SESSION V

NOBLE GASES (2)

Tuesday, August 13, 1974
CHAIRMAN: Neill Thomasson

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OPENING REMARKS OF SESSION CHAIRMAN:

I wish to welcome you to the second session on noble gases. The papers in the previous session were on noble gas collection and control systems. Two of the three papers in this section direct your attention to solving the problems associated with long-term storage of krypton-85 which has been collected from the waste gas processing systems. Or, to put it another way, now that we have collected krypton-85, what do we do with it considering safety, personnel exposures, cost, and environmental considerations, which must be balanced for an optimum solution?

It is encouraging to note that papers are to be presented dealing with storage methodology. Possibly these papers will stimulate additional interest in the research community and industry so that additional effort will be directed toward producing a technology for safe and economical storage of krypton-85. Otherwise, safety and occupational exposure problems may outweigh the environmental benefits gained through long environmental storage. The first paper has been prepared by Dr. M.M. Ćirić, Dr. Cvjeticanin and Dr. Radak, all of whom are researchers at the Boris Kidric Institute in Belgrade, Yugoslavia. This work, as well as that of the other Yugoslavs on the agenda, has been sponsored by the Environmental Protection Agency under its special foreign currency program. Dr. Ćirić could not be with us, so I will briefly summarize his paper and if there are questions, I think the best thing to do is submit them to Dr. First, who will forward them to the Yugoslavs who should be able to answer them.

RETENTION OF KRYPTON ON POLYMETHYL METHACRYLATE +

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Abstract

Retention of krypton on polymethyl methacrylate was studied as a function of kryptonation pressure (P), temperature (T) and time (t). It was found that the dependence of the retained quantity on P, T, and t is in accordance with the diffusion theory. The optimum results, i.e. the maximum retained quantity and the best stability of the kryptonate, were obtained at elevated kryptonation temperatures (200°C). The diffusion coefficients of krypton in polymethyl methacrylate, determined from the dekryptonation process, vary from 1×10^{-10} cm^{2}s^{-1} to 0.2×10^{-10} cm^{2}s^{-1} for samples kryptonated at 20°C and 200°C respectively.

The results have been discussed from the viewpoint of radiation and thermal stability of kryptonated polymethyl methacrylate. Inadequate radiation stability could be the main obstacle for practical purposes.

I. Introduction

Incorporation of the inert gas krypton into different materials is usually called kryptonation, and such materials, containing krypton, more or less stably incorporated, are called kryptonates. Up to the present more than 120 different substances have been kryptonated. These include elements, inorganic compounds, alloys, glasses, rubbers, plastics, and proteins.

Two general methods for preparation of kryptonates have been developed. The first one is the ion bombardment method. The krypton atoms are ionized in the discharge tube and impelled into a solid under the influence of a potential drop in the kilovolt range. The second method is of the diffusion type. The sample is placed in contact with the krypton gas at elevated pressure and temperature. The gas will diffuse into the sample in accordance with classical diffusion theory.

The diffusion method has some advantages in comparison to the ion bombardment method. There is no restriction in the choice of substances to be kryptonated, while the ion bombardment method is restricted to conductors. Also, the depth of penetration, and consequently the amount of gas collected by the sample is larger for the diffusion method.

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Kryptonates prepared by either of these two methods can be applied for various purposes, e.g., as suitable radiation sources, analytical purposes etc. Another potential application would be to store ^{85}Kr released in reactor fuel reprocessing or during normal reactor operation as a kryptonate. This problem, i.e. safe storage of ^{85}Kr is becoming more and more urgent, particularly at fuel reprocessing plants, where thousands of curies of ^{85}Kr are released during reprocessing of one ton of uranium fuel. Furthermore, pressurized water reactors (PWR) are now being designed to enable recycle and/or retention of reactor fission gases, in order to minimize the release of radioactivity to the environment. Whether the gases are recycled and stored in pressurized tanks or collected and concentrated cryogenically, the inplant radiation exposure problems and the potential for an accidental release of ^{85}Kr are increased. Kryptonation would reduse the hazards of long-term storage of ^{85}Kr at fuel reprocessing plants and reactors, and also the short-term inplant radiation exposure problems due to leakage of ^{85}Kr from pressurized storage tanks.

Since the problem of kryptonation has been considered from this viewpoint, the diffusion method was selected for use in our experiments. In choosing the material to be kryptonated, the results of previous investigations (1 - 4) were utilized. Another criterion was that the substance also should be amenable for experiments on a larger scale. Also, it ought to be an easily available inexpensive commercial product, suitable for transpcrtation, storage, etc. A synthetic organic polymer could perhaps fulfill these requirements, if the diffusion cahracteristics, radiation and thermal stability of its kryptonate were satisfactory.

Previous experiments with kryptonated organic polymers have been undertaken by Schäfer and Maywald (1) and Trofimov et al. (2), among others. The first authors investigated polyethylene, polystyrene, 2,6- and 2,9- acetyl cellulose, polyamid, polyvinyl chloride, polyetylene terephthalate, polycarbonate and epoxy resins. None of the obtained kryptonates was sufficiently stable, as the diffusion coefficient (D) of krypton in these materials varied from 5×10^{-8} to 1×10^{-10} cm^{2}s^{-1}, while for sufficient stability D should have the order of magnitude of 10^{-12} cm^{2}s^{-1}. Trofimov et al. (2) also investigated various polymers such as polymethyl methacrylate, polyvinyl acetate, polystyrene and teflon. The best results were obtained with polymethyl methacrylate, which exhibited a release rate of 50 % of the collected krypton in approximately 50 days.

However, this polymer was investigated only at one pressure and temperature, i.e., 1.6 atmospheres (atm) and 160°C, with kryptonation times of 1 and 2 hours. Therefore, our intention was to begin at this point, with thorough investigations of the influence of pressure (P), temperature (T), and time (t) on the kryptonation of polymethyl methacrylate.

II. Experimental

Material

Stable krypton (purity 99.9 %) was purchased from VEB Technische Gase Leipzig, Betrieb Berlin. The ^{85}Kr was purchased from the Radiochemical Centre, Amersham, England. One ampulla of ^{85}Kr, containing 3 ml gas, 250 mCi, was diluted with one large ampulla of stable krypton, containing 2 liters of gas at 500 torr.

Polymethyl methacrylate samples were prepared from the commercial product. Samples were in the form of disks, 2 cm diameter, 2 mm thick.

Apparatus

Counting Equipment. The activity of the kryptonated samples was measured on a NE 102 A Plastic Scintillator Detector. The counter efficiency (13 %) was determined by measurements of a known amount of a ^{204}Tl (0.762 MeV max. beta energy) standard solution on a 4π proportional counter and NE 102 A Plastic Scintillator counter. The Tl samples measured on the NE 102 A detector were prepared on the same material (polymethyl methacrylate disks) which was used in the kryptonation experiments.

Test Apparatus. The test apparatus consisted of two parts. The basic part was a universal apparatus for handling of gas samples at pressures up to 1 atm. It was made of Pyrex glass, with vacuum tested stopcocks (Figure 1). A rotary pump and mercury diffusion pump were used to evacuate the apparatus to the pressure of $3 - 5 \times 10^{-4}$ torr. The pressure was measured by Pirani vacuum gauge.

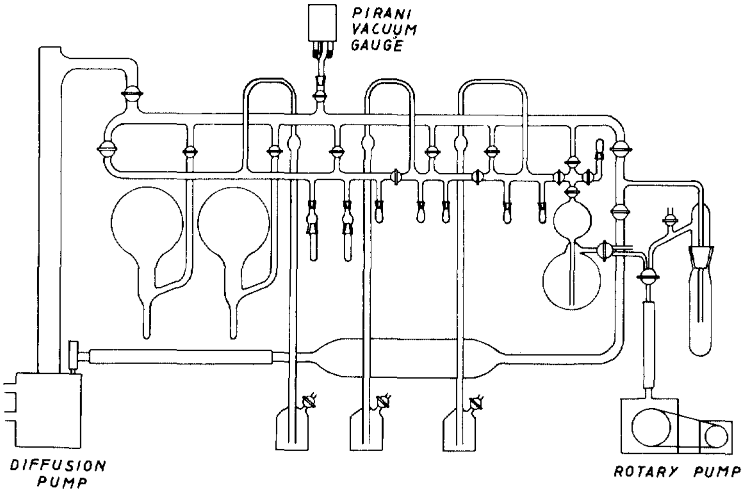

Figure 1. Basic part of the test apparatus.

For work at elevated pressures, an additional part was attached to the apparatus, which consisted of a metal ampulla (approximately 200 ml volume) for condensation of krypton, two pressure vessels for experiments at room and elevated temperatures, and a manometer for pressures up to 12 atm. One valve was used for separation of this part from the glass apparatus, and two other valves were between the ampulla and pressure vessels (Figure 2).

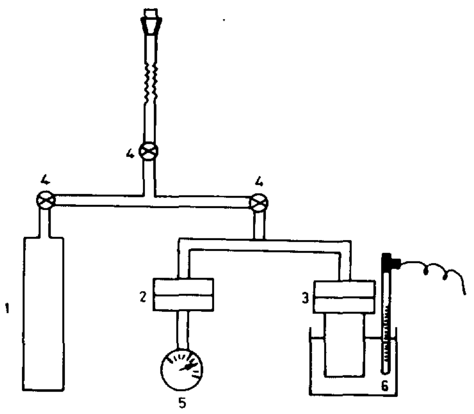

Figure 2. Arrangement pf the additional part of the test apparatus for experiments at elevated pressures and temperatures: 1. Metal ampulla, 2. and 3. pressure vessels for room and elevated temperatures, 4. valves, 5. manometer, 6. oil bath.

Procedure

The samples were placed into the pressure vessels. The whole high-pressure part was evacuated to 5×10^{-4} torr and the temperature of one pressure vessel was elevated by an oil bath. Then the krypton was condensed from the 2 liter flask (in the basic part of the apparatus) into the metal ampulla by cooling with liquid nitrogen. The whole high-pressure part was then separated from the glass part, the ampulla heated to the room temperature, and the gas released into the pressure vessels, where the pressure was adjusted to a defined value. After some time had elapsed, krypton was again condensed in the metal ampulla, the valves were closed and polymethyl methacrylate samples taken from the pressure vessels. The activity of samples was measured at regular time intervals.

III. Results and Discussion

The first series of experiments was performed at room temperature (20°C). The kryptonation time was 2 hours, and the pressure of krypton varied from 0.53 to 7 atm. Dekryptonation of these samples as a function of time is presented in the Figure 3.

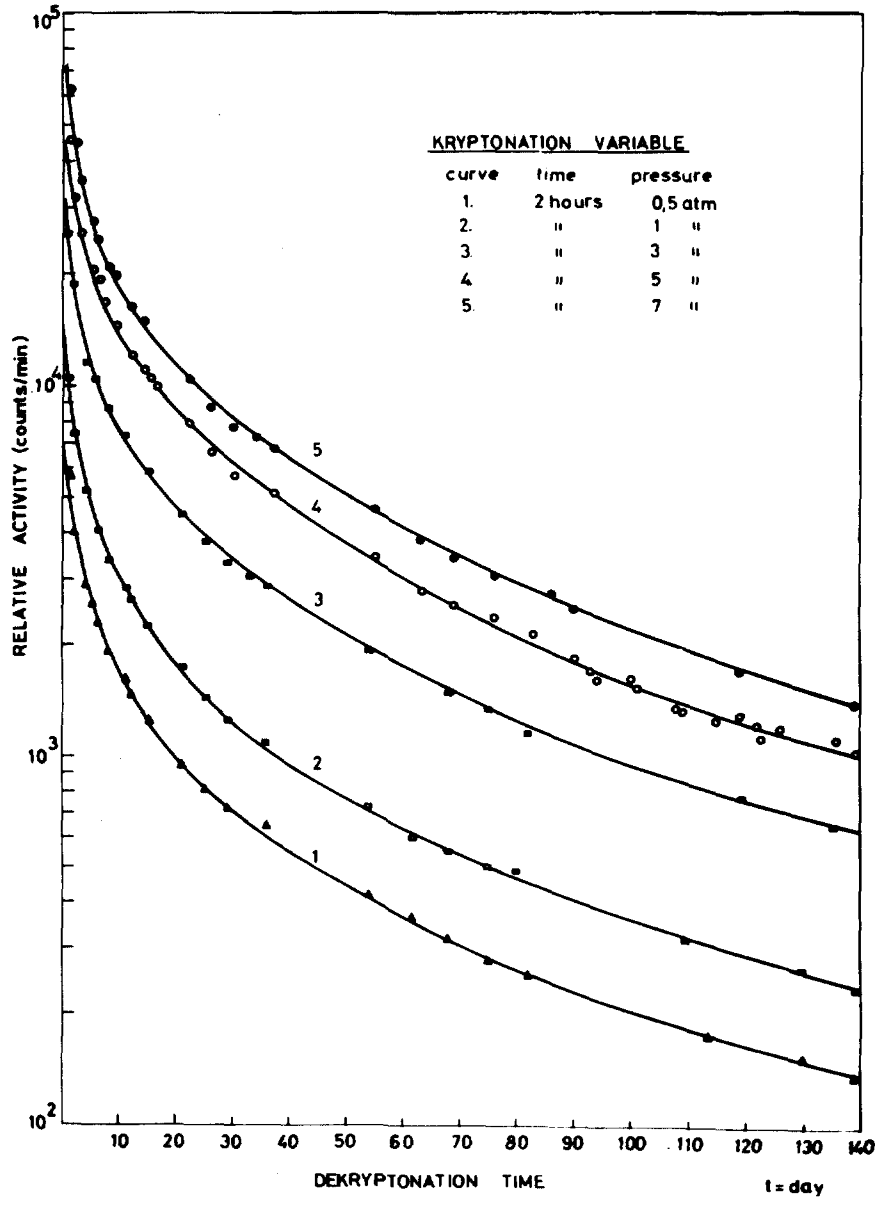

Figure 3. Dekryptonation of samples as a function of time.

