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PRELIMINARY PROPOSAL -  
EMERGENCY REACTOR OFF-GAS DECONTAMINATION SYSTEM

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## EMERGENCY REACTOR OFF-GAS DECONTAMINATION SYSTEM

Irradiation of nuclear fuel results in the production of substantial quantities of radioactive by-products. Fortunately, the bulk of the fission product inventory is retained within the ceramic matrix of the reactor fuel. A significant fraction of the noble gases and halogens, however, migrates through the fuel pellets and accumulates in the fuel rod voids. Under normal operation, small amounts of these fission products then enter the primary reactor coolant system via fuel cladding failures. Xenon-133 and Xenon-135 constitute the major source of this modest coolant activity in the usual case. Table I gives the volatile radionuclide core inventory for a representative 1000 MWe PWR nuclear power plant operated at full power for 500 days and shows the corresponding amounts of these components expected in the fuel plenum and primary coolant. During the normal operation of a PWR, essentially all of the noble gases released from the fuel concentrate in the primary coolant volume control system and are subsequently routed to an appropriate decontamination process. All ancillary equipment leaks and secondary coolant releases are commonly left untreated and are lost to the environment because under normal reactor operation they represent a relatively small amount of noble gas activity, well below federal release limits. The boiling water reactor operates on a direct steam generation cycle and the contaminated coolant passes through the reactor turbine. Entrained noble gases and other noncondensables are then removed from the turbine condenser by a steam jet air ejector. Better than 99 percent of all noble gas released from the core of a BWR normally escapes along this pathway. Consequently, the only BWR noble gas control equipment is located on the downstream side of the condenser air ejector. Other environmental emissions are again minor and mostly ignored.

Delay tanks and charcoal beds are commonly employed to limit noble gas radioactive releases from various power reactors under normal operating conditions. This method achieves decontamination through natural decay. Retention of the reactor off-gas for 45 days results in the decay of the major fraction of all short-lived isotopes and reduces the reactor radioactive emissions by a factor of near 100. Krypton-85, however, has a 10.8-year half-life and therefore moves through such a system virtually unaffected. Reactor radwaste systems are designed to effectively accommodate only the amount of activity associated with normal core releases, which corresponds to 1 percent failed fuel. On this basis, the cooling circuit waste gas retention equipment is designed to handle a nominal 1 scfm of contaminated gas in the case of a PWR and 5 to 50 scfm for a BWR.

Commercial light water reactors have been in operation for a sufficient period of time to demonstrate the effectiveness of various containment systems designed to minimize releases of radioactive by-products during normal reactor operation. Overall, the U.S. commercial power reactor operating record has been outstanding. Actual releases to the environment have only been a fraction of the permissible levels set by federal regulations. Recently, however, the Three Mile Island reactor incident

Table I

VOLATILE RADIONUCLIDE INVENTORY IN  
A 1000 MWe NUCLEAR POWER PLANT<sup>[5]</sup>

<u>Radionuclide</u>	<u>Half-Life</u>	<u>Reactor Core,<sup>a</sup> 10<sup>6</sup> curie</u>	<u>Fuel Rod Voids, 10<sup>6</sup> curie</u>	<u>Primary Coolant,<sup>b</sup> curie</u>
Iodines:				
I-131	8.05d	74.9	0.76	465
I-132	2.3 h	114.0	0.14	186
I-133	21. h	171.0	0.64	766
I-134	52. m	206.0	0.12	117
I-135	6.7 h	158.0	0.34	420
Kryptons:				
Kr-85	10.8 y	0.66	0.067	334
Kr-85m	4.4 h	33.5	0.95	439
Kr-87	76. m	64.4	0.076	261
Kr-88	2.8 h	93.0	0.149	775
Xenons:				
Xe-133	5.3 d	164.0	4.17	52,290
Xe-133m	2.3 d	4.0	0.019	692
Xe-135	9.2 h	43.6	0.084	1,488
Xe-135m	15.6 m	46.4	0.016	42

- a. 3040 Mwt PWR operating at full power for 500 days.  
b. 1 percent failed fuel.

