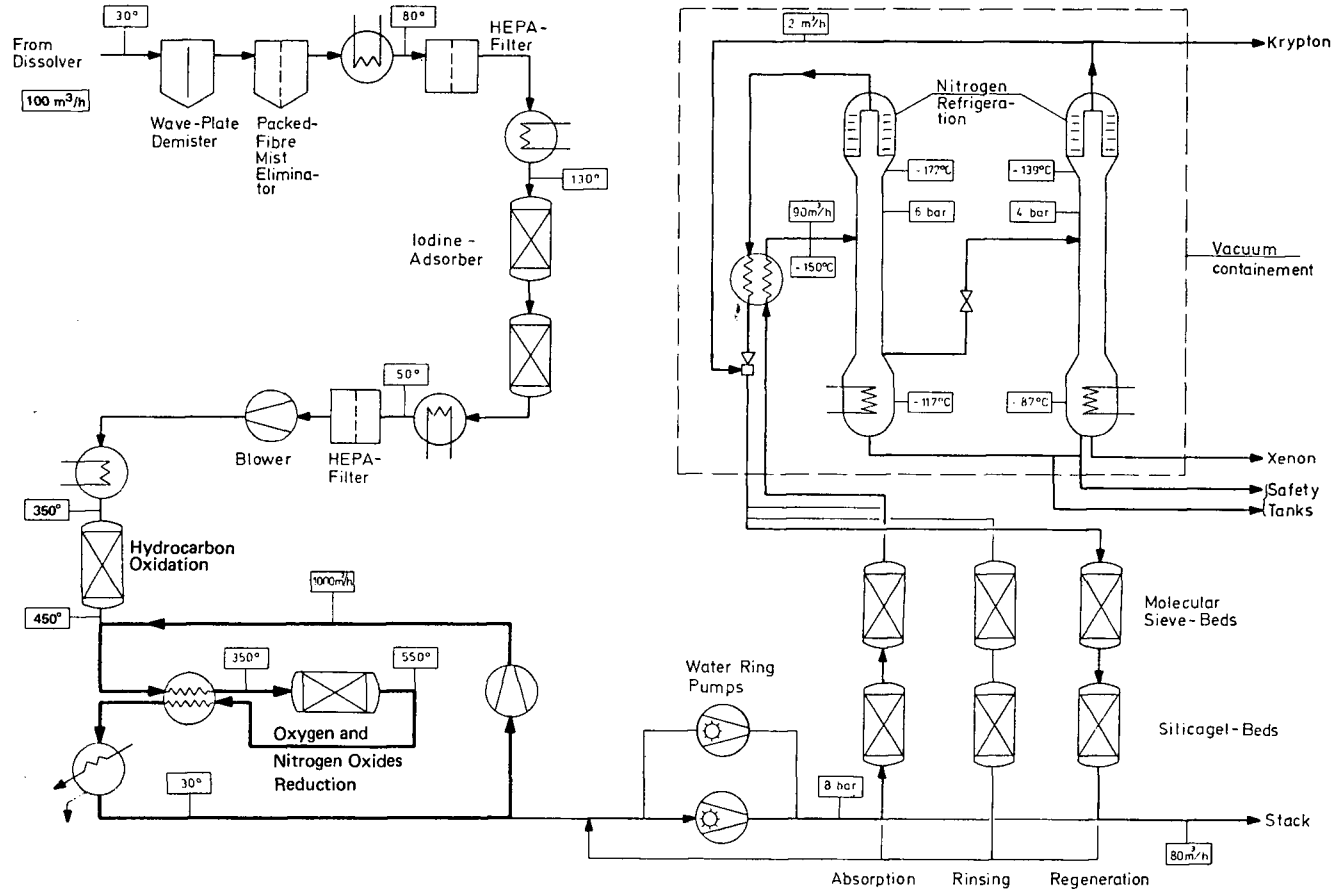


FIG.6. Schematic diagram for the AZUR cryogenic krypton separation plant.

vessels. From the storage tanks, the gas stream is passed through rhodium catalyst beds at a temperature of 540 – 650°C where nitrous oxide is reduced to nitrogen and the small amount of hydrogen in the gas reacts with oxygen to form water. Then the effluent from the catalytic reduction unit passes through a condenser, a demister and a drier before entering a cryogenic system.

The cryogenic system consists primarily of two cold traps, a distillation unit and a batch still. Feed gas flows alternately through one or other of the two cold traps, also functioning as heat exchangers, where it is cooled by the cold packing. The packing is pre-cooled by effluent cold gas from the primary distillation column. The cooled gas leaves the cold trap through a check valve at a temperature of about 162°C and enters the primary distillation column. Liquid nitrogen is introduced into the top of the column and flows downward over the sieve plates in the column, condensing and absorbing higher boiling components in the feed gas such as oxygen, xenon, krypton and argon. Waste gas (primarily nitrogen) is discharged at the top of the column while the absorbed gases are further concentrated by boiling and rectification in the kettle and lower portion of the column.

Bottoms from the primary column, containing the relatively concentrated rare gases, are transferred periodically to the batch still where the nitrogen and most of the oxygen are distilled off after each transfer. After a sufficient quantity of product has accumulated in the batch still (equivalent to that amount from six or seven liquid transfers), a complete fractionation is performed. The initial gas fraction, which contains mostly oxygen, is recycled back to the feed-gas compressor to prevent the loss of the small amount of rare gas in the fraction. Krypton is the first product fraction taken off, followed by xenon. The disadvantage of this process is the presence of oxygen. As a result ozone explosions have occurred in this plant when ozone concentrations exceeded a critical value. More recent experience with concentrations < 2% showed no explosions.

4.1.1.2. The AZUR plant (FRG) (under design)

An off-gas purification and krypton separation plant called AZUR, which will be added to the WAK reprocessing plant in the FRG, has been under design since 1976. The main object of the project is to gather experience for the installation of a cryogenic krypton separation plant at a 1400 t/a reprocessing plant yet to be built. The flowsheet is shown in Fig. 6 [16].

After the separation of liquid and solid aerosols, as well as iodine, the off-gas (60 – 120 m³ STP/h) passes a catalytic converter to remove hydrocarbons. In a second catalytic unit oxygen and nitrogen oxides are reduced by reaction with hydrogen. To prevent hydrogen/air explosions a dilution cycle with oxygen-free off-gas is installed.

After compressing the off-gas to 8 bar by means of water pumps, carbon dioxide and water, as well as impurities such as ammonia and nitrogen oxides, are removed on silica gel and molecular sieve beds.

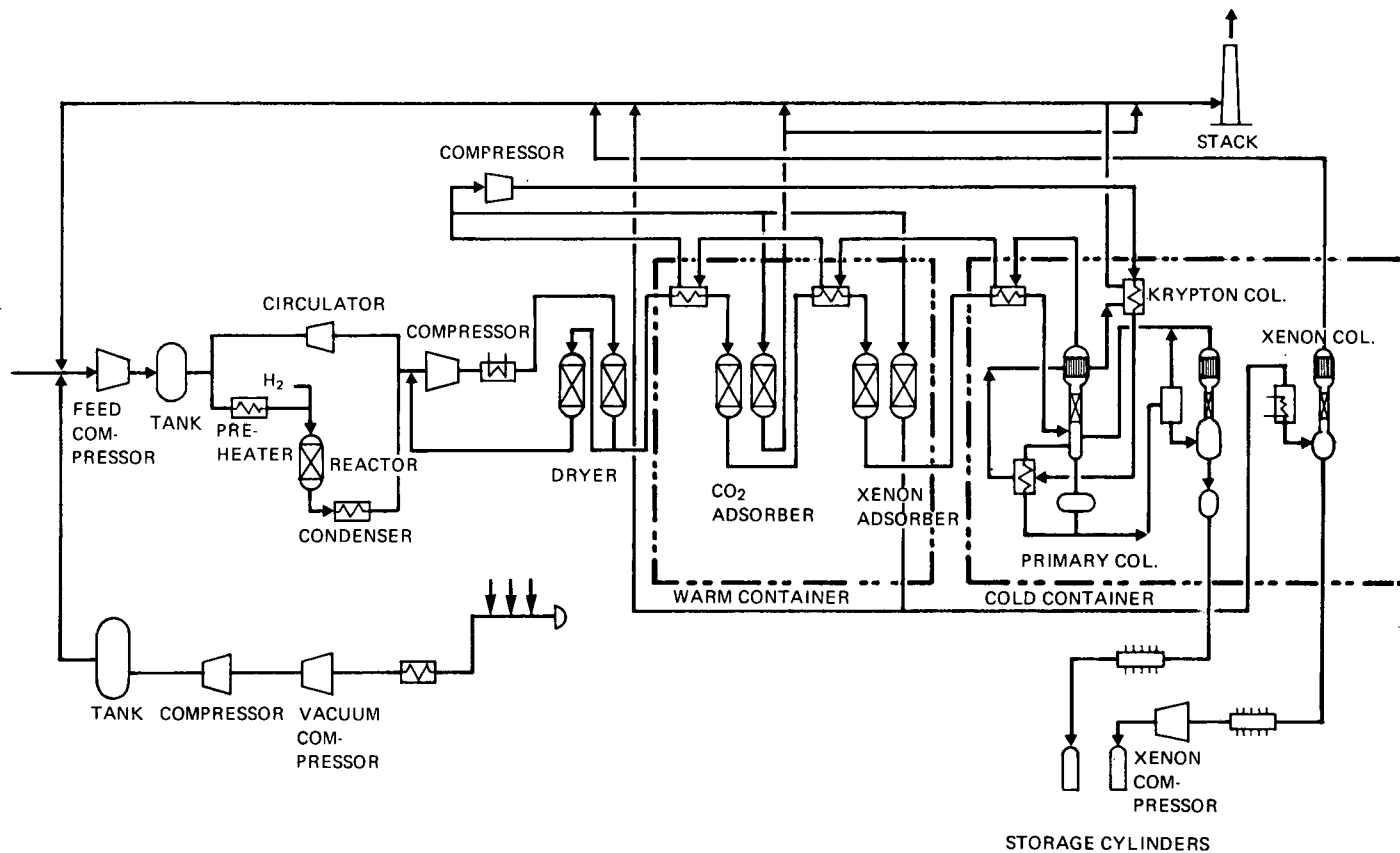


FIG.7. Process diagram for the Japanese krypton pilot plant.

Noble gases are separated in cryogenic equipment containing a distillation column for the separation of the noble gases from nitrogen and other light gases, and a second column for the separation of krypton and xenon. To prevent xenon freeze-out in the lower part of the first column a krypton stream is recycled from the top of the second column to the feed of the first column. This enables the cryogenic equipment to run continuously at thermodynamic equilibrium so that krypton peaks resulting from discontinuous dissolution of the fuel are levelled out. The krypton recycle stream will only increase the total krypton-85 inventory by a small factor, but will guarantee safe and continuous operation.

The AZUR plant consists of several hot cells and will be safe against earthquakes and power failure. Emergency tanks are installed to keep the total krypton inventory of about 6×10^5 Ci safe. Hot operation of the total system is scheduled for 1981.

Parts of the equipment are being tested in cold operation in co-operation with Kernforschungszentrum, Karlsruhe (see sub-section 4.1.2.3).

4.1.1.3. The Japanese krypton pilot plant [17]

This plant consists of four major sub-systems:

A feed gas storage system

A pre-purification system to reduce oxygen, nitrogen oxides and hydrocarbons catalytically and to remove water, carbon dioxide and xenon by adsorption

A cryogenic distillation system

A storage system.

The various steps of the process are shown on the process diagram (Fig.7).

(i) Feed gas storage system

This system will smooth out the downstream gas flow after the off-gas from the chopper enters the plant. It is designed to perform the storage and release functions automatically.

(ii) Pre-purification system

(a) Reduction of oxygen, nitrogen oxides and hydrocarbons

These impurities are catalytically reduced to very low concentrations by adding a slight excess of hydrogen, while keeping the reactor temperature high enough. Sufficient recycled nitrogen is added to maintain the oxygen concentration at the inlet of the reactor below the explosion limit.

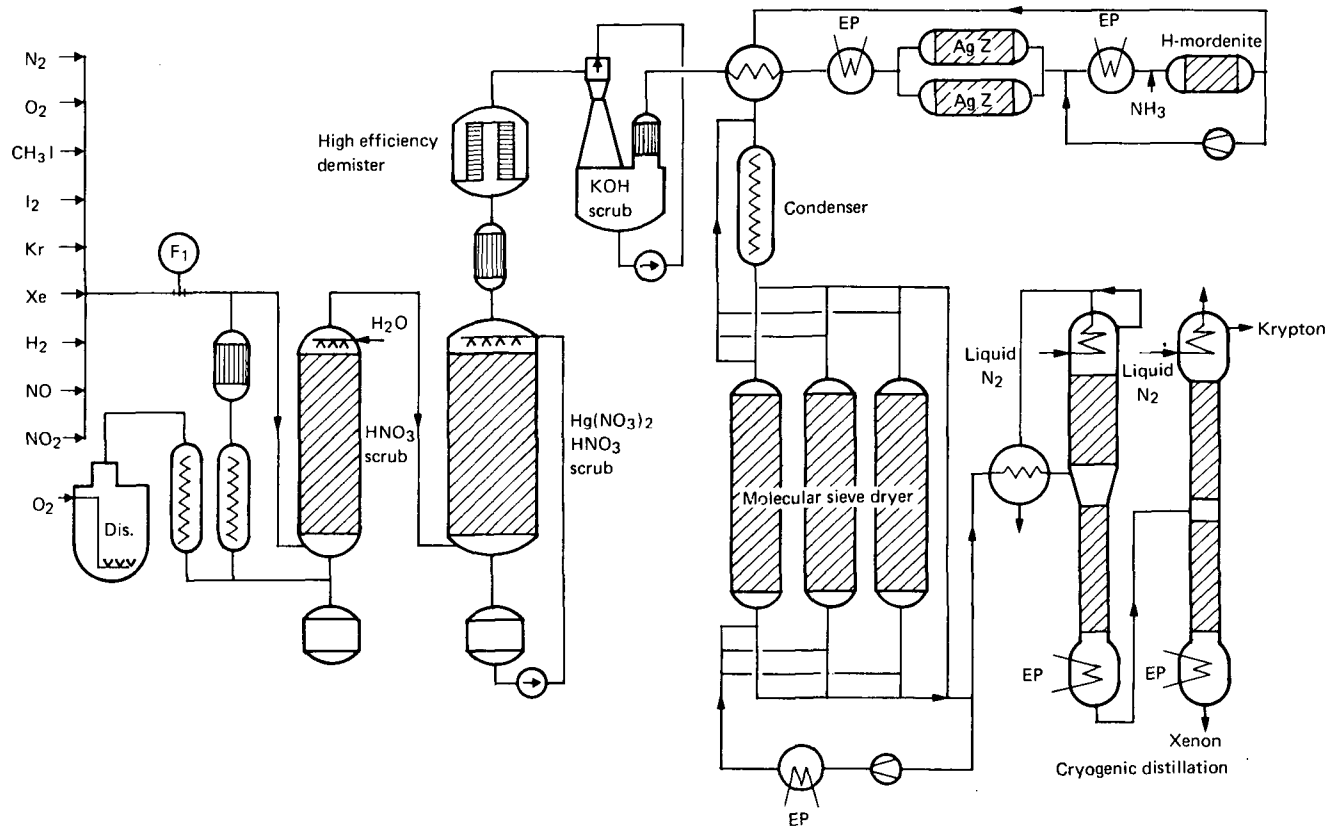


FIG.8. Off-gas clean-up test loop for the SCK/CEN Mol plant.