These results are in accordance with previous experience in kryptonation of graphite(3). The curves indicate the presence of two different processes during kryptonation: surface adsorption characterized by rapid dekryptonation, and diffusion into the depth of the sample, characterized by slower release of krypton. The quantity of krypton diffused into the sample during kryptonation can be estimated by extrapolation to the ordinate. In these experiments it was ≤ 0.3 µg per cm^2 of sample surface.

These results can be replotted as in Figure 4 where the relative activity of the samples is presented as the function of kryptonation pressure. From this plot, it can be seen that the quantity of krypton collected by the polymethyl methacrylate samples depends linearly on the pressure, in accordance with previous experience. The linear dependence in the adsorption part of the curves should also be emphasized. This indicates that the covering of the surface was far from saturation in the pressure range investigated.

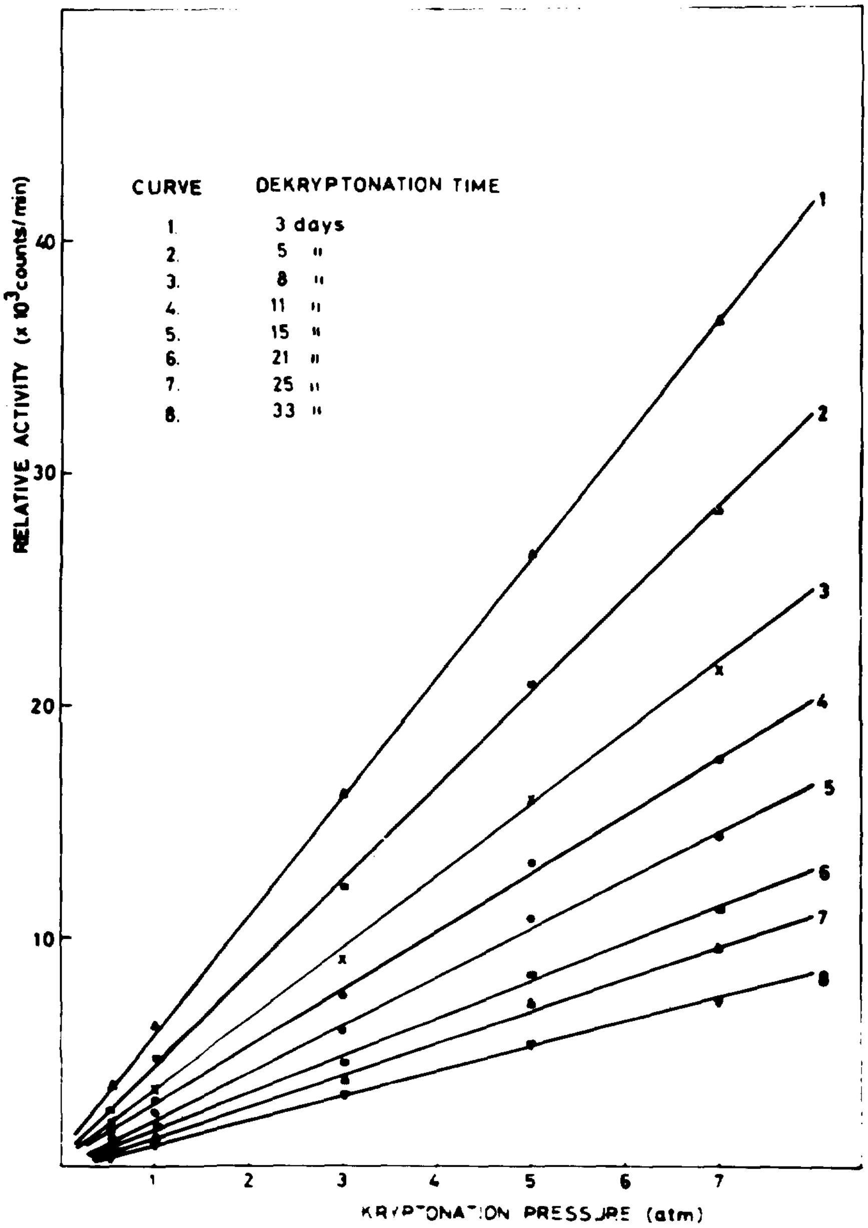

Figure 4. Relative activity of samples as a function of kryptonation pressure. Kryptonation time 2 hours.

In the next series of experiments the pressure was held constant (7 atm), while the kryptonation time was varied from 1 to 48 hours. The release of krypton from these samples was followed for 160 days, as presented in the Figure 5.

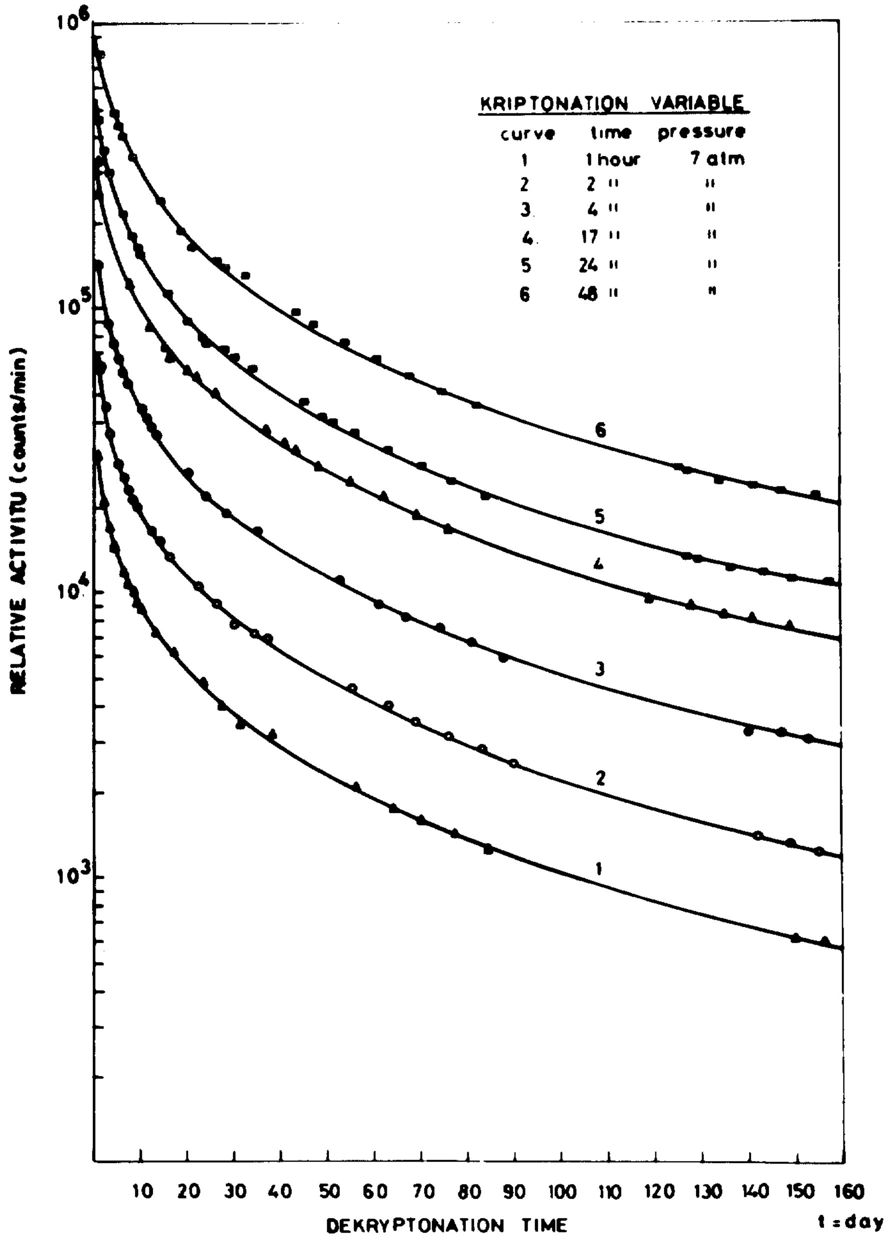

Figure 5. Dekryptonation of samples as a function of time.

The quantity of krypton diffused into the sample in these experiments varied from ~0.12 μg per cm^2 for 1 hour to ~5.4 μg per cm^2 for 48 hours.

These results, replotted as the dependence of the relative activity of samples on the kryptonation time (as $\sqrt{t}$ hours) are presented in the Figure 6. The linear dependence of the diffused-in quantity of krypton on $\sqrt{t}$ (except for t = 48 hours) can be observed.

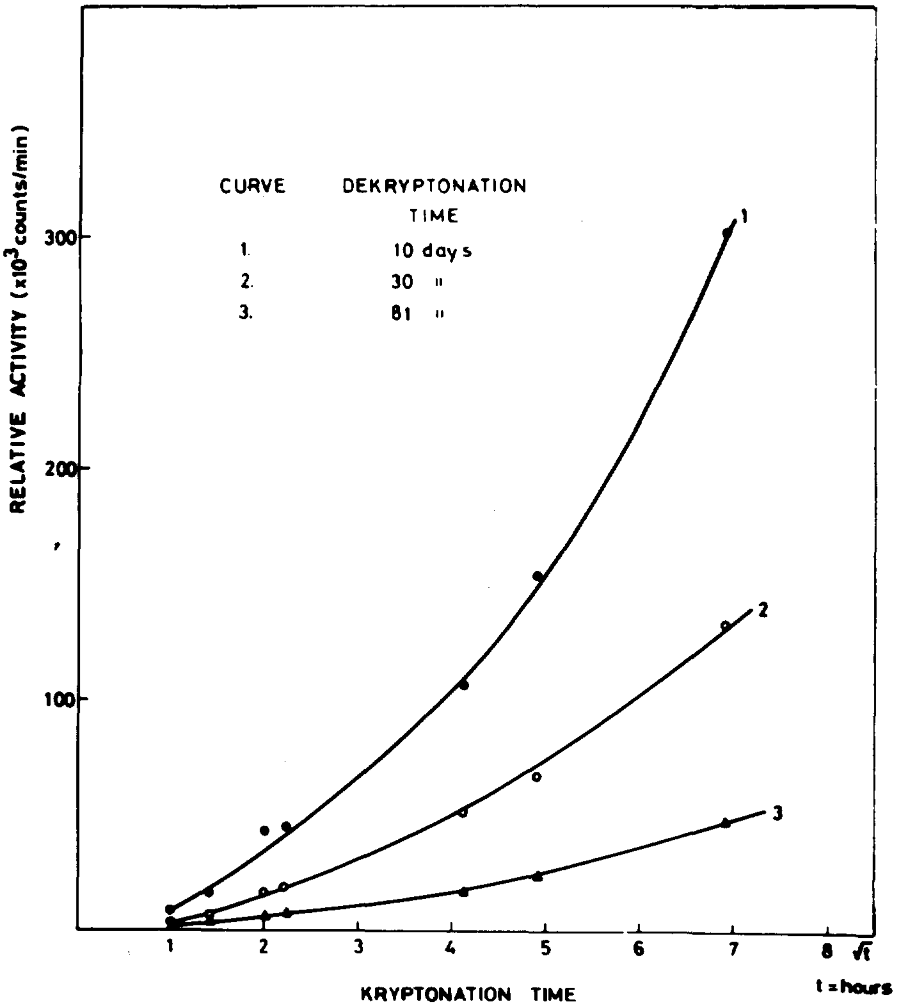

Figure 6. Relative activity of samples as a function of kryptonation time. Krypton pressure 7 atm.