demonstrated the inability of the normal reactor environmental systems to satisfactorily handle overload situations precipitated by a significant failed fuel condition. In the TMI case, nearly all of the core inventory of noble gas was released into the primary and secondary reactor coolant circuits. A large fraction of this burden was subsequently dumped into the reactor containment shell, containment sump pump housing, and turbine building. Fortunately, the TMI reactor had been in service for only 90 days prior to the accident and the krypton-85 inventory was less than 10 percent of the level given in Table I, which is based on 500-day operation. All of the short-lived isotopes, however, were present at near Table values since these radionuclides achieve rapid core equilibrium. The reactor gaseous radwaste system, while effective during routine reactor operation, was not available because this equipment is part of the reactor primary coolant cleanup system and is not generally accessible. As already noted, however, the radwaste equipment would not have offered much relief anyway because of its low capacity relative to the quantity of gas requiring decontamination. Some of the noble gas was inadvertently vented to the environment while a sizable fraction was isolated within the reactor containment shell. The reactor presently contains 35,000 curies of krypton-85.

In 1966, the Oak Ridge Gaseous Diffusion Plant (ORGDP) worked on a mobile processing system designed to be transported to the site of a hypothetical reactor within 24 hours following a fuel failure accident to recover the noble gases and other volatile radionuclides that were released to the containment vessel. The process was based on selective absorption using fluorocarbon solvents. As envisioned, all of the recovery equipment was to be located in a series of trailer trucks<sup>[11,12]</sup>. The design capacity of the mobile unit was 1000 to 1500 scfm and was based upon processing the entire reactor containment volume ( $3 \times 10^6$  cubic feet) within one week with an overall krypton decontamination factor of 100. This work did not proceed beyond the conceptual design stage, however, and the program emphasis was shifted to application of the process to routine cleanup of reactor off-gas during normal operation and to fuel reprocessing plant off-gas treatment.

The fluorocarbon process development program has since been essentially completed as part of the fuel recycle program at the Oak Ridge National Laboratory (ORNL). Considerable improvements and simplifications have been made to the original 1966 version of the process. Performance and reliability have been demonstrated on an engineering scale over many years of pilot plant operation, including tests with krypton-85, xenon-133, and iodine-131. A third generation pilot plant is currently in operation at Oak Ridge. Mass transfer data and rigorous process models have been generated that permit confident design of an emergency off-gas decontamination process applicable to essentially all types of reactors.

In view of the current interest in providing additional reactor safety features, it is believed the mobile Kr-Xe removal system deserves re-examination. This proposal specifically requests funds to study, design, and ultimately construct an emergency mobile or fixed reactor decontamination system. Further process development is not required for this application



and the design studies can be initiated immediately. An integrated system is proposed that will allow total off-gas cleanup, depending upon the particular accident, including removal of elemental and organic iodine, tritiated water, semi-volatile species, and particulates. The resulting system operation and performance will be verified and it will then be made available as directed by DOE.

## 1. BACKGROUND

The fluorocarbon-based selective absorption process for krypton and xenon removal has been under development since 1967. At that time, a test facility was built at the ORGDP to establish general process feasibility and to collect noble gas absorption data<sup>[23]</sup>. This initial equipment, while somewhat limited in operating capability, functioned exceptionally well, and valuable overall performance information was attained. In 1970, the testing program was oriented to demonstrate specific application of the process to achieve cleanup of the off-gas from light water reactors<sup>[24]</sup>. Pilot plant tests demonstrated the basic feasibility of the process and showed that better than 99.9% of the krypton and xenon could be removed from various reactor off-gases, such as air, nitrogen, argon, helium, and hydrogen, and process concentration factors in excess of 1000 could be achieved. The process was subsequently offered commercially for LWR application<sup>[7,8]</sup> but was not really required to meet normal reactor release limits that were in effect at that time.