The system is designed to allow automatically for fluctuations in the flow rate and composition of the feed gas.

(b) Water removal

This water removal system uses drying agents and is based on conventional and well-proven technology. Water is removed by alumina gel and molecular sieves from which the regenerated gas is recycled to upstream. The water leaves the system through a cooler.

(c) Carbon dioxide removal

Carbon dioxide must be eliminated to avoid plugging in the cryogenic section of the plant. Efficient and selective use of molecular sieves during adsorption and desorption makes it possible to remove this gas. Desorption gas at a relatively low temperature is recycled to the feed gas storage system and purged through the ventilation duct after its temperature becomes nearly ambient.

(d) Xenon removal

Xenon freezes easily and so plugs the equipment if its concentration increases and the temperature is sufficiently low. In order to avoid such trouble in the distillation column pre-treatment to remove xenon with silica gel is carried out. Desorption gas from the xenon adsorber is supplied to the distillation system to obtain a high concentration of xenon.

(iii) Distillation system

Two columns for krypton and one column for xenon are provided to decontaminate the gas and produce a high concentration of krypton and xenon. The primary column for krypton is continuously fed with contaminated gas, although extraction of liquid from the bottom is in batches. The primary objective of this plant is to decontaminate the off-gas and that is achieved in this column. In the secondary column (krypton column) liquid krypton of 90% concentration is produced. Desorption gas from the xenon adsorber is fed to a freeze-out vessel installed just before the xenon column.

All the distillation columns are packed columns and both products, krypton and xenon, are stored separately in high pressure cylinders.

TABLE IV. GAS FLOW RATES AND CONCENTRATIONS AT DIFFERENT POINTS OF THE CEA PILOT PLANT

	Feed column 1	Top column 1	Boiler column 1	Inlet catalytic reactor	Outlet catalytic reactor	Feed column 2	Top column 2	Boiler column 2
Flow-rate	$20 \text{ m}^3 \cdot \text{h}^{-1}$	$19.4 \text{ m}^3 \cdot \text{h}^{-1}$	$600 \text{ ltr} \cdot \text{h}^{-1}$	$30 \text{ m}^3 \cdot \text{h}^{-1}$	$28 \text{ m}^3 \cdot \text{h}^{-1}$	$11 - 33 \text{ ltr} \cdot \text{h}^{-1}$	$1 - 3 \text{ ltr} \cdot \text{h}^{-1}$	$10 - 30 \text{ ltr} \cdot \text{h}^{-1}$
Concentrations								
N ₂	79%	82%						
O ₂	21%	18%	98%	2%	1 ppm	1 ppm		
Kr	50 - 150 ppm	0.5 ppm	0.2%	9%	10%	10%	80%	$10^{-7} - 10^{-10}$
Xe	500-1500 ppm	0.5 ppm	1.8%	84%	89%	89%	10%	100%
H ₂				5%	1%	1%	10%	

4.1.2. Experimental plants

4.1.2.1. SCK/CEN, Mol plant (Belgium)

SCK/CEN in Mol, Belgium, is developing a test loop for the reduction of releases of iodine, tritium and krypton from reprocessing plants following voloxidation of the spent fuel [18]. After adsorption of tritiated water on molecular sieves, iodine removal with molecular sieves or scrubbing with $\text{Hg}(\text{NO}_3)_2\text{-HNO}_3$ -solutions, demisting with glassfibre filters, elimination of nitrogen oxides by reaction with NH_3 in the presence of H-mordenite and drying with molecular sieves, the off-gas is cooled to a temperature of 90 K and fed into the first column at a pressure of about 3 bar (Fig.8).⁴ The bottom product, enriched in krypton and xenon, can be transferred continuously or in batches to a second still working at a lower pressure. The second still operates in batches.

First nitrogen and oxygen are separated from the krypton and xenon. The separation of krypton and xenon starts after a sufficient volume of the noble gases has been collected.

No provision has been made for oxygen removal or ozone decomposition.

The cryogenic equipment has been installed and cold tests have been started.

4.1.2.2. The CEA plant (France) [19]

The CEA has built a pilot plant ($20 \text{ m}^3 \cdot \text{h}^{-1}$) at Fontenay-aux-Roses to define an inactive cryogenic distillation process.

This installation includes:

- (a) Preliminary purification of the gas to be treated, comprising:
 - (i) Alkaline scrubbing to eliminate carbon dioxide and nitrogen oxides, followed by water scrubbing;
 - (ii) Nitrogen oxide decomposition in a catalytic reactor using rhodium, absorption of traces of carbon dioxide and moisture on a molecular sieve.
- (b) Concentration column

In this column all the nitrogen and most of the oxygen are removed and the rare gases are concentrated by a factor of 20 to 30 in liquid oxygen.

Hydrocarbon traces are eliminated by an alumina filter, and a catalytic decomposition system is provided to minimize the risk of ozone accumulation.

⁴ 1 bar = 1.00×10^5 Pa.

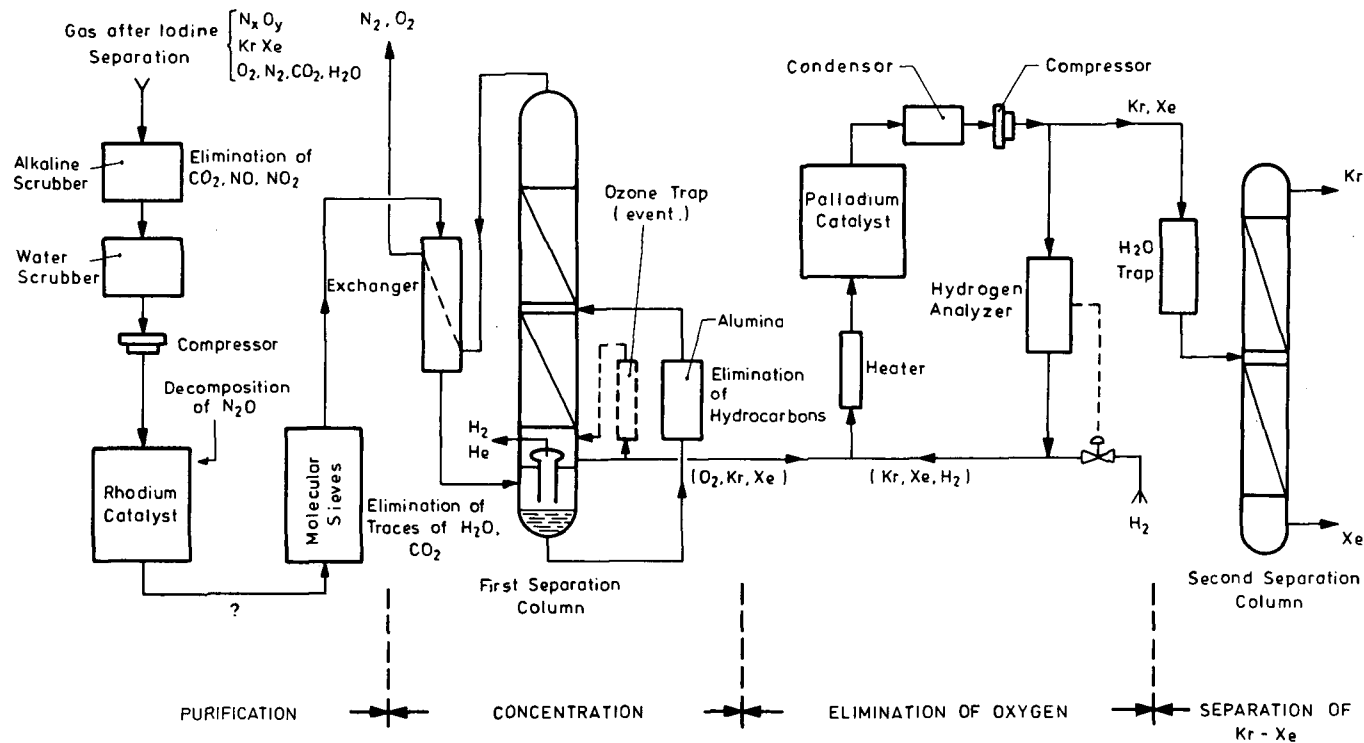


FIG.9. Schematic diagram for the CEA (France) cryogenic plant.

(c) Oxygen elimination loop

The oxygen is converted to water by catalytic reduction in the presence of hydrogen on a palladium support. To maintain the reactor temperature below 400°C, the gas is diluted by a factor of 50 by rare gas reflux.

(d) Krypton/xenon separation column

The first krypton/xenon separation by rectification is carried out in this column. Traces of moisture are retained by a cryogenic trap at the column head.

Gas flow rates and compositions at different points of the installation are given in Table IV. The schematic diagram is given in Fig.9.

4.1.2.3. *The KRETA plant (FRG)*

The Kernforschungszentrum Karlsruhe concept for the separation of krypton-85 from the reprocessing off-gas includes cryogenic distillation of the liquefied gas mixture as the final step [9]. Before this step the off-gas is cleaned by combined removal of oxygen and nitrogen oxides via catalytic reduction with hydrogen (to avoid excessive ozone formation) and by adsorptive retention of water, carbon dioxide and other impurities. The cryogenic part of the process as well as the catalytic reduction and the adsorption process are being tested on a cold, half-scale basis (gas throughput: 50 m³ STP/h) in the pilot plants REDUCTION, ADAMO and KRETA (Fig.10). The last two plants have been in operation for about 2 years.

ADAMO is a fairly conventional adsorber unit consisting of three lines with a silica gel and molecular sieve bed in each line. Before regeneration of a line a purging step with dry nitrogen is included at ambient temperature to desorb and recycle adsorbed krypton.

KRETA consists of two columns. The first is a sieve plate column (15 cm diameter, 7 m high). Here nitrogen is driven off from the top, and krypton and xenon are collected in the bottom. After transfer to the second column, which is a packed bed column (5 cm diameter), krypton is separated from xenon. The columns are contained in a vacuum tank for isolation, together with two intermediate storage vessels for the product and the heat exchanger for the feed gas.

The first column is operated at a pressure of 5 bar and the second column at a pressure of approximately 2 bar.

During operation xenon concentrations of up to 800 ppm by volume and krypton concentrations of up to 2% by volume were fed to the first column continuously for many hours without malfunctioning. A krypton decontamination factor of 10³ was achieved for a column.

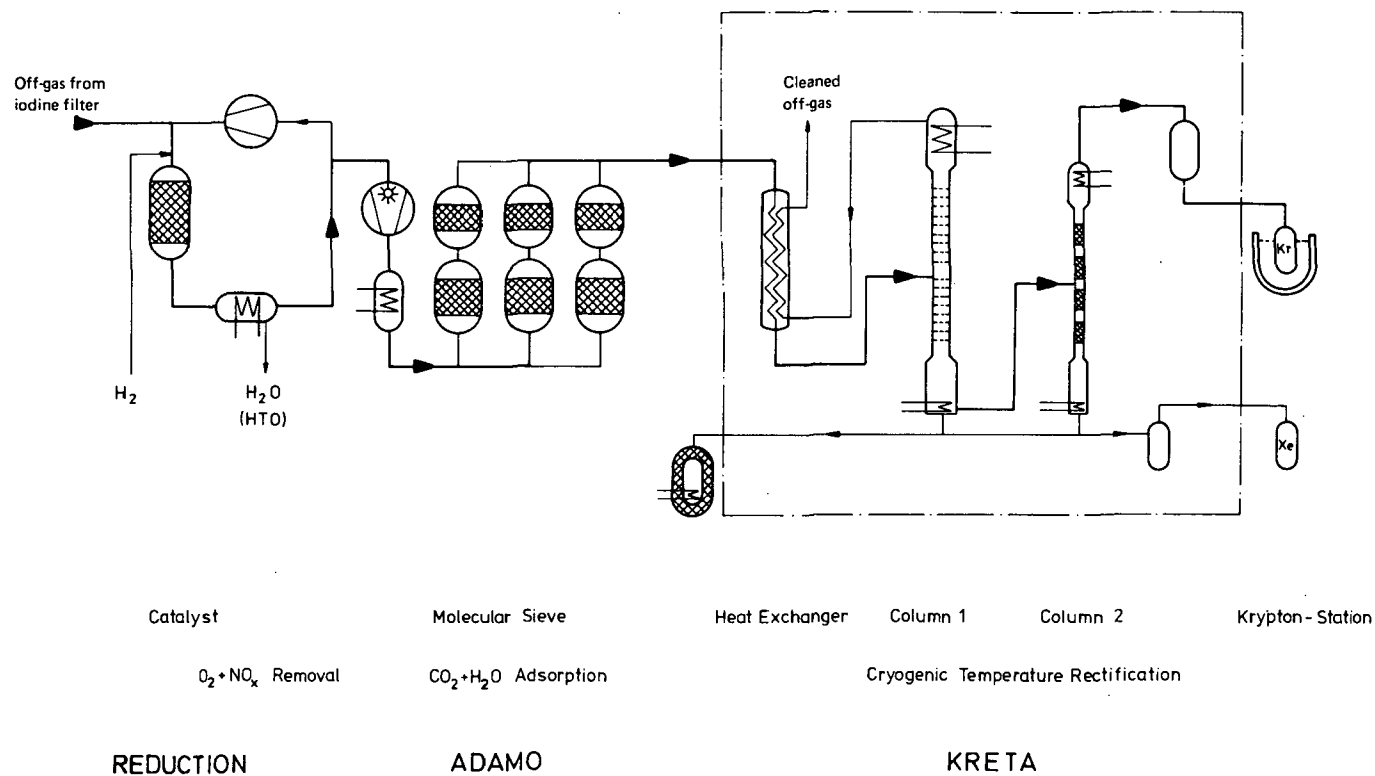


FIG.10. Schematic diagram of the cryogenic process in the pilot plants REDUKTION, ADAMO and KRETA.

Higher xenon concentrations in the feed gas resulted in freezing phenomena near the feed point. The krypton/xenon separation in the second column is carried out with high separation factors without any problems.

The krypton product is filled into steel cylinders by cryopumping and the xenon is filled by means of a membrane compressor.

The krypton product will be withdrawn from the top of the second column by cryopumping.