In the last series of experiments the effect of temperature was investigated. The pressure was 5 atm. and the kryptonation time was 2 hours.

The exponential dependence of the diffused-in quantity of krypton on kryptonation temperature is observed in the Figure 7.

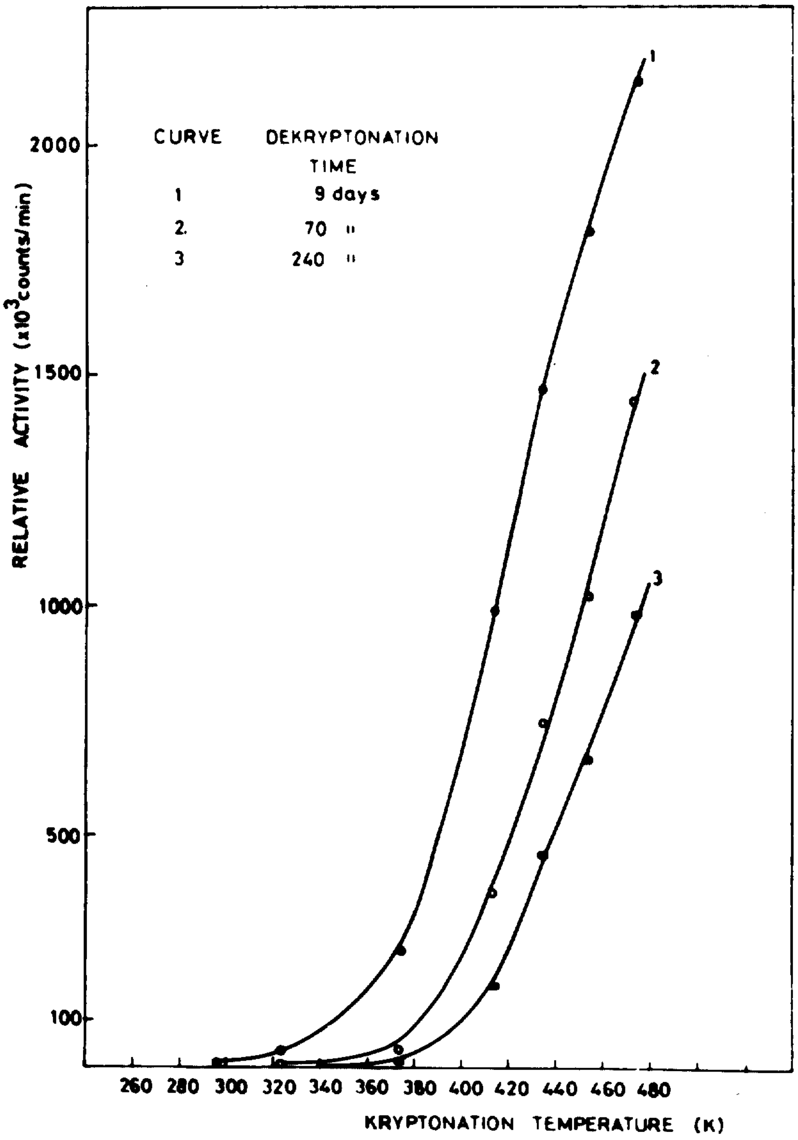

Figure 7. Relative activity of polymethyl methacrylate samples as a function of kryptonation temperature.

Slower release of krypton from samples kryptonated at elevated temperatures can be observed in the Figure 8.

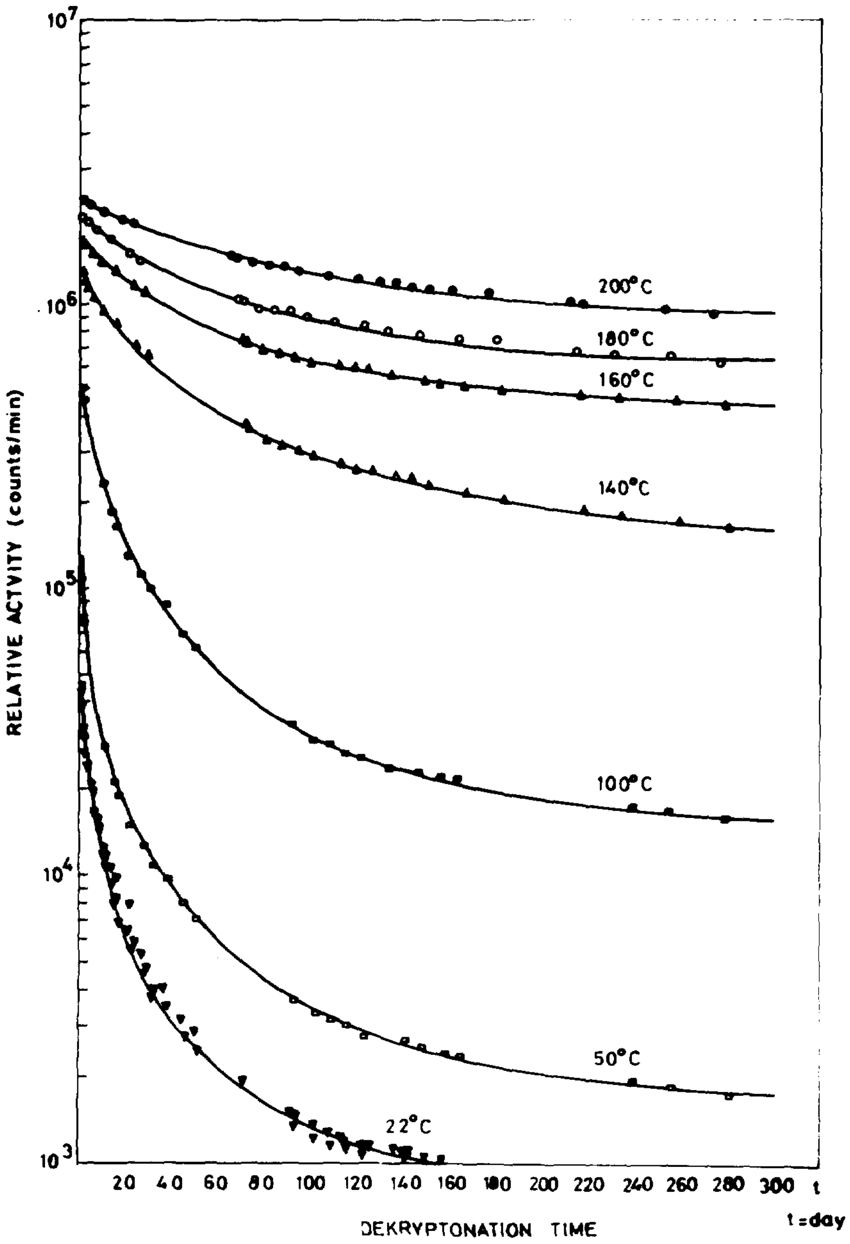

Figure 8. Dekryptonation of samples kryptonated at different temperatures as a function of time.

The amount of krypton diffused into the sample varied in these experiments from ~ 0.25 µg per cm^2 at 20°C to ~ 38 µg per cm^2 at 200°C.

Determination of the Diffusion Coefficient

In order to determine the diffusion coefficient of krypton in polymethyl methacrylate the equation (1) can be applied (5) :

$$\frac{\bar{c}}{c_i} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-2(n+1)^2 \frac{\pi^2 D t}{h^2}\right] \qquad (1)$$

where

$\bar{c}$ = average concentration of the diffused-in gas in the sample at the time t

c_i = initial concentration of the diffused-in gas in the sample

D = diffusion coefficient ($cm^2 s^{-1}$)

t = dekryptonation time

h = halfthickness of the sample (cm)

For sufficiently large t, this equation can be approximated to a form suitable for practical purposes:

$$\log_{10} \frac{\bar{c}}{c_i} = \log_{10} \frac{8}{\pi^2} - \frac{\pi^2 D t}{2.303\, h^2} \qquad (2)$$

The diffusion coefficient can now be determined from the dependence of $\log_{10}(\bar{c}/c_i)$ on t, i.e. by plotting $\bar{c}/c_i$ as a function of t on a semi-logarithmic paper.

From the dekryptonation curves presented in the Figure 3 and Figure 5 it can be seen that $\bar{c}/c_i$ is 0.5 after approximately 54 ± 1 days. Since h = 1 mm, it follows from the equation (2) that $D = 1.05 \pm 0.02 \times 10^{-10}\ cm^2 s^{-1}$.

However, the samples kryptonated at elevated temperatures exhibit much larger dekryptonation half-times (up to 300 days) (Figure 8). Accordingly, the corresponding D values are lower (Table I).

Table I. The effect of kryptonation temperature on the diffusion coefficient of krypton in polymethyl methacrylate.

Kryptonation Temperature K	Diffusion Coefficient (10^{-10} cm^2s^{-1})
293	1.05
298	0.92
323	0.39
373	0.32
413	0.27
433	0.23
453	0.21
473	0.19

Obviously, kryptonation at elevated temperatures has two positive effects: the quantity of collected krypton is increased and the stability of the kryptonate is improved. The value of D obtained at 200°C could probably match the requirements for interim storage and transport purposes.

An explanation of the improved stability could be that the pores in the polymethyl methacrylate expand at elevated temperatures, thus admitting gas molecules larger than those which are normally allowed to pass. When the sample is cooled to room temperature, the gas (or a portion of it) will be physically entrapped within the sample.

Polymerization of the methyl methacrylate monomer in the presence of krypton could also be investigated in further experiments, in order to obtain homogeneously kryptonated samples, containing larger amounts of krypton. Slower dekryptonation, i.e. better stability of these samples in comparison to those kryptonated at 200°C might also be expected.

However, the question of radiation and thermal stability of kryptonated polymethyl methacrylate samples should also be considered prior to any recommendation of this material for practical purposes.

IV. Considerations on the Radiation and Thermal Stability of Kryptonated Polymethyl Methacrylate and Epoxy Resins

Basic Data and Assumptions

In the subsequent paragraphs the radiation and thermal stability of polymethyl methacrylate and epoxy resins are considered, assuming a concentration of 1:1 by volume of carrier-free radioactive krypton in these materials.

Radioactive Krypton: gas, carrier free ^{85}Kr, beta emitter, mean value of beta energy $\bar{E}_\beta = 0.236$ MeV per disintegration, half-life 10.76 years.

Polymethyl Methacrylate: density 1.18 to 1.20, thermal conductivity between 1×10^{-4} and 10×10^{-4} cal $cm^{-1}s^{-1}deg^{-1}$ *, emissivity between 0.88 and 0.92 (6). Critical absorbed dose is assumed to be 50 Mrad, although less significant changes occur at about 10 Mrad. At 100 Mrad embrittlement is considerable and the molecular chains are broken to a very high extent, with fissures gradually developing (7). Gaseous products from the samples irradiated in air and then heated above 100°C are (in micromoles per gram per Mrad):

Hydrogen	1
Carbon Dioxide	2.5
Monomer	23
Benzene	35

Below 70°C no bubbling or foaming has been observed, whatever large the radiation exposure. The formation of gaseous products is therefore neglected in the present study and only the absorbed dose and thermal effects are considered.

Epoxy Resin. Araldit AV 121, the Ciba-Geigy (Switzerland) product is taken as a model. This compound is based on diphenyl propane and epichlorhydrine; its density is about 1.7 and the thermal conductivity varies between 1.6×10^{-3} and 2.0×10^{-3} cal $cm^{-1}s^{-1}deg^{-1}$. Emissivity is very high and can be taken as unity. The compounds of this type are highly resistive to radiation damage. The main change produced by radiation in epoxy resins is the increase of the cross-linking degree (7) which can be favourable for the given purpose. A critical absorbed dose of about 10^{10} rad can be assumed (8).

Absorbed Doses and Dose Rates, Considerations on a Model.