Based on the demonstrated operability, flexibility, performance, and tolerance for impurities that the fluorocarbon process exhibited for typical off-gas components, efforts were initiated in 1971 to adapt the process to krypton decontamination of LMFBR fuel reprocessing plant off-gas. In concert with the overall LMFBR fuel recycle program at ORNL, a more sophisticated facility was proposed for the expanded program. A new pilot plant was designed in 1972 and put into operation at ORGDP late in 1974<sup>[26,27]</sup>. This test equipment was built to be especially flexible, with the necessary analytical capabilities for overall, as well as detailed, component analysis.

Allied-Gulf Nuclear Services conducted a study of the application of advanced fission gas retention systems to the Separation Facility at the Barnwell Nuclear Fuel Plant. Flow sheets incorporating the fluorocarbon-based krypton absorption process in an overall off-gas decontamination package were subsequently developed and modifications to the Barnwell plant necessary to implement the flow sheet options were determined<sup>[18]</sup>. Nuclear Fuel Services performed a similar study to identify problems associated with providing enhanced fission product containment at the West Valley reprocessing plant<sup>[19]</sup>. These two studies confirmed the overall utility and applicability of the proposed selective absorption process to the decontamination of commercial LWR fuel reprocessing plant off-gas but also pointed out that, in the opinion of the two companies involved, sufficient environmental justification could not be found to warrant installation of noble gas removal equipment.

In 1975, it became apparent that unresolved waste management problems had become detrimental to the continuing development of commercial LWR fuel cycle facilities. After an evaluation of available waste management alternatives, an ad hoc national task force concluded that effective and reliable off-gas decontamination equipment was, in fact, also needed for the removal of krypton-85 from LWR facility off-gas<sup>[1]</sup>. Since there were only minor differences between LMFBR and LWR fluorocarbon process

applications, a joint LMFBR/LWR fluorocarbon process development program was formulated among ORGDP, ORNL, and the Savannah River Laboratory (SRL) to efficiently meet the needs of both reactor fuel cycles. During this same time, it became obvious that the fluorocarbon-based process being developed for krypton-85 removal could also be used for effective, simultaneous removal of carbon-14, as carbon dioxide, and various nitrogen oxides. Available data also indicated that the same process is an effective means for removing iodine, methyl iodide, and water. Consequently, the scope of the fluorocarbon process development effort was broadened to include further definition of this general capability of the process for application to LMFBR and LWR reprocessing plants [28].

Early in 1977, considerable interest was also expressed in the use of alternate fuel cycles, such as the one based on thorium, and various optional reprocessing schemes that would reduce the world-wide opportunity for plutonium diversion. Consequently, in order to keep the program responsive to the needs of the expanded fuel cycle effort, the fluorocarbon process development program was structured to the newly formed Advanced Fuel Recycle Program at ORNL and the Alternate Fuel Cycle Technologies Program at SRL [29]. Radon-222 was identified as a potential off-gas problem for the thorium fuel cycle, and therefore, work was then scheduled to verify that the fluorocarbon process would also be an effective means for removing this nuclide.

All nuclear fuel reprocessing work funded by DOE is currently being managed by ORNL under the Consolidated Fuel Reprocessing Program. The ORGDP fluorocarbon development program is now an integral part of this overall effort. The objective of the ORGDP fuel recycle work is to complete the process development activities and design a demonstration off-gas decontamination facility applicable to several types of reprocessing plants. In order to accomplish this task, the fluorocarbon program was divided into 4 major work areas: (1) process development, (2) process application, (3) solvent chemistry, and (4) reliability analysis. The process development work is generating the process technology required to completely define the fluorocarbon-based process and all associated peripheral equipment. Process application studies are providing the engineering models required for process optimization and demonstration plant design [9,16,31]. This work is identifying flow sheet options and pointing out the relative effects and importance of individual process elements and operating conditions on the overall system function. The solvent chemistry effort is establishing and confirming component solubilities (where these data are not available), phase relationships, component interactions, and corrosion characteristics of the fluorocarbon system. The process reliability studies are assessing the component and system reliability and recommending necessary flow sheet redundancy and backup support systems to ensure a high process on-line efficiency [33].