4.1.2.4. The CRYOSEP plant (FRG)

In Jülich, FRG, a 10 m³ STP/h CRYOSEP plant has gone into cold operation [20]. The plant has been designed for the treatment of the more concentrated HTGR dissolver off-gas. However it can also be used for the diluted LWR dissolver off-gas. Hot operation is planned for 1984 in combination with a small pilot plant JUPITER for reprocessing HTGR fuel elements. To prevent an ozone explosion, oxygen is removed before the gas enters the cryogenic unit. The flowsheet is shown in Fig. 11.

After separation of iodine with silver-impregnated silica gel absorbers and retention of aerosols by HEPA-filters, the oxygen is removed by catalytic reaction with hydrogen. By recycling the reaction product the oxygen is diluted to below the explosion limit. In this step the nitrogen oxides are also reduced, giving elementary nitrogen and small traces of ammonia. The resulting water is removed in a water-cooled condenser. After retention of surplus hydrogen on a copper oxide catalyst the gas flows through a demister and molecular sieve drier.

After this preconditioning and repeated filtering by a HEPA-filter, the gas enters the cryogenic unit. It is precooled to about 160 K by a heat exchanger. In the upper part of two alternately-operated cold traps xenon containing 0.5% krypton is deposited in solid form at 80 K. The remaining gas components are liquefied in the lower part of the xenon separator and flow to a 200-ltr storage-tank.

4.1.2.5. Linde cryogenic plant (USA)

The Linde company has presented a flowsheet (Fig.12) for a cryogenic plant which is similar to other flowsheets already described [21].

The feed gas and a krypton-rich recycle stream from the product column are combined before entering a dual stage catalytic system. Recycling of the krypton-rich stream serves the primary function of maintaining the desired krypton product purity at a minimum of 75%. This stream is taken from the overhead of the second column to remove methane and nitric oxide from the krypton product. The dual-stage catalytic system consists of a catalytic unit for the oxidation of hydrocarbons to carbon dioxide and water and a catalytic recombiner cycle for the removal of oxygen by reaction with hydrogen. The off-gas from the recombiner

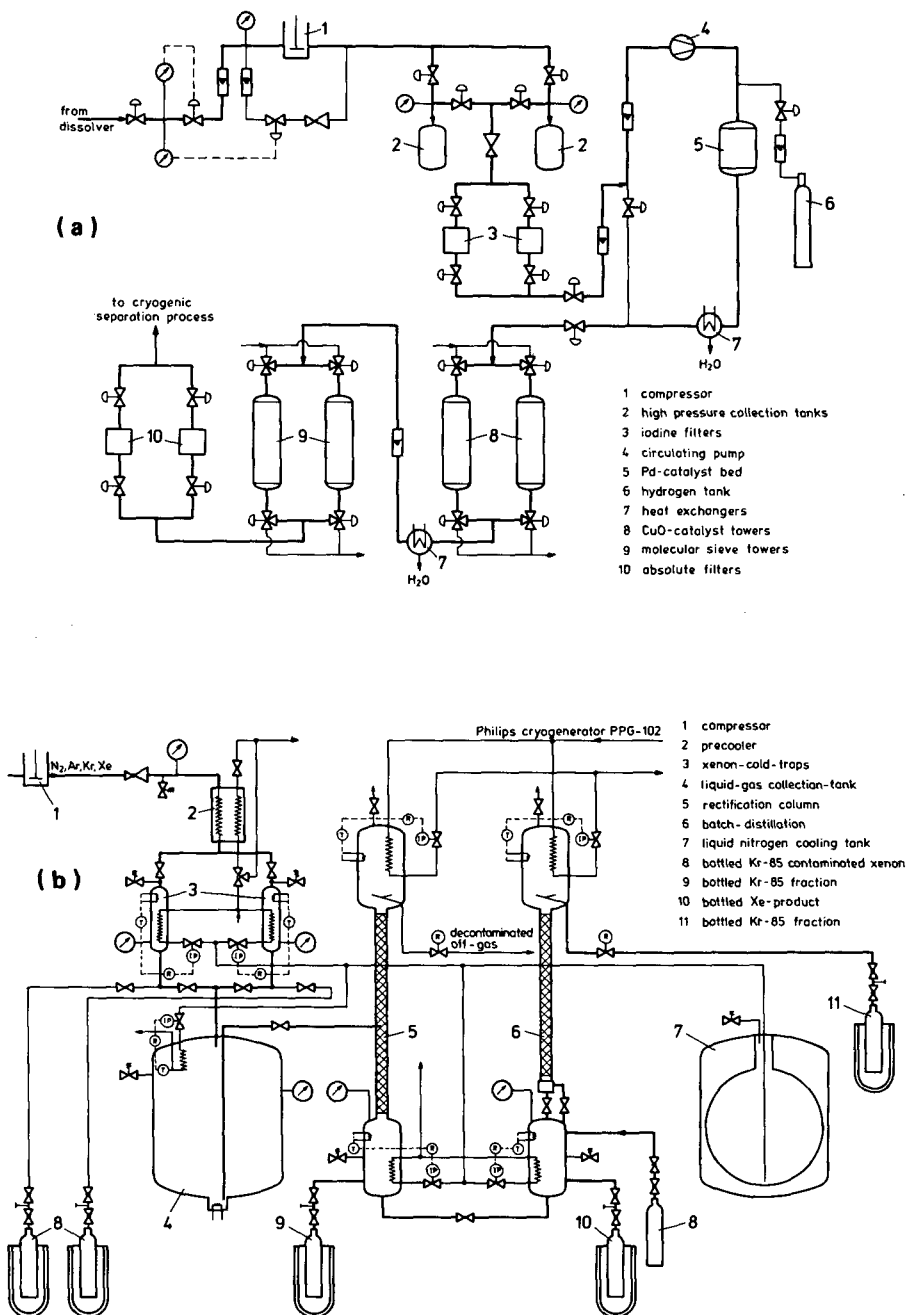


FIG.11. CRYOSEP plant in Jülich: (a) pre-purification and O_2 removal; (b) cryogenic equipment.

is essentially deoxidized air saturated with water, containing 2 – 4% residual hydrogen, 150 – 200 ppm of nitrogen oxide and the fission products krypton and xenon. After compression, carbon dioxide and water are removed from the off-gas before cryogenic processing. From this pre-purification process, the off-gas passes to the primary heat exchanger of the cold box and enters the cryogenic separation equipment consisting of two distillation columns. The decontaminated vapour stream withdrawn from the top of the first column will at a later stage be utilized in a heat exchange function against the reflux of the second column.

Liquid from the bottom of the primary recovery column, containing mainly krypton and xenon, is continuously withdrawn for processing in the product column.

The second distillation column withdraws a high purity xenon product, on a scheduled basis, from the krypton fraction.

The krypton-rich vapour, which consists of the krypton recycle and product streams, is warmed to ambient temperature. The recycled krypton stream is discharged into the feed gas before it enters the preheater of the hydrocarbon catalytic conversion unit. The krypton product stream (containing 75% krypton) is periodically withdrawn and is available at a pressure of 50 lbf/in² (g) for further compression into shielded storage cylinders.⁵ The krypton and xenon are compressed separately for ultimate storage.

4.1.2.6. *The Freon gas-liquid absorption process at Oak Ridge (USA)*

A gas-liquid absorption process using Freon has been developed at the Oak Ridge gaseous diffusion plant [22] based upon fundamental work at Brookhaven. A schematic flow diagram of the pilot plant is shown in Fig.13. Three packed columns comprise the heart of the system: an absorber, a fractionator (that is, an intermediate stripper) and a final stripper. The main separation of noble gas from the bulk carrier gas is accomplished in the absorber. Here the contaminated process gas, after being compressed and cooled, is in intimate contact with the solvent and essentially all of the krypton and xenon dissolve, along with a portion of the carrier gas. The remaining diluent gas, depleted of contaminants, is vented from the process while the loaded solvent is passed on to the fractionator. The purpose of the fractionator is to strip the bulk of the co-absorbed carrier gas from the liquid stream. The fractionator is customarily operated at a much lower pressure than the absorber and, in addition, the gas-laden liquid phase is subjected to the stripping action of counter-flowing solvent vapour. Consequently the bulk of the less soluble carrier readily desorbs. The off-gas from the fractionator must ordinarily be recycled back to the absorption step however, because it also contains a measurable amount of desorbed krypton and xenon. The enriched solvent stream

⁵ 1 lbf/in² = 6.895 × 10³ Pa.

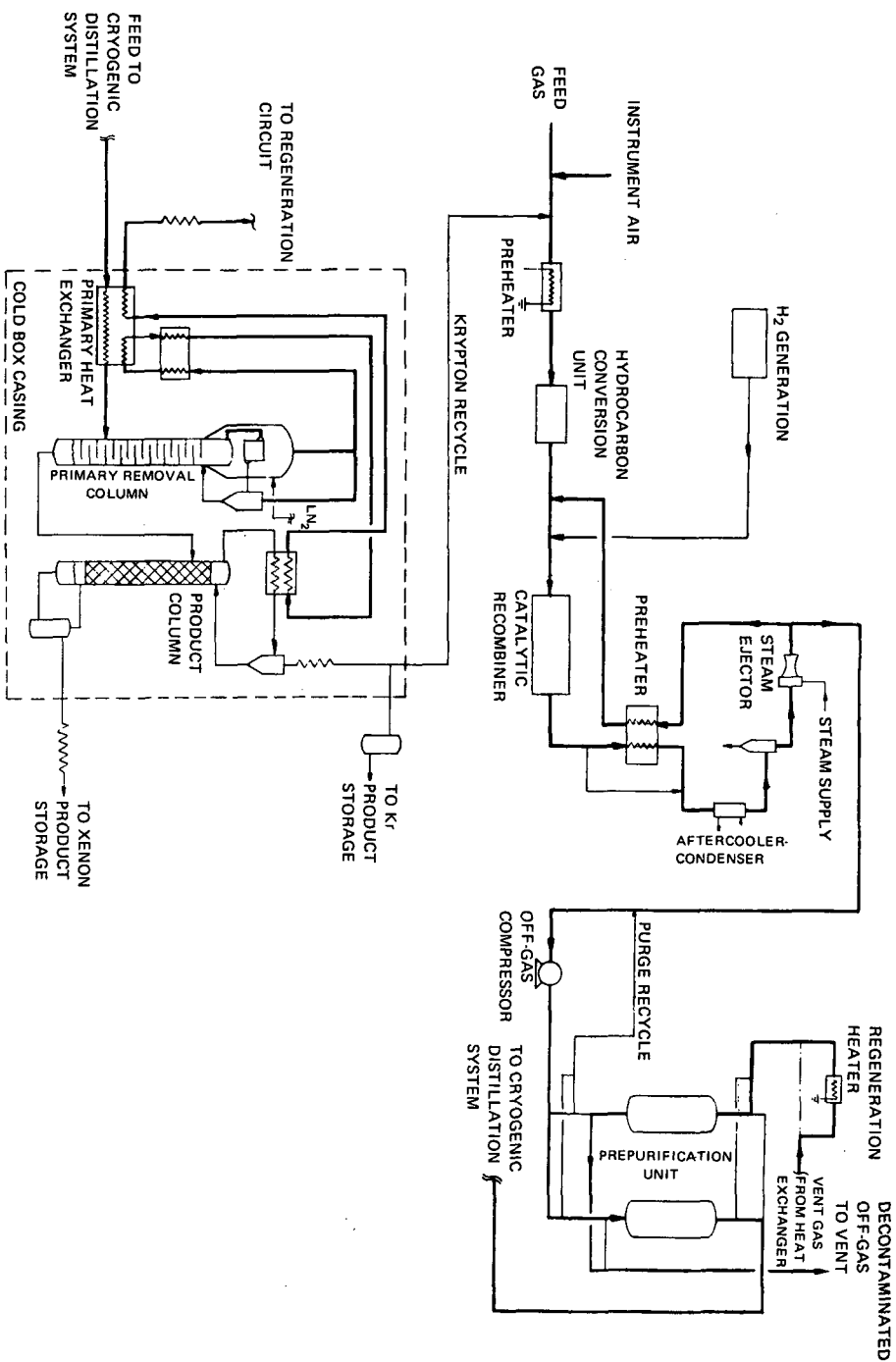


FIG. 12. Schematic diagram of the Linde cryogenic plant.

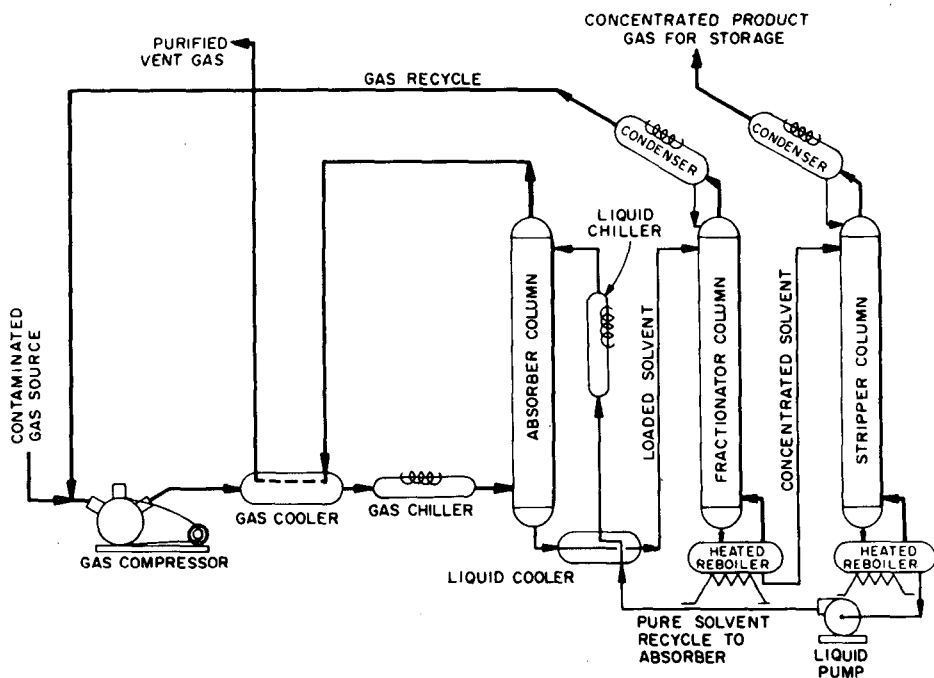


FIG.13. Krypton-xenon absorption process pilot plant schematic flow diagram.

produced in the fractionator subsequently passes on to the stripper. The purpose of the stripper is to produce a highly concentrated krypton-xenon gas product by driving the remaining dissolved gases from the solvent. The stripper is usually operated at an even lower pressure than the fractionator and with more liquid/vapour contacting to facilitate desorption of even the most soluble gases. The pure solvent leaving the stripper is pumped back to the absorber for re-use.

The pilot plant was designed on the basis of processing a nominal quantity of $24 \text{ m}^3 \text{ STP/h}$ off-gas at absorber pressures as high as 40 atm and temperatures as low as minus 70°C .