Radioactivity of 1 cm^3 of ^{85}Kr at 1 atmosphere and the ambient temperature of 300 K is obtained from the relation

$$A = \frac{0.693}{t_{1/2}} n_o$$

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* Considerations on the thermal effects are expressed in callories since the existing thermal data are tabulated in these units.

Since $n_o = 2.44 \times 10^{19}$ atoms per cm^3 at 300 K and 1 atm., and $t_{1/2} = 10.7$ years,

$$A = 1.35 \text{ Ci cm}^{-3} \quad \text{or } 5.0 \times 10^{10} \text{ dps}$$

The rate of radiation energy generation from this activity amounts to $dE/dT = \bar{E}_\beta A = 6.8$ Joule h^{-1} (or 1.63 cal h^{-1}) per 1 cm^3 of ^{85}Kr

If one liter block, kryptonated to a concentration of 1:1 by volume is considered, the heating rate for the whole liter will be 0.453 cal $s^{-1}l^{-1}$.

Assume one liter block to be a cylinder of 6 cm diameter and 36 cm long, homogeneously heated by the incorporated radioactive gas. Consider the block to be suspended in a barrel of 40 cm dia and 1 m high. The temperature distribution of a homogeneously heated "infinite" cylinder (condition is satisfied since 3 cm $\ll$ 36 cm) is given by the relation (8)

$$T_r = T_o + \frac{W}{2R\pi H \sum h_i} + \frac{W}{4\pi H \lambda}(1 - r^2/R^2) \qquad (3)$$

where T_r is the temperature at a distance r from the axis, T_o is the temperature of the ambient (wall of the barrel), W energy dissipation rate, R radius of the cylinder (3 cm), H length of the cylinder (36 cm), $\sum h_i$ sum of the heat transfer coefficients, λ_m heat conductivity of the cylinder material.

In order to calculate h_i only the heat conduction (h_c) and radiation (h_r) coefficients are considered. Convection, which can be considerable, depending on geometry and temperature differences, is taken as safety excess of cooling.

Heat conduction coefficient, h_c is obtained from the relation

$$h_c = \frac{\lambda_{air}}{\ln(1 + d/R)} \qquad (4)$$

This is an approximation for a cylinder suspended in a fluid (10,11). λ_{air} is the heat conductivity of air (8.3×10^{-5} cal $cm^{-1}s^{-1}deg^{-1}$), d is the distance to the wall of the barrel (about 20 cm), R as in the equation (3). It follows

$$h_c = 4.07 \times 10^{-5} \text{ cal cm}^{-2}\text{s}^{-1}\text{deg}^{-1}$$

Radiation heat transfer coefficient is

$$h_r = \sigma F \frac{(T^4 - T_o^4)}{T - T_o} \qquad (5)$$

where σ is the Stefan's constant (1.38×10^{-12} cal $cm^{-2}s^{-1}deg^{-1}$), T and T_o the temperatures of the cylinder surface and the barrel, respectively. Since the surface area of the barrel is much larger than that of the cylinder, and since the emissivities of polymethyl methacrylate, Araldit, and rough metal approach unity, F can be taken as unity (10). For temperatures around 300 K the value of h_r is calculated to be

$$h_r = 1.6 \times 10^{-4} \text{ cal cm}^{-2}\text{s}^{-1}\text{deg}^{-1}$$

Therefore the value of $\sum h_i$ is estimated as

$$\sum h_i = 2 \times 10^{-4} \text{ cal cm}^{-2}\text{s}^{-1}\text{deg}^{-1}$$

Polymethyl methacrylate. From equation (3), using the above mentioned heating rate and other values derived or previously mentioned in the text, the temperature difference between the surface of the cylinder and the barrel is calculated as $\Delta T_s = 3.5^{\circ}C$. The temperature along the cylinder axis relative to the barrel temperature, ΔT_a amounts to $13.5^{\circ}C$ for the minimum thermal conductivity of polymethyl methacrylate assumed (1×10^{-4} cal $cm^{-1}s^{-1}deg^{-1}$).

Based on the total rate of energy output of 6.8 Joule h^{-1} cm^{-3} and the density of 1.2, the dose rate is 0.56 Mrad h^{-1}. It means that the critical value of 50 Mrad is attained within 88 hours, i.e. about 3.5 days.

Epoxy Resin (Araldit AV 121). The surface temperature of the cylinder relative to the barrel is the same as in the case above ($\Delta T_s = 3.5^{\circ}C$) since it does not depend on the heat conductivity of the material. Along the cylinder axis, $\Delta T_a = 4.0^{\circ}C$.

Taking the density of 1.7, the dose rate is 0.40 Mrad h^{-1}, and the critical value of 10^4 Mrad is attained within 1000 days.

V. Conclusion

From the experimental results, it can be concluded that all investigated parameters, i.e., P, T, and t considerably influence the amount of krypton collected by the polymethyl methacrylate. For maximum kryptonation, the pressure and temperature used should be as high as possible (with respect to the physical and chemical properties of the investigated substance); the kryptonation time should also be protracted.

From the considerations on the radiation and thermal stability of kryptonated polymethyl methacrylate and epoxy resins, it can be concluded that thermal effects in kryptonated polymers can be neglected in practice. With respect to possible radiation damage, epoxy resin has an advantage in comparison to polymethyl methacrylate. The calculated 1000 days for the assumed critical dose of 10^4 Mrad can be **regarded** as the minimum, since radioactive krypton does not appear in practice as carrier-free, but as a mixture of krypton isotopes containing only about 8% ^{85}Kr. However, rather high diffusion coefficient of krypton in epoxy resins is a disadvantage for this purpose. Oppositely, the assumed critical dose for polymethyl methacrylate is attained after 3.5 days, but the diffusion coefficient of krypton in this polymer (kryptonated at elevated temperatures) seems to be satisfactory for interim storage and transport purposes.

Hence one comes to the concept of a container composed of polymethyl methacrylate grains which are (after kryptonation at elevated temperatures) incorporated in epoxy resin. In such a case, polymethyl methacrylate would provide a high retention of krypton, while the epoxy resin could give the mechanical strength. However, before proposing such a solution for practical storage of ^{85}Kr, additional experiments should be performed: diffusion coefficient of krypton in polymethyl methacrylate (and the same material covered with a layer of epoxy resin) should be investigated as a function of absorbed doses, by irradiating the samples with ^{60}Co gamma rays.

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LONG TERM STORAGE TECHNIQUES FOR ^{85}Kr*

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Abstract

As new nuclear fuel reprocessing plants go on stream, the collection of fission product ^{85}Kr will be required to avoid potential local release problems and long-term atmospheric buildup. Storage of the collected ^{85}Kr for a period of at least 100 years will be necessary to allow $\sim$99.9% decay before it is released. This paper discusses a program designed to develop and evaluate proposed methods for long-term storage of ^{85}Kr, and the results of a preliminary evaluation of three methods: (1) high pressure steel cylinders, (2) zeolite encapsulation, and (3) clathrate inclusion.

I. Introduction

Several isotopes of the noble gases xenon (Xe) and krypton (Kr) are produced as fission products in nuclear reactors. Occasionally, a fuel element leaks and some of these gases are released in the reactor, but most of the elements maintain their integrity, and greater than 99% of the fission product gases remain sealed inside. These trapped gases are finally released at the reprocessing plant when the fuel is dissolved. The delay between fuel discharge and fuel reprocessing is usually at least 160 days, which allows the shorter-lived fission products to decay. Most of the krypton and xenon isotopes, being short-lived, decay to insignificant levels during the delay period, but ^{85}Kr with a 10.76 year half-life remains a potential hazard for many years. To avoid potential local release problems and long-term atmospheric buildup, ^{85}Kr must be collected at the reprocessing plant and stored for a period of about 100 years, to allow substantial decay before it can be released. Recognizing these potential problems and in keeping with the "as low as practicable" limit on releases, the U. S. Atomic Energy Commission is sponsoring programs designed to develop methods for collection and long-term storage of ^{85}Kr. One such program is being carried out at the Idaho Chemical Processing Plant at the National Reactor Testing Station, where storage methods are being developed and evaluated.

II. Summary

The first step of the program involved a review of all proposed methods for noble gas containment and storage. Some methods have been studied or developed to the point where a preliminary evaluation can be made based on what has been reported. Where more information is needed for an accurate evaluation, laboratory experiments are being performed. When enough information is obtained, a written evaluation in the form of a topical report is issued.

For methods that appear promising but require further development, laboratory investigations will be performed using tracer level ^{85}Kr in Kr gas mixtures. If the method proves acceptable in the laboratory, it will then be scaled up to a

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* Work performed under USAEC Contract AT(10-1)-1375 S-72-1

pilot-plant development and demonstrated using the recovered fission product Kr of the Rare Gas Recovery Facility at the Idaho Chemical Processing Plant. As a final step in the program, a storage facility will be constructed and used to demonstrate the storage of ^{85}Kr using a method(s) determined to be acceptable in laboratory and pilot-plant evaluations.

The criteria taken as a basis for evaluating the potential storage methods are: (1) storage capacity, (2) thermal and radiation resistance, (3) installation and operating cost, (4) safety, and (5) ease of recovery.

Storage capacity of the methods is of great importance since large volumes will need to be stored. One 1500-tonne per year fuel reprocessing plant will produce about 16.8 MCi per year or 189,000 liters (6,680 cu ft) of krypton ($\sim$6% ^{85}Kr) at S.T.P.,(1) assuming 33,000 Mwd/tonne. This makes some form of storage at increased density necessary to reduce the volume of stored gas to a reasonable size.

Thermal and radiation stability are problems arising from the ^{85}Kr decay. Greater than 99 percent of the decay energy is in the form of 0.67 MeV beta particles. These particles will be stopped by most materials, and their energy converted to heat. Although less than one percent of the decay energy is in the form of gamma radiation, shielding will be necessary to protect personnel during handling because of the large quantities involved. Also, any storage method will have to be able to withstand the radiation field and decay heat and will have to allow for sufficient cooling to prevent temperatures from rising above the critical temperatures of the materials being used.

Methods of storage will differ in the amount of safety they provide during handling, transportation, and long-term storage. Nevertheless, the installation and operating costs cannot be prohibitive. Trade-offs of safety versus capacity and cost will need to be made.

The final criterion, ease of recovery, has recently become of importance in waste management philosophy. While the ^{85}Kr is decaying, it is a source of energy, which it may someday become feasible to utilize. Fission product Kr is also of value as an inert tracer gas. Also, after most of the ^{85}Kr is decayed, both the remaining nonradioactive Kr and the decay product rubidium may be of commercial value.

In the final selection of the method(s) to be used, all of the above factors will need to be considered.

III. Status of Program

The potential methods for storage of ^{85}Kr which have been identified for evaluation as discussed above are: (1) high pressure steel cylinders, (2) glass, plastic or metal capsules, (3) injection into soil or underground formations, (4) dispersions in glass, metal or plastic, (5) absorption or adsorption, (6) zeolite encapsulation, (7) clathrate inclusion, (8) ionic bombardment, (9) sputtering, (10) chemical compounds, or (11) combinations of the above.

The use of high pressure steel cylinders, such as those used to store and transport nitrogen and oxygen, is probably the most obvious method for storing gases in a compact form. This method was one of the first to be chosen for more extensive evaluation and will be discussed further below.

Using glass, plastic, or metal capsules at greater than ambient pressure is a variation of high pressure steel cylinders. This method appears to offer some safety advantage over large cylinders, but the method will have lower capacity and higher costs.

Injection into soil or underground formations is deficient in one important safety aspect: a formation has not yet been found for which the present and future integrity can be assured once the gas is injected.

Dispersions in glass, metals, or plastics offer some technological problems. Plastics can be foamed easily enough but provide poor radiation resistance. Glasses and particularly metals are more resistant to radiation damage, but they are liquid at much higher temperatures, and considerable development work would be required to develop a process that would yield high capacity.

Absorption or adsorption processes may require considerable development work also. Fluorocarbon and CO_2 absorption processes have been studied for separating fission product krypton from off-gas streams, but they do not appear to have high enough capacity to be practical for storage. The storage of liquid for about 100 years also presents some safety problems; a leak developed during long-term storage could be difficult to clean up.

The zeolite encapsulation process appears to have reasonable capacity and offers several important advantages in safety because it is a solid and can be stored at ambient pressure. Therefore, this method was chosen for further evaluation and will be discussed in more detail.

Clathrate inclusion compounds appeared to have some properties similar to the zeolite encapsulation process; further study was also done on them. The results were not as favorable, however, as will be discussed below.