## II. PROCESS BASIS

Several methods can be considered for reducing noble gas emissions from various nuclear facilities. In general, these operations can be categorized into four groups: (1) delay tanks and selective adsorption techniques using such sorbent materials as charcoal or molecular sieves, (2) cryogenic distillation, (3) selective absorption in liquid solvents, or (4) special techniques such as trapping as clathrates or separation by selective permeation. Suitable chemical processes are not available because krypton and xenon are essentially inert. Delay tanks and adsorption processes are not effective whenever Kr-85 control is demanded as previously discussed. Cryogenic distillation is a well developed commercial process for air separation in the absence of radiation effects and feed gas impurities. When processing radioactive noble gas, however, ozone formation poses a serious threat to the continuous safe operation of the cryogenic equipment. Also, xenon plugging has proven to be a common problem with this type of process when the amount of xenon in the feed gas is large relative to that of krypton, such as is characteristic of the noble gas generated in a reactor. The special techniques are not generally effective for treating dilute gas streams. Additionally, the processes that fall into this classification are not well developed at this time.

The basis of the selective absorption process is, of course, solubility differences which exist between the different gas mixture constituents and the solvent. In this regard, fluorocarbon solvents have been identified as a valuable and somewhat unique group of solvents unusually suited for separating a number of industrially important components from various gas mixtures[14,15]. The solvent preferred for noble gas absorption is dichlorodifluoromethane,  $\text{CCl}_2\text{F}_2$ , commonly referred to as refrigerant-12. This particular solvent was first selected by Steinberg, primarily because of its capacity, separation factors, and thermal and radiation stability, as well as overall process safety and economic features[21,22]. The physical properties of refrigerant-12 are well known. The basic thermodynamic properties are detailed by McHarness, et al[10], and in a duPont technical bulletin[4]. A substantial amount of equilibrium data now exists for krypton and xenon in refrigerant-12 solution. The initial work was performed at the Brookhaven National Laboratory (BNL) by Steinberg. Later work was reported from the University of Tokyo (UT) by Yamamoto and Takeda[34]. The most recent data are given by Shaffer[20] at ORNL. Merriman[17] reviewed the available data and utilized several techniques based on Hildebrand's regular solution theory to estimate krypton and xenon equilibrium coefficients. All available data and Merriman's regular solution estimates are presented in Figure 1. All investigators show good agreement.

Toth, et al[32], recently completed a laboratory study to define the general behavior of other nuclear fuel reprocessing plant off-gas components such as carbon dioxide, various nitrogen oxides, water, iodine, and methyl iodide. Their work shows that carbon dioxide is even more soluble in refrigerant-12 than xenon, and they present detailed solubility data taken over the temperature range of  $-40$  to  $+20^\circ\text{C}$  and with solute concentrations