4.1.2.7. Single column Freon-absorption system (USA)

An advanced process using Freon absorption consists of a combination of absorber, fractionator and stripper in a single three-section column. A system of this kind was designed and constructed on the basis of data from experiments with the Faster-process (Fig.14).

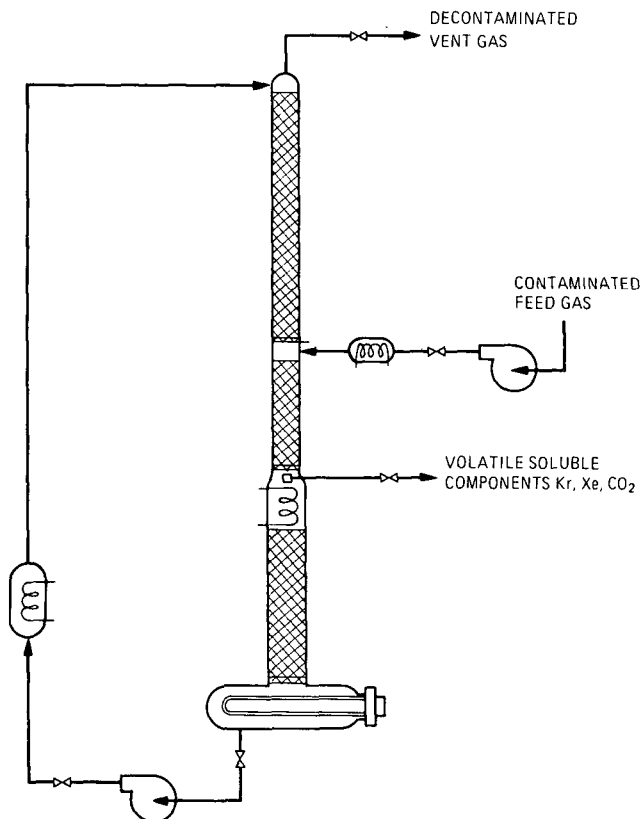


FIG.14. Single absorber/fractionator/stripper column.

The top part of the three-section column, i.e. the part above the gas feed point, is the absorption section of the process. The middle section, i.e. the part between the product take-off and the gas feed point, serves as the fractionator, and the bottom section including the reboiler makes up the stripper [8]. The plant has been installed, apart from the necessary final product cleaning system, and the first experiments are under way.

4.1.3. Other concepts

In addition to the above-mentioned production, pilot and experimental plants, several other concepts for krypton removal from LWR dissolver off-gas have been published.

A combined adsorption and cryogenic distillation process has been proposed in India by Khan [23]. The flowsheet is shown in Fig.15.

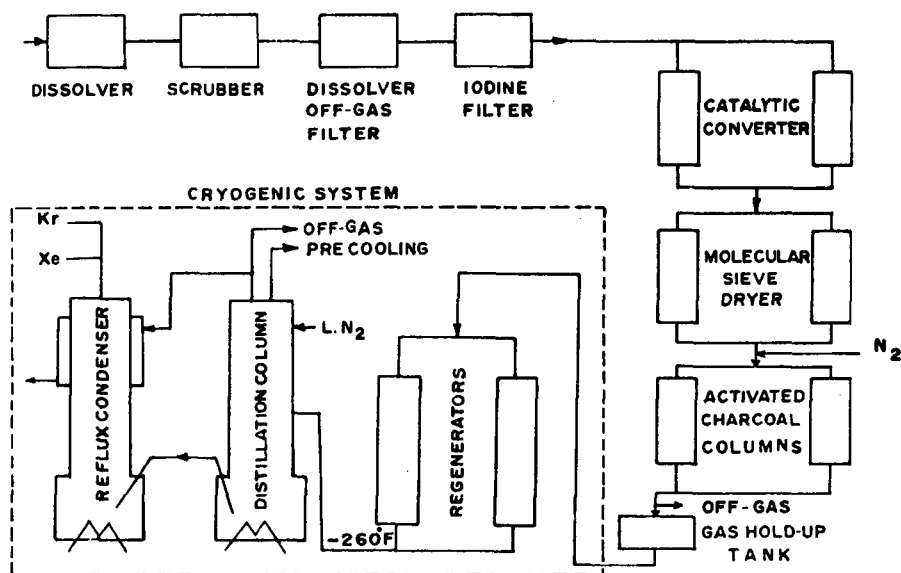


FIG.15. Flowsheet for a krypton-85 containment system in India.

The dissolver off-gas is filtered by HEPA and iodine filters. Nitrogen oxides and hydrogen are eliminated by catalytic reactions, while moisture and tritiated water are adsorbed on molecular sieves. The pre-purified gas stream is then subjected to a pressure-swing process in which it is passed through activated charcoal where krypton is concentrated. Under these conditions krypton is adsorbed and oxygen follows the carrier gas stream. After loading of the charcoal beds, the pressure is reduced and a krypton-nitrogen mixture is desorbed, and is fed into a cryogenic distillation column.

The advantage of this process is a simple separation of oxygen from krypton resulting in elimination of the risk of an ozone explosion as well as a remarkable reduction of the volume of the off-gas stream requiring cryogenic treatment.

In the Soviet Union the necessity is seen of removing krypton arising from effluents from nuclear reprocessing plants. Several concepts are therefore under consideration. Special research and development work is being done. However, a final choice has not yet been made [24].

Since noble gas removal has not hitherto been of immediate urgency, the United Kingdom has preferred not to duplicate the programmes undertaken in other countries but to concentrate the effort available on developing a novel method of krypton storage (see sub-section 5.3.1). The cryogenic, Freon, and other methods of trapping have nevertheless been kept under review [25], and

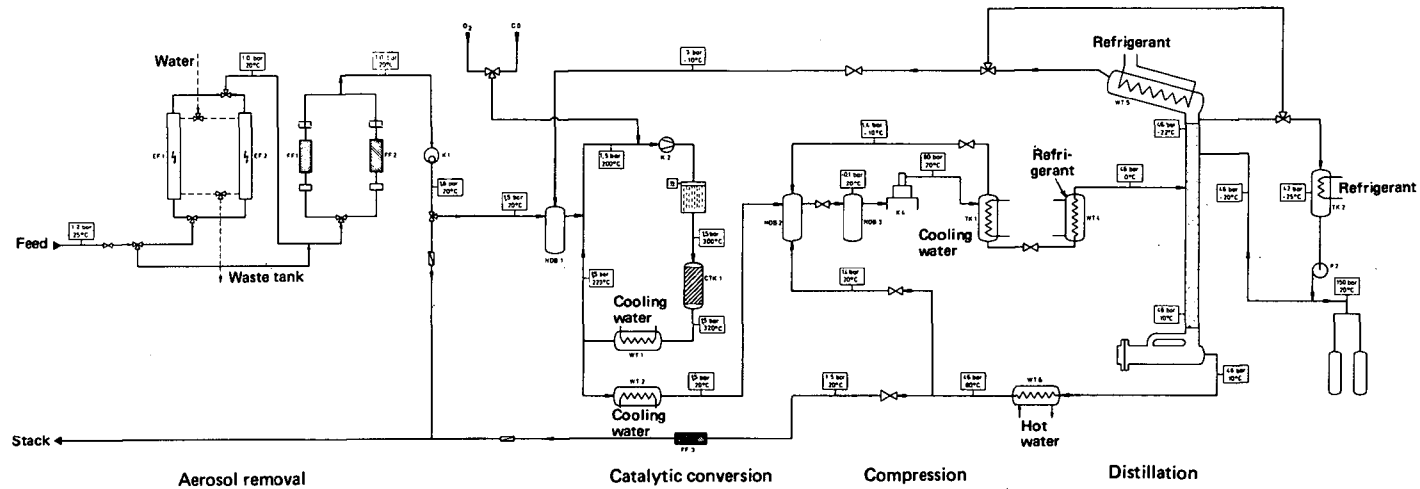


FIG.16. Schematic diagram of the AKUT process for the removal of aerosols, krypton, iodine and tritium from burner off-gas.

their application to the particular conditions of the projected THORP reprocessing plant at Windscale is now under active consideration by BNFL. In the Windscale Inquiry report it is stated that BNFL accept that "krypton removal plant will be incorporated if the technology for its removal and safe retention is available". BNFL are further enjoined in the report to devote effort to the development of this technology.

4.2. HTGR OFF-GAS

HTGR fuel elements consist of uranium/thorium ceramic fuel oxide or carbide particles coated with pyrocarbon, and in some cases also with silicon carbide, and embedded into a graphite matrix.

In the reprocessing plant the graphite and the pyrocarbon layer are first removed by burning with oxygen. The "ash", consisting of the fissile and fertile fuel, is then dissolved in Thorex reagent, 12M HNO_3 with small amounts of aluminium nitrate and hydrofluoric acid. If there is a silicon carbide layer an additional crushing step is necessary.

Krypton-85 is found in both the burner and dissolver off-gas. The distribution between the two streams depends on the fuel element concept and on the quality of the particles and coatings. In the case of oxide particles < 10% of the krypton inventory, and in the case of carbide particles without silicon carbide coating 100% of the krypton inventory is found in the burner off-gas.

Because of the extremely different compositions of the burner and dissolver off-gases, separate processes are being developed for the two gas streams, though under special conditions it may be possible to combine them.

The dissolver off-gas from HTGR reprocessing is similar to the dissolver off-gas in LWR reprocessing, so the same processes with minor changes can be used.

For the burner off-gas special processes are being developed in Oak Ridge (USA) and Jülich (FRG).

4.2.1. AKUT process

In Jülich (FRG) the AKUT process is under development for the removal of aerosols, krypton, iodine and tritium from HTGR reprocessing burner off-gas [26]. The flowsheet is shown in Fig.16. The process consists of the following steps:

- (a) Aerosol retention by electrostatic precipitators followed by HEPA filters
- (b) Oxidation of carbon monoxide with oxygen or reaction of excess oxygen with carbon monoxide, respectively
- (c) Compression and liquefaction of the process stream
- (d) Fractionation
- (e) Partial recycling of product gas into the catalytic converter
- (f) Separation of tritiated water and iodine by adsorption.

The burner off-gas consists mainly of carbon dioxide, carbon monoxide, oxygen, tritium, iodine, xenon, aerosols and small amounts of nitrogen. First it passes through an electrostatic precipitator, where the aerosols are deposited with a decontamination factor of 10^3 to 10^5 . The main advantage of electrostatic precipitators is lower deposition on the HEPA filters, so that the stand time of the HEPA filters is increased by a factor of at least 10^2 .

A catalytic converter is necessary to ensure that no explosive reaction between carbon monoxide and oxygen can take place in the high pressure part of the system.

The catalytic converter handles carbon monoxide contents up to 100% and oxygen contents up to 30%. The gas coming out of the converter consists of carbon dioxide with less than 0.25% oxygen. To achieve this low level of oxygen, the off-gas is fed into a circulating stream, where the reaction of oxygen and carbon monoxide to carbon dioxide takes place.

The gas free from carbon monoxide is compressed to 80 atm and liquefied at ambient temperature.

This liquid stream is fractionated with a low L/G-value, so that the volatile gases such as oxygen and krypton are enriched at the top of the column. This product is fed back into the catalytic converter until the krypton enrichment is high enough for economical storage. The product gas which is withdrawn at the top of the column consists of about 10% krypton, 37% oxygen and 53% carbon dioxide.

In the bottom stream leaving the column, iodine and tritium are enriched and will be separated by an iodine absorber and molecular sieves.

The residence time in the plant is sufficiently long for radon not to be separated. A HEPA filter in the stream leaving the AKUT plant will prevent breakthrough of ^{212}Pb , a daughter product of ^{220}Rn .

4.2.2. KALC process

The KALC process for the absorption of krypton in liquid carbon dioxide has been developed as a result of an early proposal by the Jülich staff [27]. The flow-sheet is very similar to that of the Freon process (Fig.17). First experiments have been executed in the ORGDP plant.

The off-gas, already cleaned of aerosols, is compressed and enters the absorber. The gas is washed by a counter current of liquid carbon dioxide, in which part of the krypton, oxygen and nitrogen are dissolved.

The gas leaving the absorber is free of krypton. The liquid stream is pumped into the fractionator where the light gases are separated from the krypton. As this separation does not operate very efficiently, the gas leaving the fractionator has to be recycled into the gas entering the absorber column.

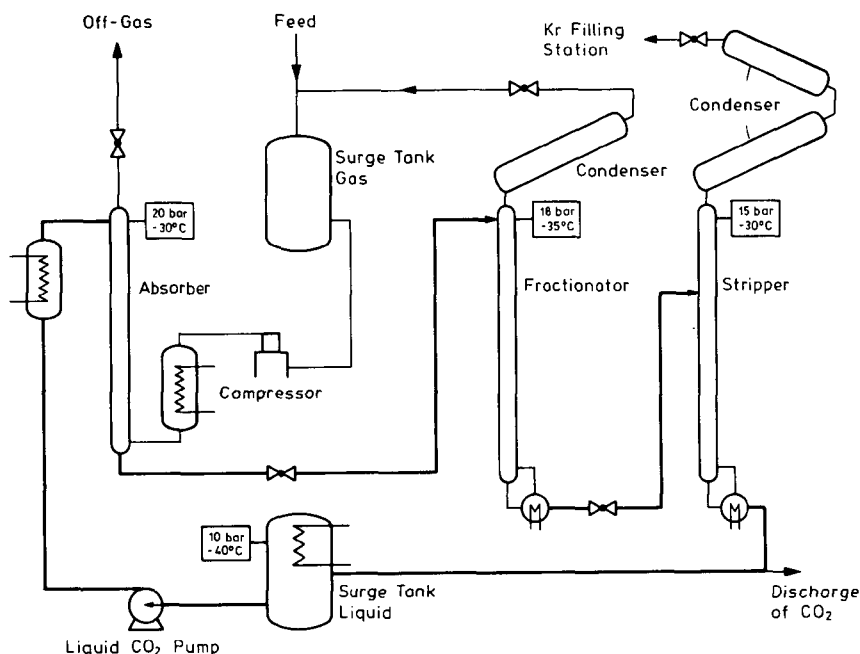


FIG.17. Krypton absorption by liquid carbon dioxide (KALC-process).

The liquid stream out of the fractionator bottom finally enters the stripper column, where krypton and other light gases which are not separated in the fractionator are enriched in the top condenser.

The stripper has to run very efficiently. As all krypton has to be removed out of the bottom stream, it is pumped into the absorber column and used as the washing liquid.

Experiments with this system are under way. Decontamination factors between 50 and 200 for krypton were measured in August 1975.

4.3. OPERATIONAL REQUIREMENTS

To guarantee the safe operation of a krypton retention plant the possibilities of malfunctioning of the equipment should be reduced as far as possible and, in the case of malfunctioning, an accidental release of accumulated radioactive krypton should be prevented. One requirement for normal operation is an extensive pre-purification of the off-gas.