Ionic bombardment is a method of driving ionized atoms of gas into a surface so that they become trapped in the crystal lattice. While this method does appear to offer a very stable form for storage and may have reasonable capacity, the method does not appear to be easily adapted to large scale operation as would be needed for the large volumes of Kr to be stored.

Sputtering involves depositing material, such as a metal or oxide, onto a substrate in a gas atmosphere and trapping some of the gas in the surface as it is built up. This method offers many of the same advantages and disadvantages as ionic bombardment.

Chemical compounds do not appear at this time to be a reasonable method for storing krypton. Being an inert gas, the formation of chemical compounds with any but the most reactive elements such as fluorine is very difficult. These compounds do not appear to be acceptable for 100-year storage because of their instability, especially with respect to water.

Finally, combinations of some of the above have been considered, such as embedding metal or glass capsules in plastics, but very little advantage seems to be gained with such methods.

Having given some consideration to each of these potential methods, three of the more promising methods were chosen on which to concentrate our initial efforts: (1) high pressure steel cylinders, (2) zeolite encapsulation, and (3) clathrate compounds.

High pressure steel cylinders and clathrates have been made the subjects of topical reports which are reviewed below, and the zeolite encapsulation process has been chosen for further laboratory evaluation.

High pressure steel cylinders offer the following advantages for storing fission product krypton: (1) well-established history of development and use in industry, (2) long life with good thermal and radiation resistance, (3) high capacity, (4) low cost, and (5) ease of future recovery.

The fact that cylinders have been used for over fifty years for storage and transportation of industrial gases makes them available for immediate application to the problem of storing ^{85}Kr. All of the other possible storage methods would require some development work before they could even be demonstrated on a production scale. A study made by Union Carbide showed that cylinders could be expected to last for over 500 years in normal industrial gas service if not subjected to abuse such as impact, high temperatures, or contact with corrosives.(2) As shown in Table I, the anticipated storage temperatures are low enough that no strength problems should arise, and the radiation flux should not appreciably affect the steel. The capacity shown in Table I is expected to be better than any other method so far reviewed. This capacity and the simplicity of the process for filling cylinders should result in low costs for equipment, installation, and operation. Cylinders contain the gas in an easily accessible form for future recovery.

Table I High pressure steel cylinder storage of ^{85}Kr (∿6% in Kr).

	Cylinder Pressure	
	∿500 psi	∿2000 psi
Wall Temperature	60°C	127°C
Heat Generation	44.5 cal/sec	146 cal/sec
Curie Content	128,000 Ci	419,000 Ci

In contrast to these advantages, there is always the possibility of a sudden release of ^{85}Kr, the use of cylinders place certain restrictions on the purity of the gas stored, and there may be problems associated with the accumulation of the decay product rubidium and external corrosion.

Cylinder failure due to abuse would result in the release of a few hundred thousand curies of ^{85}Kr. Proper procedures for handling, storage and transportation should minimize such possibilities. To minimize internal corrosion, efficient removal of substances such as N_2, O_2, NO_x and water would need to be accomplished prior to storage. These same substances also present problems in cryogenic separations equipment(3) so that their removal will probably be done in the separation process. Two unknown, but potential problems are external corrosion due to the elevated temperature of the cylinders and possible effects of the rubidium decay product; as much as a kilogram will form in the first few half-lives of storage. Stainless steel cylinders should solve the corrosion problem, and no serious structural problems should result from the exposure to rubidium although post-storage disposal of the cylinders will need to be done cautiously. This is a rather cursory review of high pressure steel cylinders, but more detailed information is available in a separate topical report on the subject by Foster and Pence.(4)

Although Kr does not readily form compounds, it can be trapped during the formation of compounds called clathrates. When quinol is prepared under a krypton atmosphere at elevated temperatures and pressures, a normally unstable beta-phase forms. The krypton is incorporated into the lattice of the quinol in a cage-like structure and apparently stabilizes the lattice by its presence. For the storage of the fission product krypton, quinol clathrate has the favorable properties of being easy to prepare, noncorrosive, and stable in the presence of radiation. In contrast to these, quinol krypton clathrate is water soluble, susceptible to oxidation, thermally unstable, and has a finite leakage rate. Water solubility and oxidation can probably be controlled, and the leakage rate can be reduced to a tolerable level. Thermal instability, however, places serious limitations on the capacity to the extent of making the method uneconomical.

The clathrate begins to release trapped gas at a temperature of about 70°C and complete release occurs at 120°C, long before the 170°C melting point is reached. The decay heat of the ^{85}Kr will limit the capacity to about 5 cc of krypton per gram of clathrate, requiring about 90,000 pounds per year for a single 1500 ton per year reprocessing plant. This will result in storage costs estimated to be greater than five times those for high pressure steel cylinders, making clathrates economically unattractive for fission product Kr storage. This subject is discussed in greater depth in a paper by Staples and Pence.(5)

The zeolite encapsulation process is a method for trapping atoms of krypton in the internal structure of a zeolite mineral.(6) The structure consists of large cages in the zeolite which are interconnected by pores. Under high pressure at elevated temperatures, the gas can be forced through the pores into the cages where it becomes trapped when the temperature is reduced. The material can then be stored at ambient pressure even though there may be considerable pressure in the cages. This ambient pressure storage would have a definite safety advantage over high pressure steel cylinders; however, the storage capacity of zeolites is not expected to be quite as high. Zeolites do have a large storage capacity for non-radioactive gases, but this may not be obtainable for fission product Kr due to the decay heat from the ^{85}Kr.

The potential for good storage capacity in a very stable form has prompted us to investigate the zeolite process further. Equipment is now being procured for laboratory studies to determine process operating conditions and product capacity and stability.

IV. Conclusions

Clathrate inclusion compounds appear to be unacceptable for storage of ^{85}Kr. The poor thermal stability limits capacity to such an extent as to make clathrates economically unattractive.

High pressure steel cylinders and the zeolite encapsulation method both look very promising. The cylinder storage is expected to have somewhat greater capacity, but the zeolite storage is at ambient pressure, so that it may be somewhat safer. Both methods have some uncertainty as to the effects of the decay product rubidium. Table II shows a comparison between 50-liter high pressure steel cylinders and 50-liter containers of zeolite used to store a mixture of 6% ^{85}Kr in Kr. The data in the table are calculated and in the case of the zeolite, are only estimates. The temperature of 100°C for the zeolites was chosen as an assumption, and it may be that a considerably higher or lower temperature will actually be determined to be the maximum storage temperature. The purpose of the planned laboratory work previously mentioned is to resolve such questions.

Table II Storage capacities for zeolites, clathrates, and high pressure steel cylinders.

	Temperature at Centerline of Container °C	Curies of ^{85}Kr Contained per 50-1 cylinder
Zeolites	100	77,400
Clathrates	55	32,300
Cylinders at 500 psi	60	128,000
Cylinders at 2000 psi	127	419,000

Future efforts in the program will center on development of the zeolite encapsulation process and evaluation of some of the other methods which were postponed while clathrates and high pressure steel cylinders were being evaluated.

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DISCUSSION

LASER: I agree with the speaker that storage of krypton in steel cylinders is a very promising method, but we also see disadvantages. I have concluded that krypton should not be stored for long times in these cylinders and, therefore, we have recommended that these cylinders be dumped into the deep sea. This, I think, is the method which has the lowest possible impact on the environment because the krypton is readily dissolved in the sea water or crystalized noble gas hydrates are formed. The probability that the radioactive gas comes into the biocycle is very low. A second comment relates to the high temperature of the cylinders which you have calculated. We have made some experiments with simulated heat sources inside a steel cylinder. I don't remember exactly the temperatures of the cylinders, but I think they were below 80° C.

FOSTER: You are correct. Temperatures were calculated. We have not had a chance to verify them in the laboratory although we are planning heat transfer experiments to do so. I have checked the calculations against the work of some people at Hanford and also the work of some people at Union Carbide and we seem to be in agreement.

LASER: What do you think may be the highest surface temperature allowable for steel cylinders for transportation and storage?

FOSTER: This has not yet been defined to my knowledge, but it will probably be 100°C or less, I would guess.

LASER: I think this is probably the maximum temperature that will be allowed in Germany, also. I don't think we can get permission in Germany for high temperatures.

FOSTER: I think there will probably be problems in the United States with dumping the steel cylinders in the sea. It's a matter of what people consider to be safe. It's more of a political-type decision.

LASER: Yes, I see this as a problem also, but I think it has the lowest impact on the environment.

ELLINGTON: I imagine there is some finite partial pressure of krypton which would be in equilibrium with the zeolites at 200°F. Do you have any information on what these partial pressures of krypton would be?

FOSTER: No. We are in the process of getting equipment to do tests on it. I haven't any information.

ELLINGTON: Let's make the assumption they will have a

ELLINGTON (cont.): partial pressure and that this partial pressure will increase with temperature. I will then say, you couldn't allow them to sit out in the open. If you did, over time, krypton would enter the atmosphere, which is what we are trying to prevent. Which leads to another question, why not encapsulate a steel cylinder inside of a steel cylinder to get the necessary protection against a catastrophe at probably 120th of the cost.

FOSTER: I think your whole question depends on your first assumption, and we don't have any information on that at this time. What I have seen indicates that over a period of 30 days after encapsulation there will be no measurable loss of krypton.

PENCE: Regarding the leakage rate, the data we have are based on published results, results which are not complete enough for a good evaluation of the leakage rate. Although the data are not as complete as we would like, there are indications that very, very low leakage rates are probable. This is a particular type of zeolite, and when the material is treated at about 300°C after the krypton has been loaded into the zeolite under pressure, the cations tend to migrate to seal the gas in the zeolite. If this is the case, krypton cannot leak out. We don't know what temperature the gas will tend to migrate back, but it will. This is basic to the usefullness of the process and, information that we hope to determine.

B.A. SMITH: I wonder if you could elaborate on the problems you foresee from formation of daughter-product rubidium? Is it correct, also, that you feel this will be more of a problem in the steel cylinders than by any other method?

FOSTER: To answer your last question, yes. We think the worst problems will be seen with cylinders, mainly because other processes distribute the rubidium throughout the material. For example, in zeolites you have very small amounts of atoms present within the cages in the molecular structure. With high pressure steel cylinders there is no material in the cylinders, but there may be a temperature at which the rubidium is liquid. You may see it condensed on the walls of the tank or in a pool at the bottom of the tank. The sort of problem that arises is the same as you see with other liquid metals in contact with stainless steel. Such problems generally occur at temperatures significantly above 400°C. This information is from people who are working in LMFBR technology. Whether it will be a problem around 100°C, we don't know, but it is the sort of thing where even a very small problem over a period of a few years can be a great problem over a period of 100 years. That is the sort of thing we anticipate might be a problem.

UNDERHILL: First, what would be the effect of moisture on the retention capacity of the zeolite you are developing? We do know that zeolites can be affected by moisture. Secondly, assume the stainless steel cylinders contained charcoal. This would have two effects: (1) reduce the partial pressure of the krypton and

UNDERHILL (cont.): 2) prevent the collection of rubidium on the walls of the cylinder.

FOSTER: I think there definitely are some materials that can be put in the high pressure steel cylinder that would have some highly beneficial effects. I don't know what would happen as far as heat transfer is concerned if you put a solid material in there. You might run at higher temperatures. I don't know how much of a trade-off there would be.

UNDERHILL: Also, I would consider putting in a different material for the collection of rubidium. I was going to suggest steel wool.

FOSTER: That has been considered to a certain extent. I guess I should say the work done on the high pressure steel cylinder was not an attempt to find the best method for using high pressure steel cylinders, but to indicate whether the use of cylinders was feasible or not.

BENDIXSEN: I am a coworker with Bruce Foster at Allied Chemical. I believe that this kind of thing ought not to be done. Clathrates or zeolites are not going to be more efficient in the long run. Regarding exposure to people, the complexity of systems required to put in zeolites are immense and the product is going to have to be doubly contained. Because of this complexity, the exposures to the operating personnel are going to increase. Why not release to the public instead of a few operating personnel?

FOSTER: I think you bring out a serious point. As I mentioned earlier in the paper, there is a tradeoff here. I don't think anything is going to have a capacity comparable to cylinders, or a lower cost. In other words, the questions are, "How safe do you consider them to be?" and "How much do you want to pay for the additional safety?" A lot is going to have to wait until we determine operating parameters for the zeolite process and see how much the process will cost and how much benefit one gets for the additional cost.