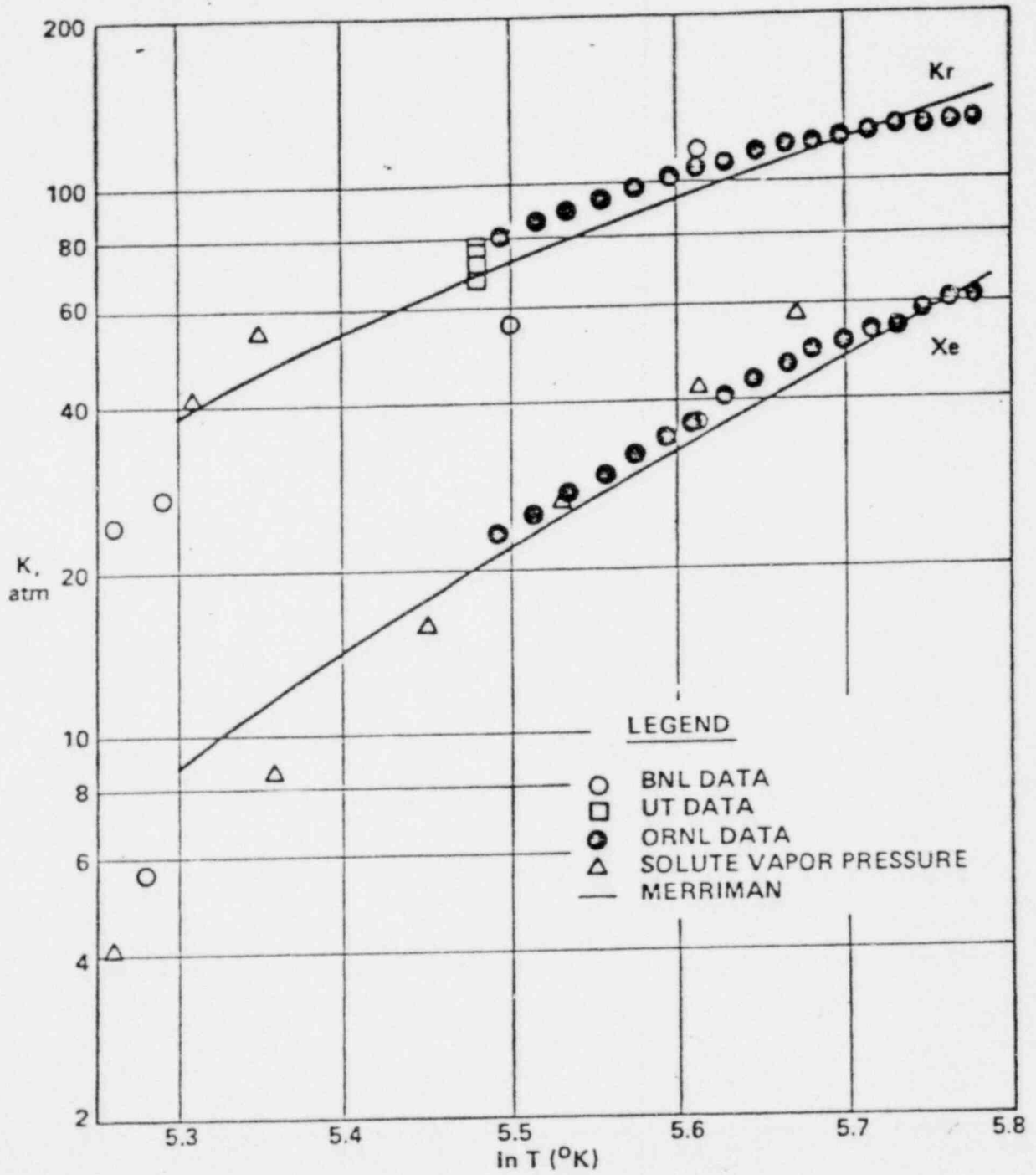


Figure 1

DISTRIBUTION COEFFICIENTS FOR KRYPTON AND XENON IN  $\text{CCl}_2\text{F}_2$

of 3 to 66%. Elemental iodine was found to be fairly soluble in refrigerant-12, while methyl iodide was totally miscible. Figure 2 shows the iodine solubility data of Toth. Beyond this work, some estimated solubility relationships have also been given<sup>[17]</sup>.

Table II summarizes the solubilities of the various components of interest in  $\text{CCl}_2\text{F}_2$ .