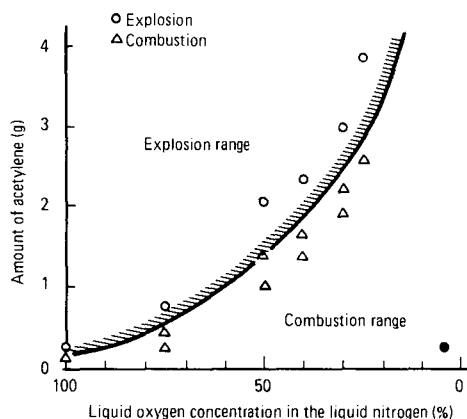


FIG. 18. Acetylene explosion limits as functions of C_2H_2 and O_2 concentrations (●: when the pre-treatment unit is operated at 90% of full performance).

4.3.1. Removal of hydrocarbons

Hydrocarbons are present in the air to a small degree or are dragged into the dissolution off-gas with recycled nitric acid. They can plug the pipes in cryogenic equipment and, in the presence of oxygen and nitrogen oxides, severe explosions can occur in the cryogenic unit. Consequently the hydrocarbons must be efficiently removed.

In several concepts it is assumed that hydrocarbons are oxidized before or during the catalytic oxygen removal [16, 20, 21]; however, a positive statement cannot be made without further experience. It must be recognized that the presence of even 1 ppm of hydrocarbons after passing the catalyst can result in hydrocarbon levels of the order of 1% after final enrichment. These problems with the hydrocarbons are known in conventional gas handling.

Systematic experiments on the explosion of acetylene in liquid nitrogen-oxygen mixtures, for instance, have been made by Yusa et al. [28]. Their data are given in Fig. 18.

4.3.2. Removal of oxygen

Oxygen forms ozone under the action of ionizing radiation. After enrichment ozone can cause explosions, so several flowsheets provide for an oxygen removal step. Furthermore oxygen enhances rubidium corrosion. Oxygen removal can be achieved by cryogenic distillation or by reaction with hydrogen. In the latter case catalytic burners are used which allow reliable operation under changing conditions, especially if a so-called "dilution cycle" is used.

In such a cycle the oxygen is diluted with oxygen-free reaction product to $< 4\%$ so that the possibility of an explosion is excluded. Oxygen and hydrogen concentrations upstream and downstream of the catalyst must be monitored.

Oxygen removal according to this principle is a well-proven technology. A disadvantage is the possible poisoning of the catalyst by iodine, iodine compounds and organics (especially tributyl phosphate and its degradation products), and the formation of ammonia; reliable trapping of aerosols and iodine is therefore essential. Test units are in operation in Jülich [20] and Karlsruhe [29], FRG.

Poisoning of the catalyst can be detected by direct or indirect measurements of the gas compositions. If the equipment fails, it is only necessary to stop the dissolution of the spent fuel when the ozone concentration reaches a critical level in the cryogenic system. Redundant equipment is not necessary.

To reduce the volume of oxygen in the French flowsheet, oxygen removal occurs after a first cryogenic distillation column in which all of the nitrogen and a large amount of the oxygen is stripped.

To prevent the formation of ozone a catalytic by-pass cycle has been proposed. At present, however, there is not enough experience of using a catalyst at cryogenic temperatures.

In the Freon process the oxygen removal is of minor interest; however, it should be recognized that during the storage of krypton, ozone can be formed in the containers in the presence of oxygen.

4.3.3. Removal of nitrogen oxides

Nitrogen oxides are formed during the dissolution of the spent fuel by the decomposition of nitric acid. They can plug the pipes in the cryogenic equipment and, in the presence of hydrocarbons, severe explosions can occur, so they must be removed efficiently.

Nitrogen oxides are partially decomposed during oxygen removal [16, 20, 21], but it seems to be difficult to achieve levels of 1 ppm or even lower. Experiments and calculations show that ammonia, which might be formed during nitrogen oxides reduction, and nitrogen dioxide can be removed together with water and carbon dioxide. Nitric oxide will follow the krypton stream in the cryogenic unit.

4.3.4. Removal of carbon dioxide and water

Carbon dioxide and water are present in the carrier gas. In cryogenic units they can cause plugging and prevent operation of the plant. They must therefore be removed efficiently.

The adsorption of carbon dioxide and water is a well-proven technique although possible co-adsorption of krypton-85 might cause some chemical engineering problems.

4.4. SAFETY CONSIDERATIONS

In the cryogenic units a large amount of krypton-85 is accumulated and in the event of a power failure a temperature and pressure rise is possible. Means to prevent the accidental release of an appreciable amount of the krypton inventory should be provided. The box used for the thermal insulation of cryogenic units should be designed as a second containment and should, therefore, be able to withstand the maximum credible pressure.

In the case of loss of coolant the inventory of a cryogenic unit should be put into containers which can withstand the resulting pressure at ambient temperature. Means for the removal of the decay heat must be provided.

Under these conditions it is not necessary to install redundant equipment for safety reasons. However, it is advisable to install stand-by containers in another cell to which the radioactive inventory can be transferred to allow access for maintenance and repair.

4.5. ACCIDENTAL RELEASES

Special attention must be drawn to the accident situation because the possibility of the release of the total inventory in the plant, while of very low probability, cannot be ignored. The short-time release of megacurie amounts of krypton-85 at ground level, under the most adverse weather conditions, could lead to excessive skin doses if no preventive measures were taken. It will therefore be necessary to protect parts of the plant against the effects of external or internal events so that the total krypton-85 inventory cannot be accidentally released. It may also be possible to design the plant in such a way that only a small part of the krypton-85 inventory is released at ground level. Internal emergency plans should be drawn up so as to reduce as far as possible exposures resulting from the accidental release of krypton-85.

5. CONDITIONING METHODS

For transportation and storage/disposal the krypton gas must be suitably conditioned. The most direct method is the filling of pressurized containers, which for non-radioactive gases is a well-proven technology. However, a number of special problems arise in applying the method to radioactive krypton, e.g. the containment is generally required to last for 100 – 200 years, failure of the containment will contaminate the environment with radioactivity, the decay heat must be dispersed and the rubidium decay product may cause corrosion.

As the solutions to these problems are not obvious, consideration has been given to various alternative conditioning methods, on the one hand to introducing adsorbents into the pressurized containers, and on the other hand to encapsulation of the krypton in a solid matrix.

5.1. PRESSURIZED CONTAINERS

5.1.1. Types of containers

The type of container chosen must meet the requirements regarding heat dispersal, corrosion etc. discussed in the following sub-sections, and must be able to withstand the conditions to which it will be exposed during transportation and storage/disposal. Thus, a container designed for an engineered store may well be different from one intended for sea disposal.

Two types of container have in fact been proposed. Most schemes envisage the use of standard 50-ltr gas cylinders, which may be modified for instance to suit different filling methods. The main exception is a proposal by ECN, Petten, the Netherlands, for a massive spherical container, specifically intended for sea dumping; a sphere is the shape best suited to withstand high internal and external pressures.

The design and operation of pressurized containers for radioactive krypton is limited by the factors discussed in the following sub-sections.

5.1.2. Heat transfer

Provision must be made for the removal of the decay heat from the containers; this amounts to 1.7 W/kCi. There is experience of filling and transporting up to about 25 kCi of krypton in a 50-ltr cylinder [30], when the decay heat can generally be ignored, but from an economic point of view it seems necessary to fill the containers to a considerably higher degree.

The problem of calculating the rate of heat transfer, the nature of the convection currents in the containers, and hence the temperatures which will be reached, is a novel one, since the heat is evolved homogeneously throughout the gas. Although calculations have been made, it is not possible to place complete confidence in the results and efforts are being made to simulate the conditions experimentally, though this appears to be difficult.

Air cooling is always the first choice for heat removal. Convective air cooling is incorporated in the German proposals, while in Japan blowers giving a forced draught will be used. Water cooling is another possibility to remove the decay heat. However, there would then be a problem due to reaction of water with the rubidium decay product in the event of container failure.

TABLE V. STORAGE CONDITIONS FOR KRYPTON-85 IN DIFFERENT COUNTRIES

Country and sub-section	Quantity of krypton per container (kCi)	Pressure (bar)	Maximum calculated outer wall temperature (°C)	Geometric volume (litres)
USA (6.1)	128	34	60	50
FRG (6.2)	350	145	140	50
AZUR (4.1.1)	100	180	120	20
Netherland (for sea disposal) (5.1.2)	500	250	80	50

Moreover standard gas cylinders are not designed for long-term storage under water; corrosion and other problems might arise.

Cooling will only be necessary for the first 30 – 50 years of storage, after which the rate of heat evolution will have fallen by an order of magnitude.

The conditions envisaged in different proposals are listed in Table V.

These figures are for the particular krypton enrichments and storage schemes envisaged. The quantity of krypton per container in the AZUR plant is limited by the low arisings from the WAK reprocessing plant.

In the concept of the ECN, Petten, the Netherlands, there is an inner stainless steel container of 50-ltr capacity and an outer carbon steel container. The containers are concentric spheres of the following diameters:

Inner container:	inner	460 mm
	outer	600 mm
Outer container:	inner	620 mm
	outer	860 mm

The space between the containers is filled with air or nitrogen and can be used for leak detection of the inner container. 1% of the volume of the inner container is occupied by a special metal foil (EXPO foil) to improve the heat transfer.

5.1.3. Corrosion

The pressurized containers must withstand the storage/disposal conditions for 100 – 200 years. In particular the container materials must resist:

- rubidium metal,
- humid air (if air cooling is adopted),
- water (if water cooling is adopted and possibly under abnormal conditions if air cooling is adopted),
- sea water (if sea disposal is adopted).

The most important corrosion problem is probably that of the rubidium metal. It should be noted that this arises early in the storage period, because half the rubidium is produced in one krypton half-life, viz. 10.76 years. Experience with sodium corrosion may provide useful pointers, but it is essential to study rubidium itself. It is also important to investigate rubidium corrosion under stress conditions and as a function of the oxygen concentration in the product gas. The subject of rubidium corrosion is being studied at KFA, Jülich, under a CEC contract [31] and at KFK, Karlsruhe.

Corrosion by humid air and/or cooling water is probably of minor concern, provided high quality materials are used.

Corrosion by sea water must be investigated if sea disposal is adopted.

5.1.4. Filling of containers

The filling operation may be conducted by pumping or by condensation of the gas at liquid nitrogen temperatures. The former leads to a more complicated installation, while in the latter case it should be noted that the vessels and their fittings will be required to withstand temperatures from about -140°C during filling to several hundred degrees above zero during certain accident conditions. In conventional processes stainless steel will be used for this purpose. After filling, the container can be hermetically sealed or can be provided with a high duty valve having a leakrate of the order of $1 \times 10^{-8} \text{ torr} \cdot \text{l} \cdot \text{s}^{-1}$ ($1 \text{ torr} = 1.333 \times 10^2 \text{ Pa}$).

In the Japanese engineered storage concept, groups of twelve steel cylinders are pressure-filled directly in the storage room. These groups of cylinders remain connected by means of valves to the filling pipe during the whole storage period. Manual filling valves have been chosen for ease of maintenance.

In the Federal Republic of Germany a filling station is part of the AZUR plant, described in sub-section 4.1.1.2. The filling station consists of a hot cell with equipment to fill krypton bottles using cryopumping and apparatus to test the filled bottles for leaks.

In the ECN concept a filling procedure using gas under pressure at normal temperatures is preferred; nevertheless other techniques will be taken into consideration.

In the USA a special valve, designed by Kerotest for high temperature applications, has been used for cylinders [30]. The materials are forged monel for the body, copper tinsel for the stem packing and stainless steel for the remaining parts. The expansion coefficient for the valve seat (monel alloy) is smaller than that of the valve stem, so that any increase in temperature results in a tighter seal [30].

5.2. ADSORBENT FILLINGS FOR PRESSURIZED CONTAINERS

Charcoal and molecular sieves have been suggested as adsorbent fillings for pressurized containers for krypton. The possible (though unconfirmed) advantages are:

- reduction in the internal pressure for a given amount of stored krypton;
- reduction in corrosion of the container;
- improved heat transfer with certain fillings, e.g. metal-impregnated charcoal;
- smaller and/or slower releases in the event of container failure.

Against this is probably the added complication of introducing the adsorber. The rubidium problem will, moreover, change in character.

It appears that charcoal is typically 3 – 4 times as effective as a molecular sieve, and would therefore probably be preferred, despite the potential fire hazard. Preliminary data indicate that pressure reduction by a factor of about 2 could be achieved with charcoal at low krypton-85 levels. Studies of krypton adsorption on charcoal for storage have recently been concluded at SCK/CEN, Mol under a CEC contract [31].

5.3. ENCAPSULATION IN A SOLID MATRIX

A solid conditioned form of krypton may have advantages in lower releases during storage/disposal. In the event of fracture of such a material, only a small release is to be expected, compared with the possible total release of the contents of a pressurized container.

Moreover, a solid form may be more readily acceptable for disposal in geological formations or in the deep ocean. No amendment to the London Convention would be needed in the latter case if the dumped activity does not exceed 100 Ci/t (see sub-section 8.2.1).

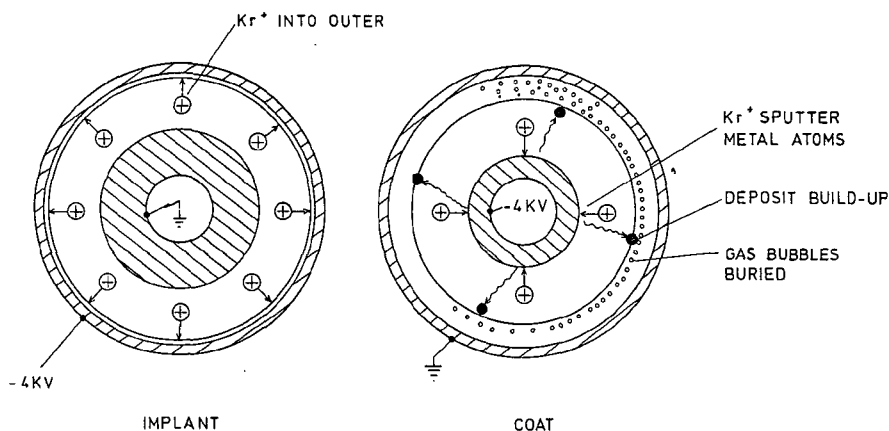


FIG.19. Principles of the process for encapsulation in a metal matrix.

5.3.1. Encapsulation in a metal matrix

It has been shown at the Atomic Energy Research Establishment, Harwell, UK, under a programme partly funded by the CEC [31], that krypton can be encapsulated in the form of minute bubbles ($\leq 2\text{ nm}$ in diameter) in a metal matrix by using a combination of ion implantation and sputtering [32]. The principle is illustrated in Fig.19. There are two cylindrical electrodes, with krypton gas at ca. 10 Pa between them. A negative potential of $3 - 5\text{ kV}$ is applied alternately to each electrode, inducing a glow discharge and generating krypton ions. When the outer electrode is negative, krypton ions are implanted in it, and when the potential is reversed, a fresh layer of metal is deposited on the outer electrode by sputtering from the inner electrode. By repeated switching, a thick layer of deposit is built up containing $5 - 10\%$ by atoms of krypton, i.e. at least 170 nanolitres of gas per litre of metal.