THOMASSON: I would like to add one thing to the point Mr. Bendixsen just made--"Why not release Kr-85 to the environment and let the general public have a dose versus the operators?" I indicated earlier that this is one consideration in determining the optimum solution of the problem of the best disposal method. One thing to be kept in mind is that once the material is in the environment, it is too late to do anything with it. In future years, when we start getting a buildup, we will have no choice. Also,this results in involuntary exposures. You can engineer a proper system in the plant. You can control personnel exposure through proper plant design. This is basically a political decision by the regulatory people in the government and also a decision that has to be made by the plant operators and designers.

COST OPTIMIZATION FOR BWR AND PWR OFFGAS SYSTEMS

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Abstract

Technical aspects of the Offgas Systems for both Boiling Water Reactor (BWR) and Pressurized Water Reactor (PWR) are well covered in many published articles. (1) (2) (4) (7) However, in very few cases, cost aspects of the Offgas Systems are discussed. Both technical and economic factors must be included in any evaluation of the system. Factors such as reliability, maintenance, regulatory codes, future needs and public relations should also be considered.

The intent of this paper is to provide some cost optimization methods for the offgas systems. Discussion is focussed more on the BWR systems as they are more expensive and larger in size. The PWR systems are relatively smaller in size as the activity reduction is achieved with processing of the cover gas compared to that of the air in-leakage (up to 40 times) in the BWR systems.

I. Introduction

Today, every nuclear power plant has installed or is planning to install a sophisticated offgas system to reduce the radioactivity emissions to the environment. The intent is to meet the AEC Guideline 'as low as practicable'. A majority of the BWR plants will have the charcoal delay type offgas system with few plants selecting the cryogenic distillation system which separates the noble gases, prime contributors for the radioactivity. PWR plants opt for one of the many different types of offgas systems; compressed storage to cryogenic type.

It is not within the scope of this article to provide economics for all types; and as such for the BWR, only the charcoal delay type offgas system and associated subsystems (pretreatments) are discussed. For the PWR, a generalized cost comparison is made of all practical systems. Major effort, however, is devoted to the BWR offgas system economics.

Cost optimization is based on differential costs (savings or losses) rather than absolute numbers. Initial equipment cost, operational and maintenance costs and wherever possible structural cost (space and/or building) are incorporated. The operating cost is adjusted to the present worth utilizing a multiplication factor of 12. The equipment cost reflects the cost of redundant components wherever redundancy is required.

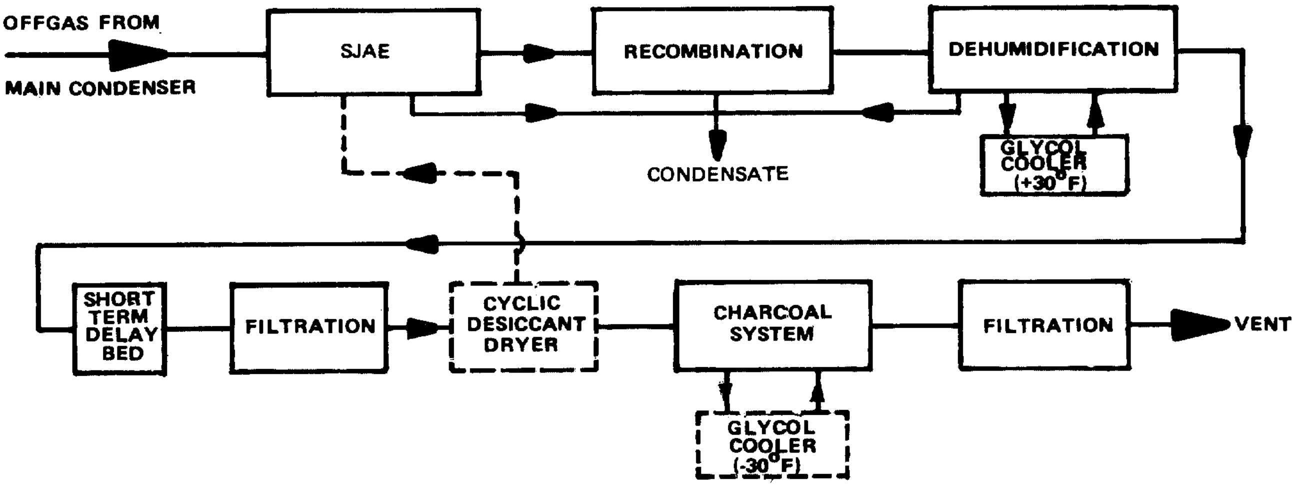

FIG 1. TYPICAL BWR OFFGAS SYSTEM

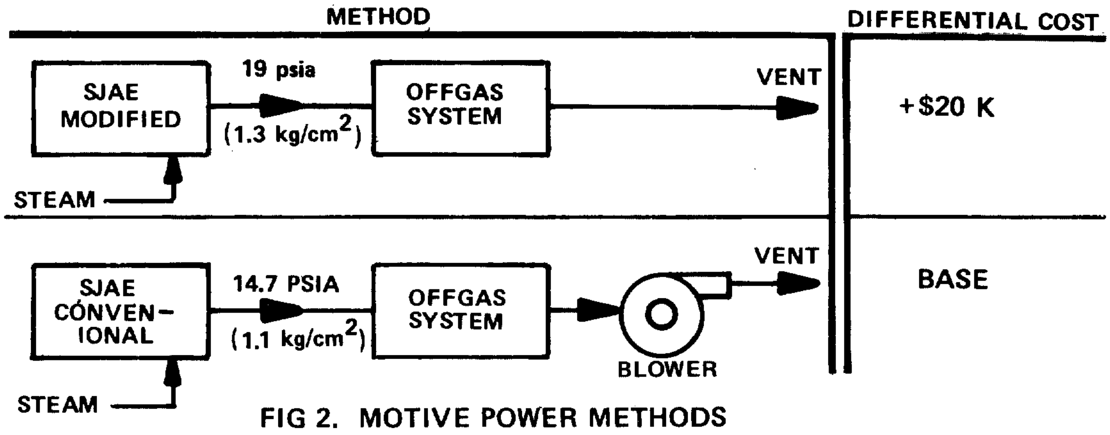

FIG 2. MOTIVE POWER METHODS

II. BWR Offgas System

A typical 800 MWe plant such as Cooper, Shoreham and Zimmer is selected as a model. The offgas flow and composition are as follows:

Hydrogen	-	32 lb/hr (14.5 kg/hr)
Oxygen	-	254 lb/hr (115 kg/hr)
Air in-leakage	-	45 to 180 lb/hr (21 to 81 kg/hr)
Water Vapor	-	Saturated
Noble Gases	-	Trace
Iodine	-	Trace
Activation Gases	-	Trace

The activity level of this stream is 2.45×10^6 μCi/sec at t = 0 and 1×10^5 μCi/sec at t = 30 minutes based on the modified diffusion mixture (1). The air in-leakage is shown as variable which depends on good housekeeping and size of the condenser shells. Also the system cost is very much dependent on the air in-leakage flow rate. The system design code is ASME Section VIII, Division 1 with seismic design category 2.

Figure 1 is a typical block diagram for the charcoal delay system. Subsystems such as steam jet air ejection (SJAE), recombination, dehumidification, short-term delay and filtration are prerequisites prior to charcoal delay. The requirement for the drying subsystem depends on the operating temperature of the charcoal delay system. Specific optimization methods are discussed in the following paragraphs.

Motive Power

About 4 to 5 psi (0.3 kg/cm^2) pressure differential is required to process the offgas stream. Two ways to provide this force are SJAE and blower as shown in Figure 2. The SJAE which is normally required to maintain a vacuum on the main condenser can be designed to boost pressure to the required level. Alternately, a small discharge blower can be used to exhaust the gas to the atmosphere. In this case, the offgas system operates at negative pressure which is attractive from leakage prevention point of view. However, from reliability and maintenance aspects, the SJAE is recommended over the blower even though the cost increases by $20,000. This is primarily due to the difference in SJAE pumping the total offgas stream as compared with blower pumping only the air in-leakage stream.

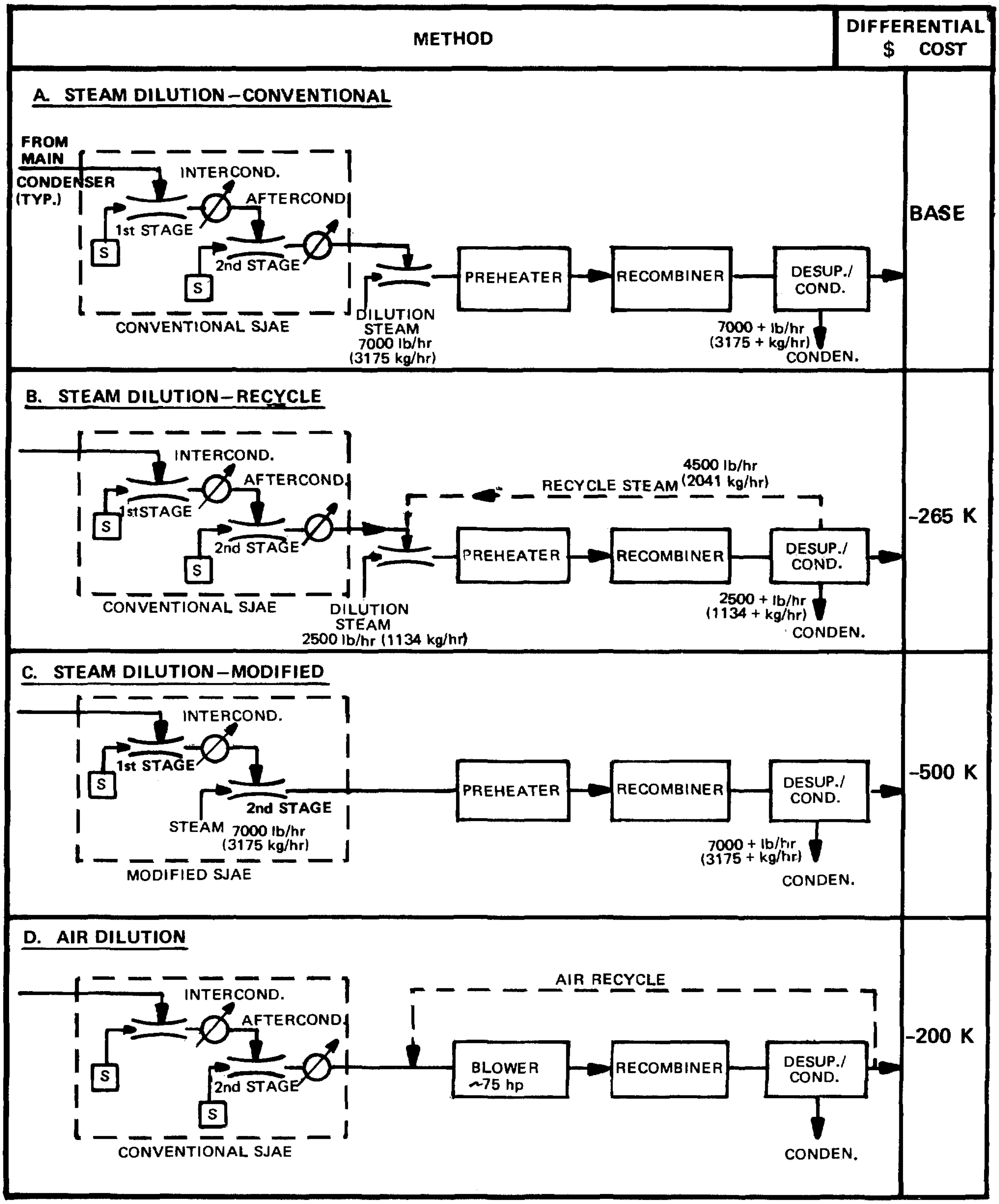

FIG 3. DILUTION METHODS

Dilution

Prior to recombination, dilution of the offgas is necessary to lower the hydrogen concentration to less than 4% by volume from about 50 to 60%. Figure 3 shows various schemes utilized for dilution. Steam dilution is more commonly used compared to air dilution. This dilution requirement represents a major factor in operating and initial equipment costs.

First generation offgas systems utilized the conventional method of steam dilution which represents a cost of $400, 000 based on 60 cents/1000 lb of steam. The second method reduces this cost to $135, 000 by recycling about 67% of the dilution steam. The third method, which is recommended by the authors for the new plants, involves modification of the SJAE by which the aftercondenser of the SJAE is eliminated and the second stage motive steam is also used as the dilution steam. A total saving of $500, 000 is realized with this approach. Even the air dilution method, very unlikely candidate for the new plants, gives about $200, 000 savings over the conventional method.