A conceptual plant is indicated in Fig.20. The size is not critical, but a vessel 0.25 m in diameter and 1 m long has been considered for comparison with alternative storage methods. Such a plant is expected to be able to encapsulate the krypton arisings from 4 GW(e) of installed nuclear capacity, with a useful lifetime of 3 months, when the matrix will contain 2.5 m^3 of gas of activity 0.25 MCi . Power consumption would be ca. 100 kW .

A variety of metals can be used, e.g. copper, nickel, iron, molybdenum, tantalum; the choice can be made on the basis of the desired matrix properties. Krypton release is naturally less from the more refractory metals, but even with copper release does not begin until just below 600°C .

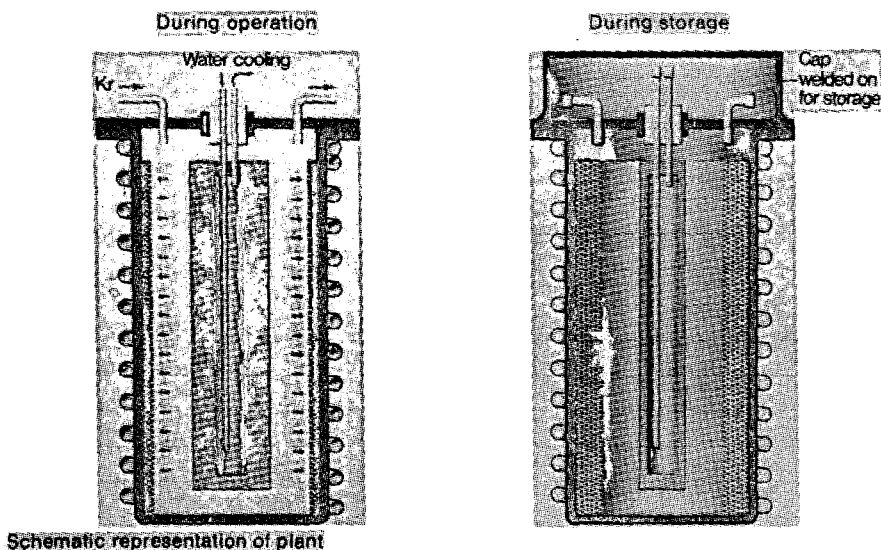


FIG.20. Schematic conceptual plant for krypton-85 storage.

Among the advantages of this system are the metallic strength and thermal stability of the matrix, integral secondary containment, and operation and storage at low temperatures and pressures.

After a successful laboratory programme to establish good operating conditions, a nominal half-scale (50 kW) pilot plant is being built.

5.3.2. Encapsulation in molecular sieves

Krypton can be encapsulated in the cavities of materials such as certain zeolites by exposing them to high temperatures and pressures, e.g. 400°C and 1000 bar. The temperature is then reduced, while maintaining the pressure, in order to close the pores and trap the krypton atoms. The system is not an equilibrium one, unlike a simple adsorption system. There is a small irreversible leakage rate, and this will be greater if the temperature rises owing to self-heating of the product. If necessary, the product can be stored in gas-tight containers, or coated with an impervious layer.

A quantity of 40 ml of krypton can be encapsulated in 1 g of zeolite, corresponding to storage at a pressure of 65 bar.

The conditions of encapsulation in molecular sieves, particularly the high pressure required, make the method unattractive. Calculated krypton leakage rates are very low [33], but these do not take into account possible radiolytic effects. Direct experimental evidence on leakage rates is not available.

5.3.3. Encapsulation as a foam in glass

In early work at the Oak Ridge National Laboratory [34] it was shown experimentally that at a pressure of 1 bar argon used as a stand-in for krypton could be dispersed in glass at a temperature of 550°C to give a foam containing 23% of gas by volume, corresponding to 0.083 ltr STP of krypton per litre of glass. Dispersion at a pressure of 100 bar and a temperature of 550°C would presumably increase this to 8.3 ltr STP of krypton per litre of glass. Dispersion was achieved by agitating the gas/liquid interface with an impeller at a speed of 5000 rev/min.

Further work on this concept has been carried out at the Massachusetts Institute of Technology [35], but again only with argon as a stand-in.

The prospective operating conditions do not seem favourable with a radioactive gas. A high temperature is essential and, if a high pressure is used, gas leakage becomes a problem, while with a low pressure a large volume of foam is generated.

5.3.4. Other methods of encapsulation

A variety of other methods of encapsulation of krypton in solids have been suggested [34] but none of them seem promising.

All known krypton compounds [36] and clathrates [37, 38] are insufficiently stable.

Foams consisting of krypton in epoxy resins would be unable to withstand accidents involving fire, and might break down and release the krypton owing to self-irradiation.

The incorporation of krypton-loaded steel capsules (20.5 ml capacity steel bulbs are commercially available in the US) into a metal, glass, or resin matrix seems rather clumsy and though suggested does not appear to have been tested.

6. ENGINEERED STORAGE

The purpose of an engineered store for krypton is to isolate the material from the environment for 100 – 200 years. It must have means of:

- removing the decay heat;
- detecting leakage of krypton;
- dealing with leaking containers.

Another highly probable feature is sub-division into small compartments to limit the consequences of accidents. The store must moreover either be a gas-tight building or must be provided with a chimney stack. In the former case means are required for cleaning krypton from the air in the building.

In the four concepts described in the following sub-sections the krypton is stored in 50-ltr cylinders, either of standard type or fairly similar. The quantities of krypton per cylinder and other details are given in sub-section 5.1.2. These four concepts are believed to be the only schemes worked out in any detail so far.

6.1. THE IDAHO STORAGE FACILITY

The reference concept developed by the Operations Office of the Idaho Chemical plant is described in considerable detail in Ref. [39]. The store is designed for 5600 cylinders in shielded cells, each cell with a capacity of 104 cylinders arranged horizontally. The main storage area is a long, gas-tight building provided with krypton monitors and allowing limited access through an air-lock for loading the cylinders through ball-valves into the shielded cells. Each cell has a self-contained air circulation and heat removal system, with an externally-mounted blower, and is maintained at a slight negative pressure; each cell also has a radiation monitor and an alarm system. The cells provide primary krypton containment and the main storage area provides secondary containment.

The cylinders are received and inspected in a small shielded hot cell, which is also used for the periodic inspection of stored cylinders and is equipped with a means for transferring krypton from leaking cylinders to clean, empty cylinders.

The store is designed to accept 40 years' arisings of krypton and to store them safely for a minimum of a further 50 years. The maximum inventory at any one time is estimated as 253 MCi.

6.2. THE STORAGE FACILITY FOR THE FRG's NATIONAL FUEL CYCLE CENTRE

The NUKEM company in the FRG has proposed to build an air-cooled storage facility for the planned National Fuel Cycle Centre [40].

The store will have a capacity of 800 steel containers of pressurized gas, each filled with 350 000 Ci of krypton-85, corresponding to 20 years' operation of the reprocessing plant. The storage time of the gas containers will be unlimited (~ 100 years).

The total height of the building is about 24 m of which about 17 m is above ground level. The containers, mounted in shock absorbers, enter the storage room through a lock (Fig.21) and are placed in a shaft of the storage

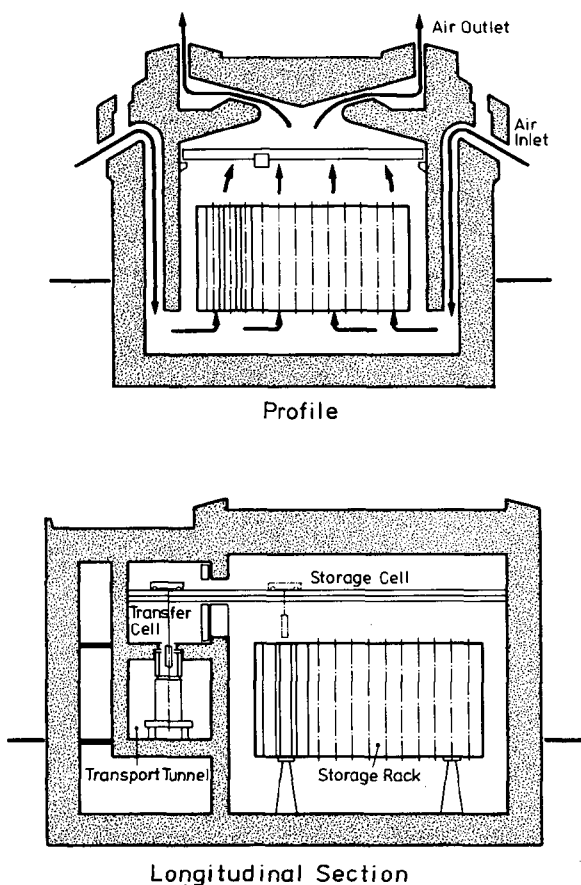


FIG.21. Air circulation in the storage facility for the FRG's National Fuel Cycle Centre.

rack. Five containers are stored in each shaft, one on top of the other. The wall temperature of the containers is about $90 - 110^{\circ}\text{C}$.

The decay heat is removed by natural convection. The ambient air enters at a height of 10 m and is distributed to the bottom of the shafts (Fig.21). In the shafts the air is warmed to about 60°C and convection currents are set up. The resulting air stream is about $350 \text{ m}^3/\text{h}$ in each shaft. The warm air is released at the top of the storage room at a height of about 15 m.

Every storage position is tested continuously to detect leaking cylinders. If a leaking cylinder is found it is welded into a second containment. All these operations are carried out remotely.

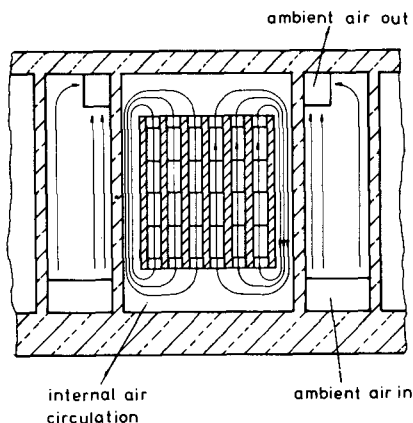


FIG.22. Gas-tight storage cell.

The building is designed to be safe against an aircraft crash. A 30-min fire in the neighbourhood of the building can reduce the convection air cooling of the gas containers. However, the temperature and pressure inside the containers will not exceed 190°C and 145 bar, respectively. The entry of kerosene from such a fire into the building can be prevented by suitable design.

6.3. THE ALTERNATIVE CONCEPT IN THE FRG

At KFA Jülich an alternative storage concept is being developed under a CEC contract [31]. The facility is designed to store the krypton-85 arising from a 1400 t per year reprocessing plant in operation for 15 years, and to store it for about 150 years. This corresponds to a maximum krypton inventory of about 163 MCi.

The krypton, in pressurized steel cylinders, is stored in a gas-tight concrete building containing six storage cells. Each shielded cell has redundant radiation monitoring and alarm systems and a slight negative pressure is maintained. The cylinders, provided with shock-absorbing mountings, are stored within the cells in vertical shafts containing four cylinders each. In case of leakage, means have been provided for identifying the leaking cylinder and transferring its remaining inventory to a new one.

A self-induced internal air circulation provides heat transport to the walls of each cell, cooled on the outside with ambient air by natural convection (Fig.22).

The pressurized steel cylinders represent the first barrier against the release of krypton to the environment and the gas-tight building represents the second barrier.

6.4. THE JAPANESE STORAGE FACILITY

An on-site engineered store is planned at the reprocessing plant of the Japanese krypton pilot plant for the noble gases from a cryogenic separation unit. It is the only plant in which xenon as well as krypton will be stored.

For krypton a building with a valve room and three storage rooms, each with a capacity of 24 cylinders, is envisaged. The estimated annual krypton arising from the pilot plant is 24 cylinders. Filling of the cylinders will be carried out in the storage room (see sub-section 5.1.4). Heat removal will be by forced air draught (see sub-section 5.1.2) leaving the building through a high chimney stack.

6.5. ACCIDENTAL RELEASES

An accident in an engineered storage facility could involve the release of krypton from one pressurized container. The resultant radiation doses will vary considerably depending upon the height of the release. For example, the release of 350 kCi at a height of 15 m under the most adverse weather conditions will give a skin dose of about 4 rem and a whole body dose of about 0.2 rem at the place of maximum radiation level outside the building.

7. TRANSPORTATION

7.1. EXISTING REGULATIONS AND RECOMMENDATIONS

Regulations for the transport of gases containing krypton-85 are given in the IAEA Regulations for the Safe Transport of Radioactive Materials [41]. These Regulations were first published in 1961 and were revised in 1964 and 1967. They were incorporated into international and national legislation. In 1973 the Regulations were revised again. These revisions will also be included in international legislation. In the case of krypton-85 the following clauses must especially be considered.

In a Type A package not more than 1000 Ci of uncompressed or 5 Ci of compressed gas may be shipped (para 109). Test conditions for Type A packages for gases are given in paras 709 to 717. They include a water spray test (para 711), a free drop test from a height of 9 m (para 716), a compression test (para 713) and a penetration test from a height of 1.7 m (paras 714, 717). The loss of the radioactive content from packages subjected to these tests is thus prevented.

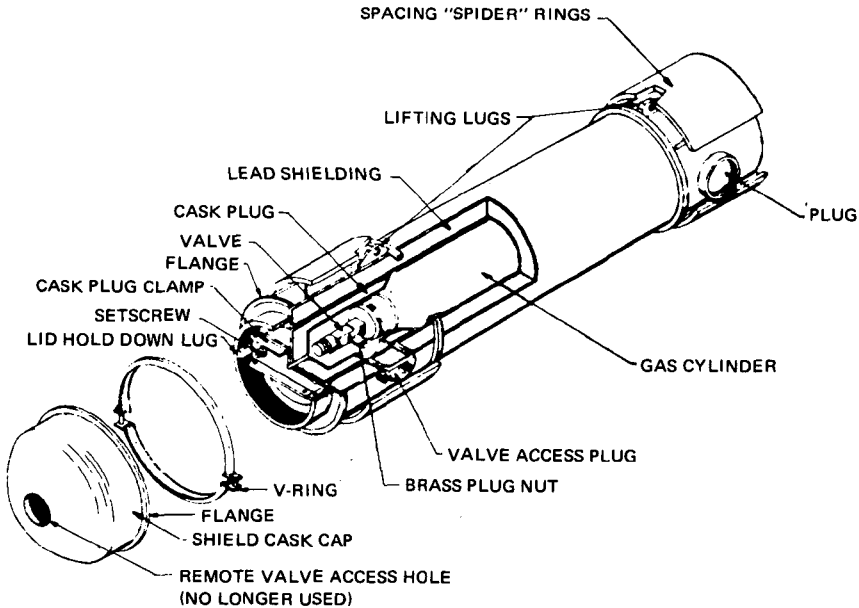


FIG.23. Schematic drawing of the ICPP shipping cask.

For shipping higher activities of krypton-85, Type B packaging is necessary. Additional test conditions are given in paras 718 to 721. They include a mechanical test, consisting of two drops on to a target (para 719), a thermal test (para 720) and a water immersion test (para 721).

After the tests given in paras 709 to 717, the loss of radioactive gas shall not exceed 1 mCi/h of krypton-85 from a Type B(M) package not designed for continuous venting, or 50 mCi/h from a Type B(M) package specially designed to allow continuous venting.

After the tests given in paras 718 to 721 the loss of krypton-85 shall not exceed 10 000 Ci/week (para 243, table IV). According to para 239 a Type B package shall not have a maximum normal operating pressure in excess of 7 kg/cm².

Pressurized gases however might be exempted because a limit of 7 kg/cm² in the case of transport from a reprocessing plant to intermediate or final storage would be very expensive.

In addition, national regulations have to be considered. In the Federal Republic of Germany, for instance, the Druckgasverordnung (Compressed Gas Ordinance) regulates the design of transportable pressure vessels, test and inspection procedures and administrative requirements for the shipping of compressed inactive gases.

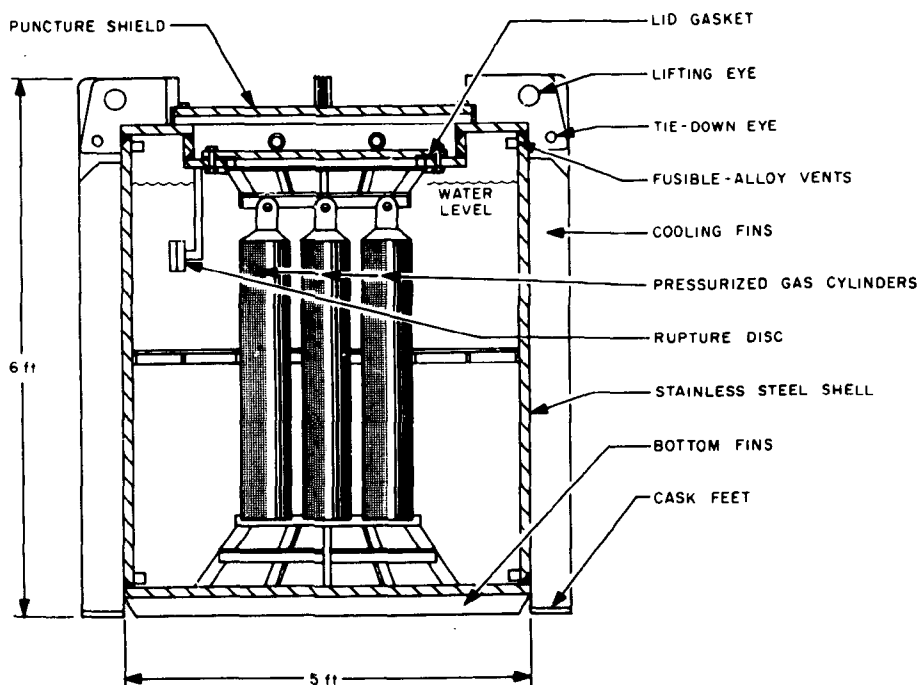


FIG.24. Conceptual design of shipping cask for cylinders of compressed fission-product gases.

7.2. SHIPPING CASKS

Krypton shipping casks are licensed in the USA and used for the transport of krypton-85 from the Idaho Chemical Processing Plant (ICPP) to the Oak Ridge National Laboratory (ORNL) [30]. A cask consists of three concentric cylinders (Fig.23).

The inner container is a compressed gas cylinder with a nominal volume of 42.5 litres. It is certified for a load of 138 atm (2015 lbf/in² (g)), however the maximum pressure allowed for krypton containing gas is 34 atm (500 lbf/in² (g)). The heat generation limit is 293 W (1000 BtU/h) which corresponds to about 170 000 Ci of krypton-85. (Erroneously given as 74 000 Ci in ICP-1077.) The cylinder is equipped with a special valve (see sub-section 5.1.4). The shielding container is a lead-filled carbon-steel shell 0.64 cm thick with 5.1 cm of lead shielding on the sides and 10.2 cm of lead on the top plug and the bottom base.

The thermal insulating container is a cylindrical end-loading unit with a 15.2 cm thick layer of high temperature phenolic foam plastic with fibreglass additive. It is designed like the protective shipping packages for 76.2 cm diameter UF₆ cylinders. During transport the temperature rises to a maximum of 177°C. In an accidental fire the temperature increase of the steel cylinder is very small.

A water-cooled shipping cask has been proposed by Blomeke and Perona [42]. The cask is a tank with a diameter of about 1.5 m, filled with water. It is made of 2.5 cm thick stainless steel and is equipped with external fins to increase heat dissipation (Fig. 24). The water provides shielding, serves as a heat transfer medium and provides the heat capacity needed to withstand a 800°C fire for 30 min. The impact and puncture resistance meet the national and international specifications. A similar shipping cask has been licensed in the USA for the transport of curium oxide.

7.3. ACCIDENTAL RELEASE

Since shipping casks must withstand normal and accident conditions as specified by the IAEA (type B container) or the AEC (AECM 0529), no release is to be expected.

8. DISPOSAL

In principle krypton-85 can be disposed of into geological formations or into the deep ocean.

8.1. DISPOSAL INTO GEOLOGICAL FORMATIONS

Two methods of disposal into suitable geological formations may be considered:

- injection of krypton gas;
- insertion of encapsulated solids.

Insertion of pressurized containers in tunnels or shafts in geological formations would generally be unacceptable, because krypton leakages would prevent access for further disposal.

8.1.1. Injection of krypton gas

Gases containing krypton have been injected into underground formations overlain by strata of low permeability at the National Test Reactor Site at Idaho [43]. However the diffusion rate, and hence the release to the atmosphere, was very high.

In the USSR, consideration is being given to the injection of the krypton from a cryogenic separation plant into water-bearing strata overlain with an impermeable layer [44]. The impermeable layer may be of clay and should form a dome-shaped roof over the water-bearing rocks. The gas will displace the water and form a gaseous cavity. Exhausted oil or natural gas lenses might be used similarly.

Matters requiring study in such concepts are the geology, seismology and hydrology of prospective disposal sites, rates of krypton release, and possible consequences of radiolytic effects in the gas-filled cavities. It is conceivable that radiolysis could in some instances produce an explosive gas mixture.

8.1.2. Insertion of encapsulated solids

Krypton in encapsulated solid form, especially in a metal matrix, would generally be comparable after disposal to other $\beta\gamma$ -active solids, but with a possibility of very slow release of radioactive gas. Studies now in progress on the disposal of $\beta\gamma$ -active solids to geological formations will therefore provide most of the data required for assessment in the krypton case, and it is considered probable that formations selected for other $\beta\gamma$ -active solids will also be acceptable for krypton-containing solids.

8.2. SEA DISPOSAL

Dumping of pressurized steel cylinders in the deep ocean has been recommended as one of the alternative methods for the final disposal of krypton-85 [45]. First calculations indicate that a significant detriment to the ecosystem by the annual dumping of 15 MCi of krypton-85 at one site is extremely improbable, although no information is available on the chemical and physical form of releases in sea water at these depths, on the subsequent movement of the krypton-85, or on the effects on the benthic organisms. The solid encapsulated forms of krypton (sub-section 5.3) are another alternative for sea dumping. No radioactive waste dumping operations so far have included krypton-85.

8.2.1. Regulations

Dumping of radioactive waste into the sea must comply with the London Dumping Convention [46]. The relevance of this Convention to the disposal of krypton-85 is discussed in the Appendix to this report. Briefly, under the provisions of the London Dumping Convention, krypton-85 can be dumped as a long-lived beta-emitter if it is in solid form, if the waste contains no more than 100 Ci/t, and if an appropriate environmental assessment has been made. The amount dumped at any site must not exceed 10^7 Ci, and will in practice be limited to a small fraction of this quantity.

Dumping in pressurized cylinders is not covered by the existing terms of the Convention, but modification of the terms at a future date should be considered. Such modification would fall within the scope of the IAEA as the international authority competent to define levels and types of waste unsuitable for ocean dumping.

In Europe the OECD/NEA is responsible for dumping operations, in accordance with IAEA guidelines. Recently the Council of the OECD formalized its administrative arrangements for sea dumping of radioactive waste [47].

8.2.2. Proposed methods

In the Federal Republic of Germany special pressurized steel cylinders with volumes of up to about 50 litres are under consideration for sea dumping of krypton. Valves which open at a predetermined depth have been proposed [45], so that the pressure is equalized. The water penetrates into the cylinder and presumably forms crystalline gas hydrates. The material used for the cylinders must be resistant to sea water.

For the dumping of these containers special shipping casks with a discharge through the bottom must be developed. Complete work on the technical concept is at an early stage.

In the Netherlands spherical containers without pressure equalization have been proposed [48] and were described in sub-section 5.1.2.

In this conceptual design the pressure vessel and the radiation shielding are both spherical and considered to be a unit. The complete unit will be dumped into the deep ocean.

A feasibility study on both concepts is in progress under a CEC contract [31], covering all management steps involved in the sea disposal.

9. CONCLUSIONS

Despite the relatively small impact of krypton-85 on man, the trapping of fission krypton from the off-gas of fuel reprocessing plants must be considered. As an adjunct to xenon delay, the retention of krypton-85 seems to be possible also in nuclear power plants. Cryogenic processes are favoured worldwide because the technology has been well proven over several decades in air liquefaction and separation plants. Relatively small modifications are required to adapt these processes to fission gas separation. Some fundamental data however are still needed for the design of a plant.

Besides the cryogenic processes, a liquid adsorption process for reprocessing off-gases and charcoal adsorption and membrane processes for reactor off-gases are under discussion.

The retained krypton can be stored in pressurized containers with air or water cooling. The containers can be kept in engineered storage facilities for an intermediate period or until the krypton-85 has decayed. Alternatively the krypton may be encapsulated in a solid.

In the future it might be advisable to dump krypton-85 in the deep ocean. However, this problem requires further investigations in the light of the London Dumping Convention.

The injection of gases containing krypton into suitable geologic strata may also be possible. The impact of accidental releases of krypton-85 from nuclear installations can be limited by technical means to an acceptable level. Special equipment for the retention of krypton-85 from accidents is not then necessary.

Much of the equipment required for the separation and storage of krypton is well known from ordinary technology, though some adaptation is often required. However there are some problems which are specific to highly concentrated fission krypton which need further R&D work. The most important items are summarized below.

For storage in pressurized containers

Study of heat transfer to outer walls, if possible by experimental simulation of the conditions.

Study of rubidium corrosion inside the containers. This should be done with rubidium itself, and should include measurements in the presence of radiation under stress conditions and as a function of oxygen concentration.

If a charcoal filling of the containers is adopted, study of heat transfer and rubidium corrosion in the presence of charcoal, and investigation of rubidium/charcoal interactions.

For encapsulation in a metal matrix

Demonstration of the implantation/sputtering process on a larger scale.
Study of leakage rates as functions of temperature, and on fracturing. Study of rubidium/metal interaction.

For encapsulation in molecular sieves

Study of conditions for encapsulation.
Study of leakage rates as functions of temperature.

APPENDIX

SOME ASPECTS OF THE LONDON DUMPING CONVENTION RELEVANT TO THE DUMPING OF KRYPTON-85 IN THE OCEAN

The major concern is with unnecessary pollution of the sea due to radioactive disposal activities, since all contracting parties believe that the marine environment and the biota it supports are vital to man and that the seas' capacity to assimilate these wastes is not unlimited. Therefore any future disposal operations of krypton-85 must comply with Annexes I–III of the London Dumping Convention.

It must first be observed that the London Dumping Convention is concerned only with solid radioactive wastes. Krypton-85 encapsulated in a solid could thus be considered for sea disposal under the Convention, but krypton-85 in pressurized containers would not be covered by the existing terms of the Convention. However, modification of the terms at a future date is a possibility, and the present Technical Committee regards this as desirable. It can certainly be argued that there is no essential difference between the two cases of encapsulation in solids and the use of pressurized containers, since the controlling feature in either case is the krypton-85 release rate.

In Annex I, according to the recent revision by the IAEA (INFCIRC 205/Add.1/Rev.1) of the definition of high-level radioactive waste, miscellaneous beta-emitters of long half-life are stated to be unsuitable for dumping at sea if the concentration exceeds 100 Ci/t. This is based on an assumed upper limit of 10^5 t/a at a single site, combined with an upper limit of 10^7 Ci/a at that site. If the concentrations are lower than those given in the definition in Annex I, then a special permit for dumping these wastes can be granted according to Annex II after careful consideration of the aspects of Annex III. This includes detailing the characteristics of the krypton-85 material as regards its form,

toxicity, dispersion and biological effects as well as characterizing the dump site for its capability to accept these packages. Sea dumping must also be weighed against possible land-based alternatives. Once this environmental assessment has been made to the appropriate State authorities a special permit may be granted to dispose of these wastes.

It must, of course, be appreciated that krypton-85 is only one of a number of long-lived beta-emitters coming forward for disposal and that, generally, only a fraction of the total activity in any one disposal operation will consist of krypton-85. Furthermore, the quantities of long-lived beta-emitters disposed of hitherto have been very much below the 10^7 Ci/a limit implied by Annex I. Realistically, the quantities of krypton-85 disposed of at any one site are only likely to constitute a small fraction of 10^7 Ci/a.

At present little information is available on the marine radio-ecology of krypton-85 and the possible impact of dumping krypton-85 either on the marine ecosystems or on man through using the marine environment.

Sites recommended for disposal of radioactive wastes have a minimum average depth of 4000 m and the design of pressure-resistant containers for krypton-85 must be in accordance with this condition. The ocean water at this depth originates from the cold polar seas, and moves generally towards equatorial zones. The direction of the flow is largely influenced by the topography of the sea bottom. Measured bottom currents are about 2 – 5 cm/s. Mixing in this region is fast, occurring by eddy currents due to friction with the bottom.

The upper layer of the ocean is well-mixed to a depth of 100 – 200 m. The direction of the surface flow is largely determined by the winds.

In between the two layers is the thermocline, a stratified layer with practically no vertical convection. The horizontal displacements here are mainly due to pressure differences and the earth's rotational forces. In the polar regions the thermocline does not exist. Near the coastal margins upwelling of water from greater depths occurs. The time required for a parcel of deep ocean water to reach the surface waters is estimated to be of the order of 100 – 1000 years.