Catalyst

Palladium/platinum type catalyst with either a metal or ceramic base is used for recombination of radiolytic hydrogen and oxygen. Most of the BWR offgas systems utilize a metal base catalyst, although cost difference between the two is insignificant. The catalyst cost can be reduced by optimizing factors such as influent temperature, effluent hydrogen concentration on a dry basis and a maintained minimum air in-leakage. Figure 4 shows the effect of the influent temperature on the catalyst cost. Part of the cost savings realized by higher inlet temperature is offset by the increased cost of preheating. However, as shown by the upper curve in Figure 4, it is still economical to increase the influent temperature. Higher than the indicated temperature may or may not be economical depending on limitation of vessel material normally used.

Selection of the effluent hydrogen concentration is important as it affects the catalyst cost. For example, the cost increases by about 20% if the effluent hydrogen concentration requirement is reduced from 0. 5 to 0. 1% by volume (dry basis). Also because the effluent hydrogen concentration is normally specified on a dry basis, the maintained minimum air in-leakage flow affects the catalyst cost. For example, the cost reduces by about 15% if the specified minimum air flow is increased from 6 to 30 scfm.

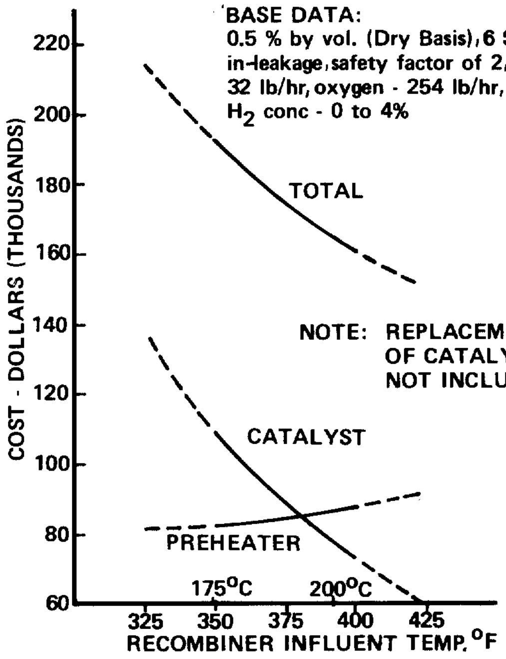

FIG 4 COST EFFECTIVENESS OF RECOMBINER INFLUENT TEMPERATURE

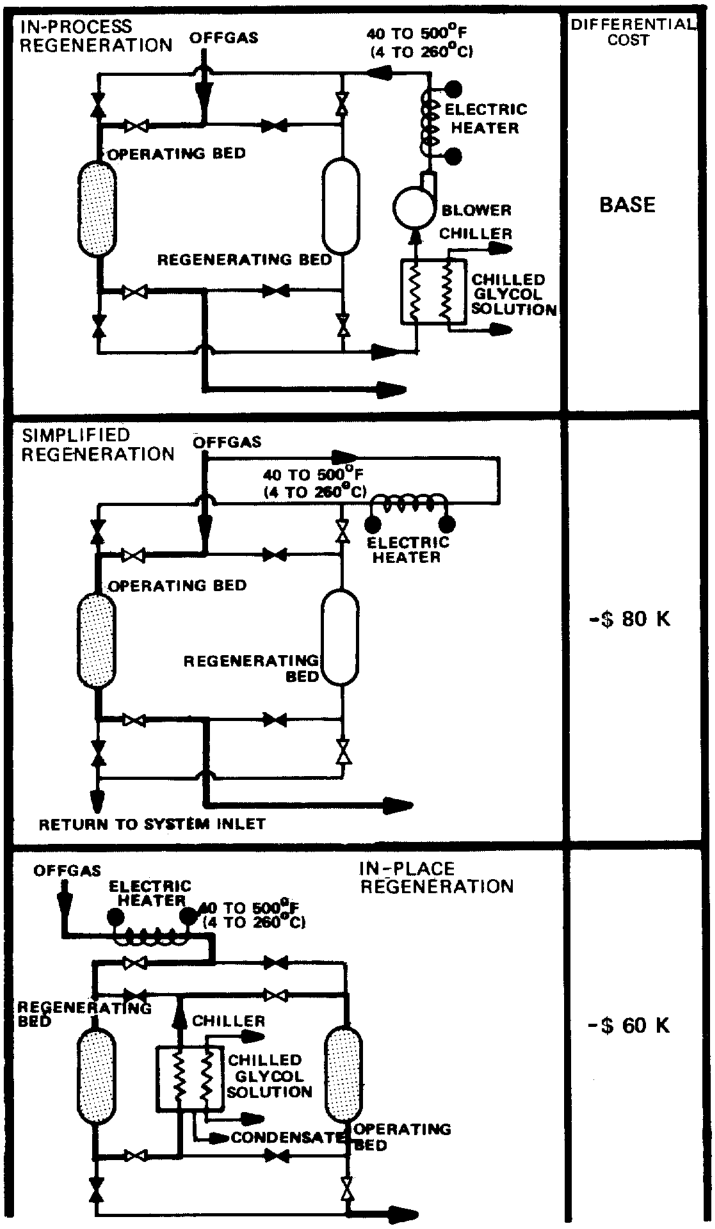

FIG 5. DESICCANT DRYER SYSTEMS

Moisture Removal

Final dehumidification of the offgas stream, primarily air after the recombination process, is normally accomplished with a chilled glycol solution circulating through a heat exchanger. Refrigeration for the glycol solution is supplied by a standard mechanical refrigeration system, a part of the glycol cooler system. Appreciable cost savings can be realized if the plant chilled water is utilized thus eliminating the glycol cooler system.

Short-Term Delay

The conventional holdup pipe in early plants delays the total stream for about 30 minutes. With the recombination subsystem the volume is reduced about sevenfold, therefore the delay line, if required, could be 7 times smaller in size. Since a delay line is expensive, unless required for transporting the gases, the short term delay bed is recommended and it can save up to $200, 000.

First proposed by the authors, the delay bed (or maternity ward where the fission product daughters are born) is a charcoal tank sized to delay the noble gases sufficiently to let more than 95% of the solid daughter products form and permit the activation gases to decay to much lower levels. The residual activity is therefore localized and the radiation levels downstream are reasonable. Another benefit is the lowered dose rates during maintenance.

Drying

Drying of the offgas stream, particularly necessary for refrigerated temperature charcoal delay systems, is accomplished, in most cases, with a desiccant type cyclic dryer. Cost of this subsystem depends on the drying cycle period and the method of regeneration. The quantity and the cost of desiccants, such as molecular sieves or silica gel, primarily depend on the cycle period which may vary anywhere from 2 to 6 days.

Figure 5 shows various methods of dryer regeneration. The conventional in-place regeneration method utilizes a chiller, a blower and an electric heater. The residual air in the closed loop is used for regeneration of the exhausted dryer. This air is heated and recirculated to desorb the moisture and then cooled to condense it. The second method, conceived by the authors, depicts a simpler way of accomplishing the regeneration without blower or chiller. A portion of the process gas is heated to drive out the moisture and returned to the front end. This return flow also maintains a minimum air flow through the catalyst, thereby reducing its size and cost. In plants where this stream cannot be returned to the front end, a modified version of the second method, in-process regeneration, may be used. In the third method, the process gas itself regenerates the saturated dryer. A chiller is required between the regenerating and drying beds.

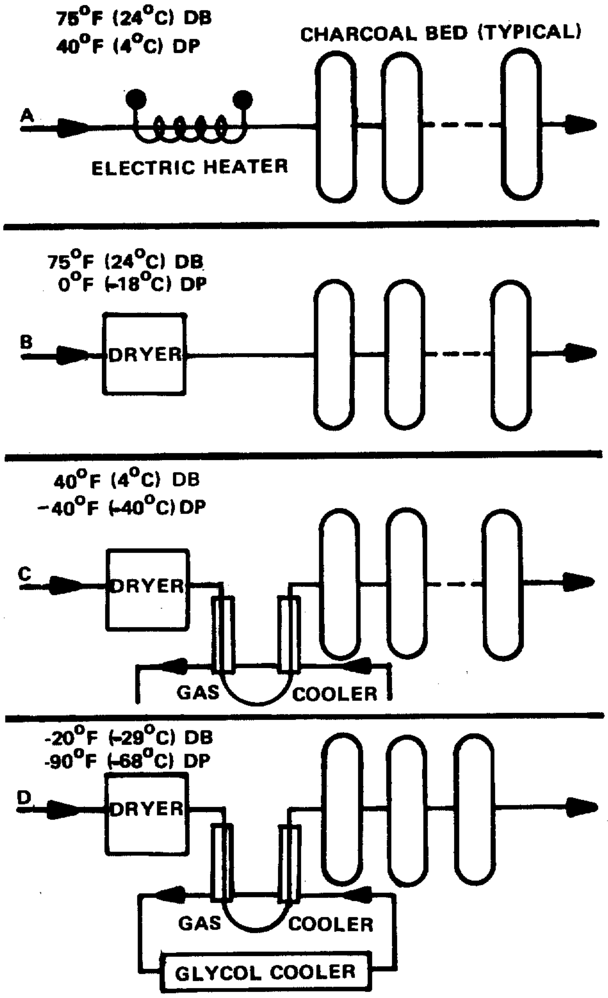

FIG 6: CHARCOAL DELAY SCHEME

Drying (Continued)

Obviously, the latter two regeneration methods have a significant cost advantage over the conventional method, as shown in Figure 5.

Precooling

Precooling of the offgas required for the refrigerated charcoal delay is accomplished by two methods. One is with a chilled glycol solution from a low temperature glycol cooler which also provides refrigeration for the charcoal beds.

The second method to achieve precooling is by routing the offgas through a cooler placed in a refrigerated vault containing the charcoal beds. The vault air must be first dehumidified to prevent ice buildup and then chilled for circulation. The bare charcoal tanks are placed in the vault which must be insulated.

The economics favor the first method, however it depends largely on the number of charcoal tanks and the vault size.

Charcoal Delay

The decay of noble gas radioactivity is accomplished by adsorptive delay using activated charcoal. The noble gases are selectively delayed for a longer time in relation to delay of the bulk carrier gas. The theory and process are explained more thoroughly by many authors. (3) (5) (6)

The first generation charcoal delay systems operate at ambient temperature. However, since the charcoal beds represent a significant portion of the total system cost, ways should be found to reduce this cost. It is known that charcoal exhibits higher adsorption efficiency with decreasing temperature; thus operation at lower than ambient temperature would reduce the size and cost. But, lowering the temperature also increases the system complexity by the addition of components such as cyclic dryer, precooler and low temperature glycol cooler system. Figure 6 shows a number of system configurations and the increasing complexity with decreasing temperature. The dynamic adsorption coefficients, corresponding to different operating conditions, are given below:

Configuration	Operating/Gas Dewpoint Temp. °F	Dynamic Adsorption Coefficient (cc/gm)	
		Krypton	Xenon
A	75/40	18.5	330
B	75/0	25	440
C	40/-40	40	850
D	-20/-90	100	3000