The containers for krypton-85 disposal should have sufficient corrosion resistance; more data are needed for calculation of corrosion rates (material data and deep sea water velocities). Generally the release of krypton-85 from the corroded container will take place in a short time, compared with dispersion times. Owing to the eddy currents near the bottom of the sea the dispersion of the dissolved gas (or crystal hydrates if they are formed) is fast and a plume will travel with the deep-sea current. Mixing with water from the thermocline will be minimal. Because the half-life of krypton-85 is comparable to the travel times good knowledge of the currents is needed for the choice of the disposal site. If for example krypton-85 has a residence time of 100 years in the bottom layer, the amount of krypton-85 still present which might reach the upper layers is about one thousandth of the original amount.

A first step in the assessment study should be the calculation of krypton-85 concentrations according to existing models of the ocean currents for a release rate of 1 Ci/s at one site. The outcome of such a study will give an indication of the amount of krypton-85 acceptable for sea disposal. If dumping is continuous, a steady state will be reached between release and decay of krypton-85.

The limiting levels of krypton-85 in sea water are determined by pathways leading to radiation exposure of man, e.g. the human consumption of marine food contaminated with krypton-85. The chemical and biological inertness of krypton make it unlikely that the concentration of krypton-85 in marine organisms will greatly exceed the concentrations reached in the sea water. Accordingly a concentration factor not much greater than unity for krypton-85 in marine organisms can be used in estimating the transfer of krypton-85 to man through the consumption of marine food. Because of the known relatively high lipid solubility of krypton a slightly higher concentration factor cannot be excluded.

If there is no significant biological accumulation the dose rate from krypton-85 in marine organisms will be about equal to the dose rate in the surrounding water, which will depend on location, release rate and dispersion. It should be verified by dose estimates that populations of marine organisms are adequately protected if the limits for man are observed.

We believe that the procedure just outlined will lead to realistic estimates of prospective doses to man. However, it must be noted that the oceanographic and biological reconcentration models used by the IAEA as the basis for the definition of high-level wastes that may not be dumped, are simplified and conservative in order to ensure that the doses to man from actual dumping are less than the calculated predictions.

In the report of the advisory group on the oceanographic basis of the definition* it was recommended that both the long-term average concentration in the bottom water for the appropriate part of the ocean basin and the appropriate maximum concentration arising from short-term events should be used for all exposure pathways regardless of the depth at which these pathways actually originate. The model suggested to obtain the long-term concentration in the bottom waters is a finite, horizontally well-mixed ocean with the vertical concentration gradient determined from a simple one-dimensional diffusion calculation, using a small value for the diffusion coefficient. The maximum concentration from short-term events is obtained by assuming the release to

* The Oceanographic Basis of the IAEA Revised Definition and Recommendations concerning High-level Radioactive Waste unsuitable for Dumping at Sea. Report of an Advisory Group. An unpublished document, IAEA, Vienna, Technical Document IAEA-210, 1978.

constitute a plume which is continuously directed towards the nearest fishing ground for a period as long as 1 year; the dilution within the plume is restricted by assigning small values to the vertical and horizontal spreads. The resulting water concentrations are used as input to the biological reconcentration or other pathway models and the most restrictive value is taken for control purposes.

REFERENCES

- [1] NATIONAL COUNCIL ON RADIATION PROTECTION AND MEASUREMENTS, *Krypton-85 in Atmosphere*, NCRP Report No.44, NCRP, Washington, DC (1975).
- [2] KELLY, G.N., JONES, J.A., BRYANT, P.M., MORLEY, F., *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*, Doc. V/2676/75, Commission of the European Communities, Brussels (1975).
- [3] BOECK, W.L., *Science* **193**, No.4249 (1976)
- [4] GERMAN RADIATION SAFETY COMMISSION, *Recommendation of the Separation of Krypton-85 out of the Off-gases from Reprocessing Plants*, Bundesanzeiger, Federal Republic of Germany, No.132, 7123 (1975).
- [5] *Environmental Radiation Protection Standards for Nuclear Power Operations*, Federal Register **42**, No.9 (1977) 2860.
- [6] McILROY, R.W., GLUECKAUF, E., de NORDWALL, H.J., PUMMERY, F.C.W., "The recovery of radiokrypton from dissolver waste gases by fractional extraction into solvents", *Peaceful Uses of Atomic Energy (Proc. Int. Conf. Geneva, 1958)* **18**, UN New York, 190.
- [7] TAYLOR, R.F., WALL, G.P., *Development of a Production Process for Radiokrypton Recovery by Fractional Absorption*, UKAEA Research Group, Harwell (1956).
- [8] RAINEY, R.H., CARTER, W.L., BLUMKIN, S., FAIN, D.E., "Separation of radioactive xenon and krypton from other gases by use of permselective membranes", *Treatment of Airborne Radioactive Wastes (Proc. Symp. New York, 1968)*, IAEA, Vienna (1968) 323.
- [9] BLUMKIN, S., *Oak Ridge Gaseous Diffusion Plant, TN, Report No. K-OA-1552 (Rev.)* (1967).
- [10] SCHMAUCH, G.E., "A cryogenic system of collection of noble gases from boiling water reactor off-gas", *Symp. on Noble Gases, Las Vegas* (1973).
- [11] STUMPF, W., QUEISER, H., JÜNTGEN, H., SCHRÖTE, H.J., KNOBLAUCH, K., *Verfahren und Anlage zur Behandlung von Abgasen, die radioaktive Verunreinigungen, insbesondere Krypton und Xenonnuklide enthalten*, Deutsches Patentamt, Munich (Germany, F.R.) 23 16 831 (1975).
- [12] WILE, G., Kraftwerk Union A.G., Erlangen (Germany, F.R.), private communication.
- [13] KANAZAWA, T., SOYA, M., TANABE, H., AN, B., YUASA, Y., OHTA, M., WATANABE, A., MAGAO, H., TANI, A., MIHARADA, H., "Development of the cryogenic selective adsorption-desorption process on removal of radioactive noble gases" (*Proc. 14th ERDA Air Cleaning Conf., 1976*), CONF 760822, Energy Research and Development Administration, Washington, DC (1976) 1017.

- [14] TAKASHIMA, Y., SEGAWA, T., TSUTSUMI, K., YUSA, H., NISHIZAWA, Y., OHNO, M., "Research and development on removal of radioactive noble gases in Japan", Management of Radioactive Wastes from the Nuclear Fuel Cycle (Proc. Symp. Vienna, 1976) Vol. I, IAEA, Vienna (1976) 115.
- [15] BENDIXSEN, C.L., ROHDE, K.L., Proposed Demonstration Program for Recovery and Disposal of Fission Product Krypton and Xenon at the Idaho Chemical Processing Plant, Allied Chemical Corp., Idaho Falls, ID, Rep. ACI-119 (1972).
- [16] BEAUJEAN, H.W., ENGELHARDT, G., ISRAEL, G., TILLESSEN, U., "AZUR – Eine Anlage zur Reinigung von Auflöserabgas der WAK", Radioactive Effluents from Nuclear Fuel Reprocessing Plants, CEC/GRS/KPK Seminar, Karlsruhe (1977).
- [17] KON, T., MOTOYAMA, S., "Recovery and storage of radioactive noble gases from the off-gas of fuel reprocessing plant in Japan", Removal, Storage and Disposal of Gaseous Radionuclides from Airborne Effluents (Proc. Techn. Comm. Vienna, 1976), IAEA, Vienna (1976).
- [18] BROOTHAERST, J., COLLARD, G., BRUGGEMANN, A., GOOSSENS, W.R.A., BAETSLE, L.H., "Treatment and control of gaseous effluents from light water reactors and reprocessing plants", Management of Radioactive Wastes from the Nuclear Fuel Cycle (Proc. Symp. Vienna, 1976), IAEA, Vienna (1976).
- [19] CHESNE, A., KROEBEL, R., LE BOUHELLEC, J., MIGUEL, P., SCHNEIDER, E., "Progrès réalisés dans les domaines intéressant le traitement des effluents gazeux des usines de retraitement", Management of Radioactive Wastes from the Nuclear Fuel Cycle (Proc. Symp. Vienna, 1976), IAEA, Vienna (1976).
- [20] BOHNENSTINGL, J., HEIDENDAEL, M., LASER, M., MASTERA, St., MERZ, E., "Cryogenic separation of krypton and xenon from dissolver off-gas", Management of Radioactive Wastes from the Nuclear Fuel Cycle (Proc. Symp. Vienna, 1976), IAEA, Vienna (1976).
- [21] DAVIS, J.S., MARTIN, J.R., "A cryogenic approach to fuel reprocessing gaseous radwaste treatment", Symp. on Noble Gases, Las Vegas (1973).
- [22] MERRIMAN, J.R., STEPHENSON, M.J., DUNTHORN, D.I., PASHLEY, J.H., "Removal of krypton-85 from reprocessing plant off-gases by selective absorption" (Paper given at Symp. on Management of Radioactive Wastes from Fuel Reprocessing, OECD/IAEA 1972), Oak Ridge Gaseous Diffusion Plant, TN, Report No. K-L-6201 (1972).
- [23] KHAN, A.A., et al., Krypton-85 Enrichment by Adsorption Desorption Process, Bhabha Atomic Research Centre, Bombay, Report No. BARC-879 (1975).
- [24] NAKHUTIN, I.E., OTCHKIN, D.V., "Removal, storage and disposal of krypton-85 arising from nuclear plants", Removal, Storage and Disposal of Kr-85 (Proc. Techn. Comm. Vienna, 1978), IAEA, Vienna (1978).
- [25] SCARGILL, D., "United Kingdom studies on the arising behaviour and control of the gaseous radionuclides tritium, krypton-85 and iodine-129", Storage and Disposal of Gaseous Radionuclides from Airborne Effluents (Proc. Techn. Comm. Vienna, 1976), IAEA, Vienna (1976).
- [26] LASER, M., BARNERT-WIEMER, H., BEAUJEAN, H., MERZ, E., VYGEN, H., "AKUT – A process for the separation of aerosols, krypton and tritium from burner off-gas in HTR fuel reprocessing" (Proc. 13th AEC Air Cleaning Conf. 1974), USAEC Technical Information Center, Oak Ridge, TN, CONF-740 807 (1974) 246.
- [27] GLASS, R.W., BEAUJEAN, H.W.R., COCHRAN, H.D., Jr., HAAS, P.A., LEVINS, D.M., WOODS, W.M., "Development of the krypton absorption in liquid carbon dioxide (KALC) process for HTGR off-gas reprocessing" (Proc. 13th AEC Air Cleaning Conf. 1974), USEAC Technical Information Center, Oak Ridge, TN, CONF-740 807 (1974) 232.

- [28] TAKASHIMA, Y., SEGAWA, T., TSUTSUMI, K., YUSA, H., NISHIZAWA, Y., OHNO, M., "Research and development on removal of radioactive noble gases in Japan", Management of Radioactive Wastes from the Nuclear Fuel Cycle (Proc. Symp. Vienna, 1976) Vol.I, IAEA, Vienna (1976) 115.
- [29] AMMON, R. von, HUTTER, E., LEICHSENRING, C.H., WEINLÄNDER, W., "Auslegung der Tieftemperatur-Rektifikationsanlage KRETA, einschließlich der Vorreinigungsanlagen ADAMO und REDUKTION und erste Betriebserfahrungen", Radioactive Effluents from Nuclear Fuel Reprocessing Plants, CEC/GRS/KPK Seminar, Karlsruhe (1977).
- [30] NIELSEN, C.W., Safety Analysis Report for Packaging Krypton Shipping Container, Allied Chemical Corp., Idaho Falls, ID, Report No. ICP-1077 (1975).
- [31] COMMISSION OF THE EUROPEAN COMMUNITIES, R and D Programme on Radioactive Waste Management and Storage, Commission of the European Communities, Brussels, EUR 6128EN (1978).
- [32] WHITMELL, D.S., NELSON, R.S., WILLIAMSON, R., SMITH, M.S., UKAEA Research Group, Harwell, Report No. AERE-R 9314 (1979).
- [33] ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION, Washington, DC, Report No. ERDA-76-43 (1976) 14.3-14.7.
- [34] CLARK, W.E., BLANCO, R.E., Encapsulation of Noble Fission Product Gases in Solid Media Prior to Transportation and Storage, Oak Ridge National Lab., TN, Report No. ORNL-4473 (1970).
- [35] JORRIS, M.H., et al., Study of Dispersion of Gases in Viscous Liquids, Oak Ridge National Lab., TN, Report Nos. ORNL-MIT-81, ORNL-MIT-84.
- [36] BEZMELNIN, V.N., LEGASOV, Y.A., MARININ, A.S., Yadrena Energiya, Moscow, Report No. YAE-2854 (1977) 17.
- [37] STAPLES, B.A., PENCE, D.T., Allied Chemical Corp., Idaho Falls, ID, Report No. ICP-1045 (1974).
- [38] FOSTER, B.A., PENCE, D.T., STAPLES, B.A., (Proc. 13th AEC Air Cleaning Conf., San Francisco, 1974), USAEC Technical Information Center, Oak Ridge, TN, CONF-740 807 (1974) 293.
- [39] BROWN, R.A., KNECHT, D.A., THOMAS, T.R., Allied Chemical Corp., Idaho Falls, ID, Report No. ICP-1126 (1978).
- [40] NUKLEAR-CHEMIE UND -METALLURGIE GmbH, Sicherstellungslager für Krypton-Druckgasflaschen, NUKEM Report No. 8.095.
- [41] INTERNATIONAL ATOMIC ENERGY AGENCY, Regulations for the Safe Transport of Radioactive Materials, Safety Series No. 6 - STI/PUB-323, IAEA, Vienna (1973).
- [42] BLOMEKE, J.O., PERONA, J.J., Management of Noble Gas Fission Product Wastes from Reprocessing Spent Fuels, Oak Ridge National Lab., TN, Report No. ORNL-TM-2677.
- [43] SCHMALTZ, B.L., Injection of Gas into the Lithosphere at the NRTS, USAEC Idaho Operations Office, Idaho Falls, ID, Report No. IDO-12069 (1969).
- [44] YUDIN, F.P., PIMENOV, M.K., "Disposal of gaseous radioactive wastes in the ground", Waste Management Research Abstracts No.5, IAEA, Vienna (1970), HSW-3, 23-25.
- [45] LASER, M., BEAUJEAN, H., BOHNENSTINGL, J., FILB, P., HEIDENDAEL, M., MASTERA, St., MERZ, E., VYGEN, H., "Off-gas treatment and krypton disposal in HTGR-fuel element reprocessing" (Paper given at Symp. on Management of Radioactive Wastes from Fuel Reprocessing, OECD/IAEA, Paris, 1972).
- [46] Convention on the Prevention of Marine Pollution by Dumping of Wastes and other Matter (drawn up at the Intergovernmental Conference on the Dumping of Wastes at Sea, London, 1972).

- [47] Decision of the OECD-Council establishing a multilateral consultation and surveillance mechanism for sea dumping of radioactive waste (adopted by the Council of the OECD at its 449th meeting, 22 July 1977).
- [48] Verkerk, B., 1st Annual R&D programme proposed for funding by the CEC (1977).

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