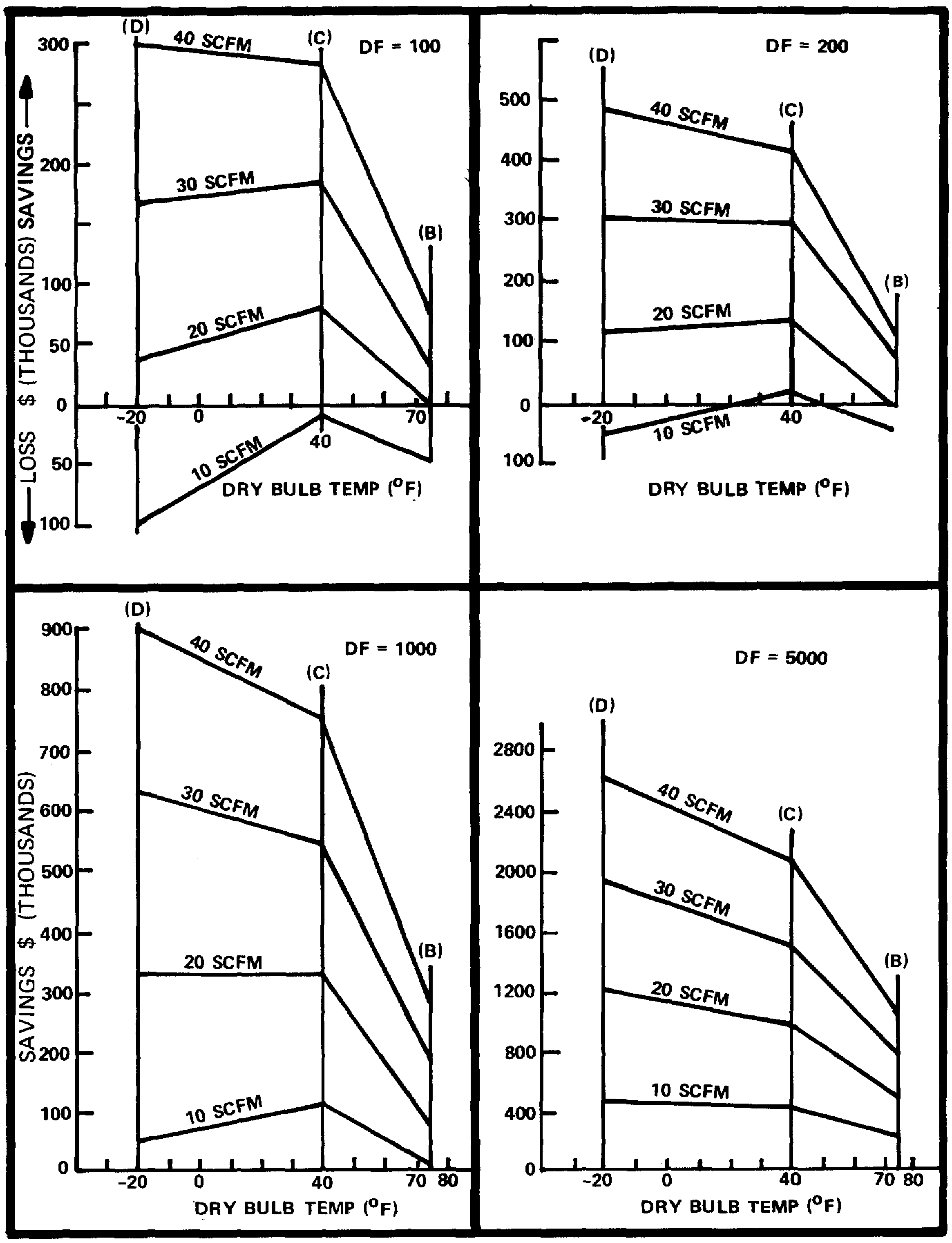

FIG. 7. BWR OFFGAS SYSTEM COST ANALYSIS

(REFER TO FIGURE 6 FOR COMPARISON BASE: SYSTEM A AT 75°F DB, 40°F DP. INCLUDES EQUIP. & SPACE COSTS.)

Charcoal Delay (Continued)

An economic analysis of these configurations uses the ambient temperature system A as the base. Figure 7 shows the cost savings of operation at low temperature when the air in-leakage flow rate and DF are higher. However, for lower flow rate and DF, it is economical to operate at near ambient temperature. This analysis includes the equipment cost with the space cost at $300/ ft^2 but does not consider the operating cost; however, the results will not be significantly different. Figure 8 shows the integrated results of the analysis and may be used for the selection of the optimum operating temperature for a given flow rate and DF.

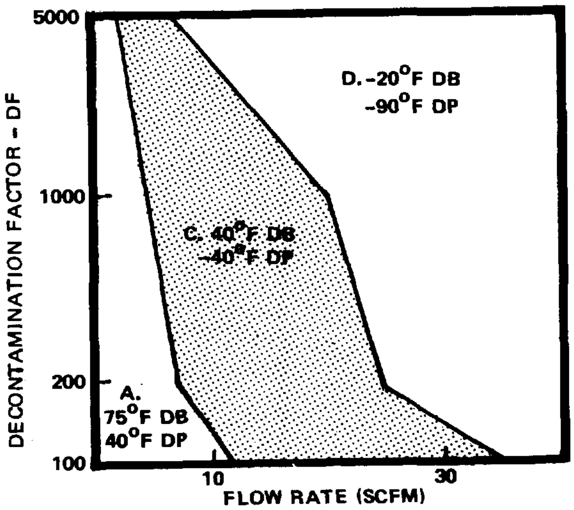

FIG 8. SELECTION CRITERIA FOR AN OPTIMIZED BWR OFFGAS SYSTEM

III. PWR Offgas System

For the PWR, the user has a wider selection of offgas systems. The system differs from a BWR in that the flow rate is about 1 scfm instead of 40 scfm and that hydrogen is the main gas, usually 95% or more. The various systems are shown in Figure 9 and described below.

Storage

Pressurized storage is a simple way and was used first. The offgas is compressed to about 10 atmospheres and stored in large (5, 000 gallon) decay tanks for 30 to 90 days. Some of the problems are the high pressure compressors, leakage and hydrogen inventory. Tanks require large volume, are operationally inflexible and inexpensive (except for off-design conditions).

Storage After Recombination

This method requires that oxygen be added to recombine with the bulk hydrogen. It eliminates explosion potential and reduces the offgas stream by a factor of twenty. Recombination is therefore a good method to greatly increase the holding time for older plants with fixed volume storage.

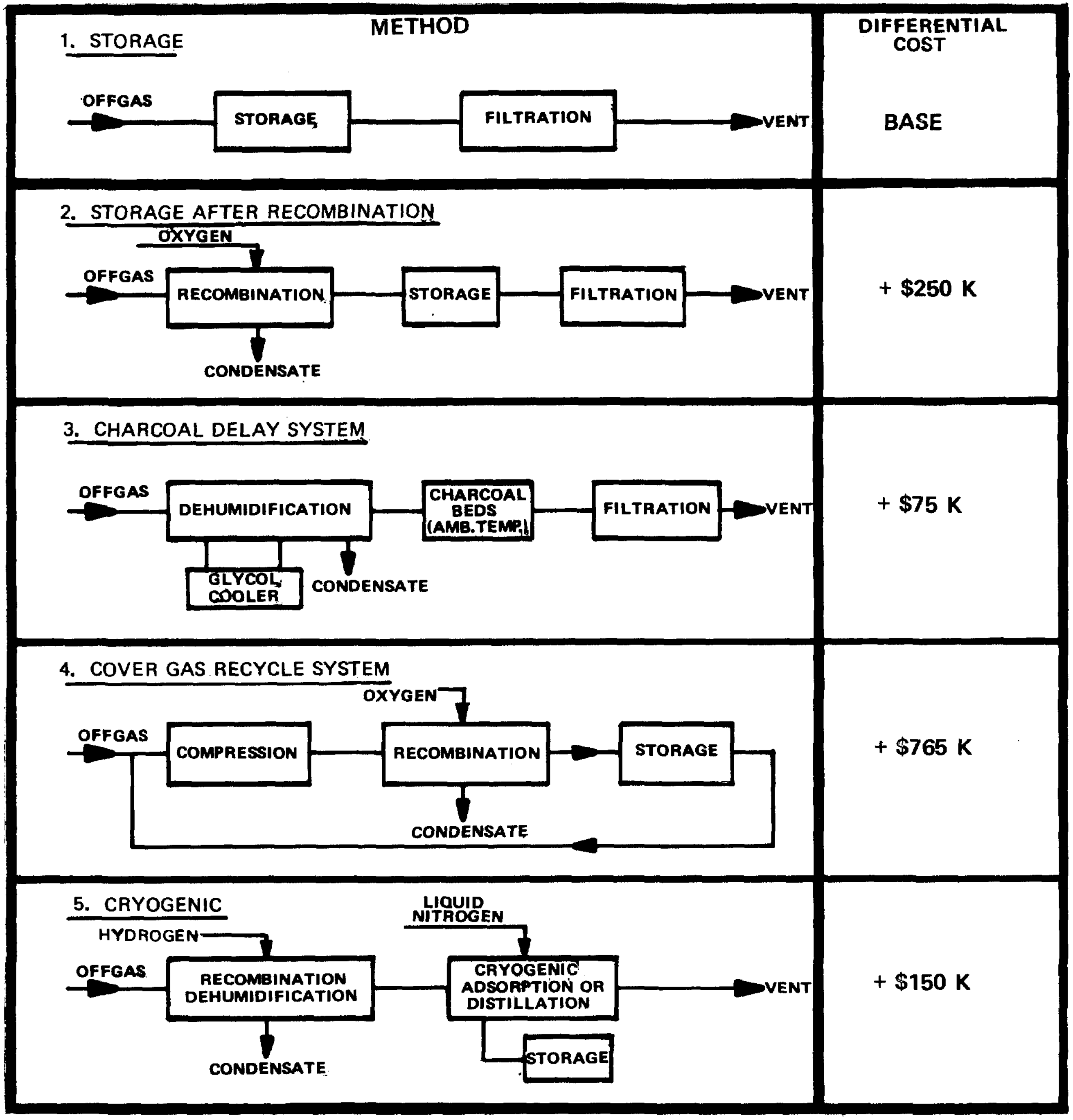

FIG. 9 PWR OFFGAS SYSTEM CONFIGURATIONS

Charcoal Delay

By using the charcoal delay system, most high pressure compressors can be eliminated as near atmospheric pressure is adequate. The system is passive as the gases flow through charcoal beds and the radioactive noble gases decay while being delayed.

Cover Gas Recycle System

With the previously described systems the Kr-85 activity is released to the atmosphere. However, the cover gas recycle system retains all activity within the system for up to 40 years. The system essentially includes a combination of recombiner and storage systems.

Cryogenic Adsorption or Distillation

It is a method by which all noble gases are separated and bottled up indefinitely. The cryogenic process is well proven and the small space requirement enhances its choice. The process is flexible and can handle the offgas, cover gas or any other gases.

Figure 9 also shows relative costs of these systems as compared with the conventional storage method.

IV. Conclusions

This paper has presented certain options and their associated costs. Most are based on servicing a single unit. However, twin or multiple units may use the same gaseous radwaste system that is modified to handle the larger volume with the same reliability but with substantial savings in building space and operational complexity.

When the utility selects the reactor type (BWR or PWR), then the selection of auxiliary equipment commences. The authors recommend that the utility consult early with the engineers and/or equipment suppliers to optimize their systems. An example, especially true for the BWR, is that by modifying the SJAE and locating the recombiners in the same room, the safety is enhanced, extra shielding walls are eliminated and the large and expensive interconnecting piping is substantially reduced. Upwards of a million dollars may be saved by these early optimizations.

V. Acknowledgement

The authors wish to thank M. K. Khandhar, Bob Bradley and others for technical assistance and the management of Cosmodyne for their encouragement and support.

VI. Bibliography and References

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DISCUSSION

MICHELS: I wonder if you would care to comment on what these costs might be if the annual cost was treated on a six year basis rather than a twelve year basis, and also, if the cost of nuclear steam was less than 60 cents per thousand pounds. I think the incremental cost of steam might be considerably less than 60 cents per thousand. On these bases, the difference in cost between alternates would be far less.

STEWART: It doesn't make a lot of difference, really. We use a factor of twelve. Today's interest costs are very high but in the past they were very low. It's something I wouldn't speculate on. It's based on eight percent over forty years, and if you use a shorter period of time, it brings the cost down. If the cost of steam goes from 60 down to 40 cents, you roughly multiply by two-thirds.

CHAIRMAN'S SUMMATION:

Based on the papers given in this session, there are serious limitations in the use of quinol, a clatharate, and polymethyl methacrylate for permanent storage of Kr-85. Limitations include radiation stability, volume of material required, and short retention times compared to the 10.76 year half-life of Kr-85. The technique of incorporating krypton in zeolite media under high pressure followed by storage at ambient pressure appears promising and will be investigated further. This technique, although providing a lower capacity than storage in pressure cylinders, would provide apparent improved safety benefits over pressurized tank storage. Hopefully, the papers presented today will stimulate additional efforts in this work, which will produce a practical technique for safe and economical storage of the long-lived Kr-85. Otherwise, the possible safety and occupational exposure problems associated with in-facility storage may outweigh the environmental gains. The ultimate solution to the problem should be reached on a cost/effectiveness optimization; that is, to maximize benefits and reductions in exposures at acceptable costs. Also, in order to achieve this goal, the applicable regulatory agencies must develop pertinent safety and environmental criteria on a timely basis so that the plant designers and owners will know the design requirements.