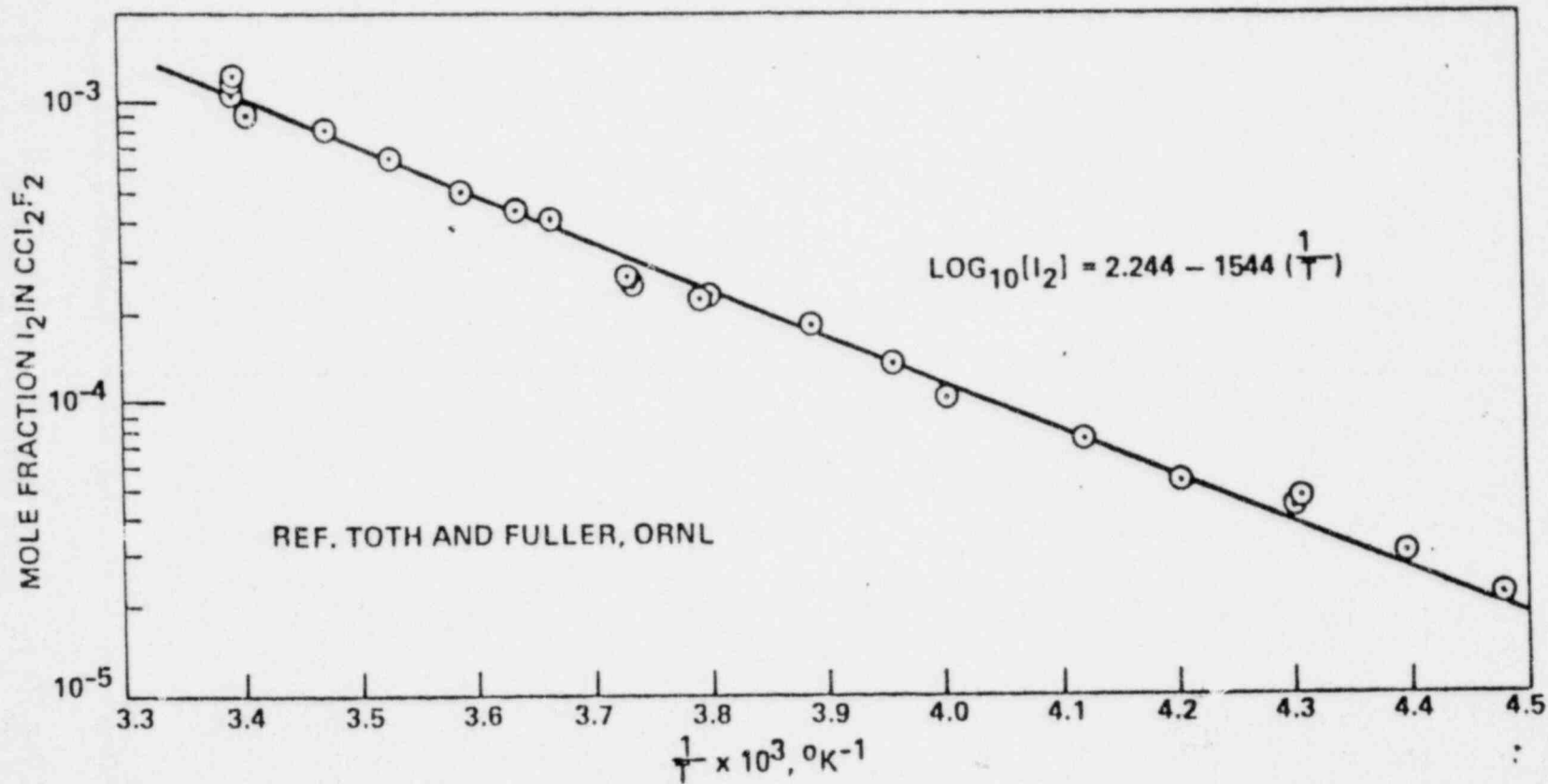


Figure 2  
SOLUBILITY OF  $I_2$  IN LIQUID  $CCl_2F_2$

Table II

SUMMARY OF COMPONENT SOLUBILITIES IN  $\text{CCl}_2\text{F}_2$ 

<u>Component</u>	<u>Solubility<sup>1</sup> mole fraction x 10<sup>4</sup></u>	<u>Reference</u>
H <sub>2</sub>	5.5 <sup>2</sup>	15
N <sub>2</sub>	23	17, 31
O <sub>2</sub>	40	17, 31
CO	41	17
Kr	131	17, 20, 31
O <sub>3</sub>	290	17
Xe	465	17, 20, 31
CO <sub>2</sub>	700	17, 32
I <sub>2</sub>	0.71 <sup>3</sup>	32

1. Based on a solution temperature of -25°F (-31°C) and component partial pressure of 1 atm except as noted.
2. 75°F (24°C)
3. Saturated solution.



## III. PROCESS DESCRIPTION

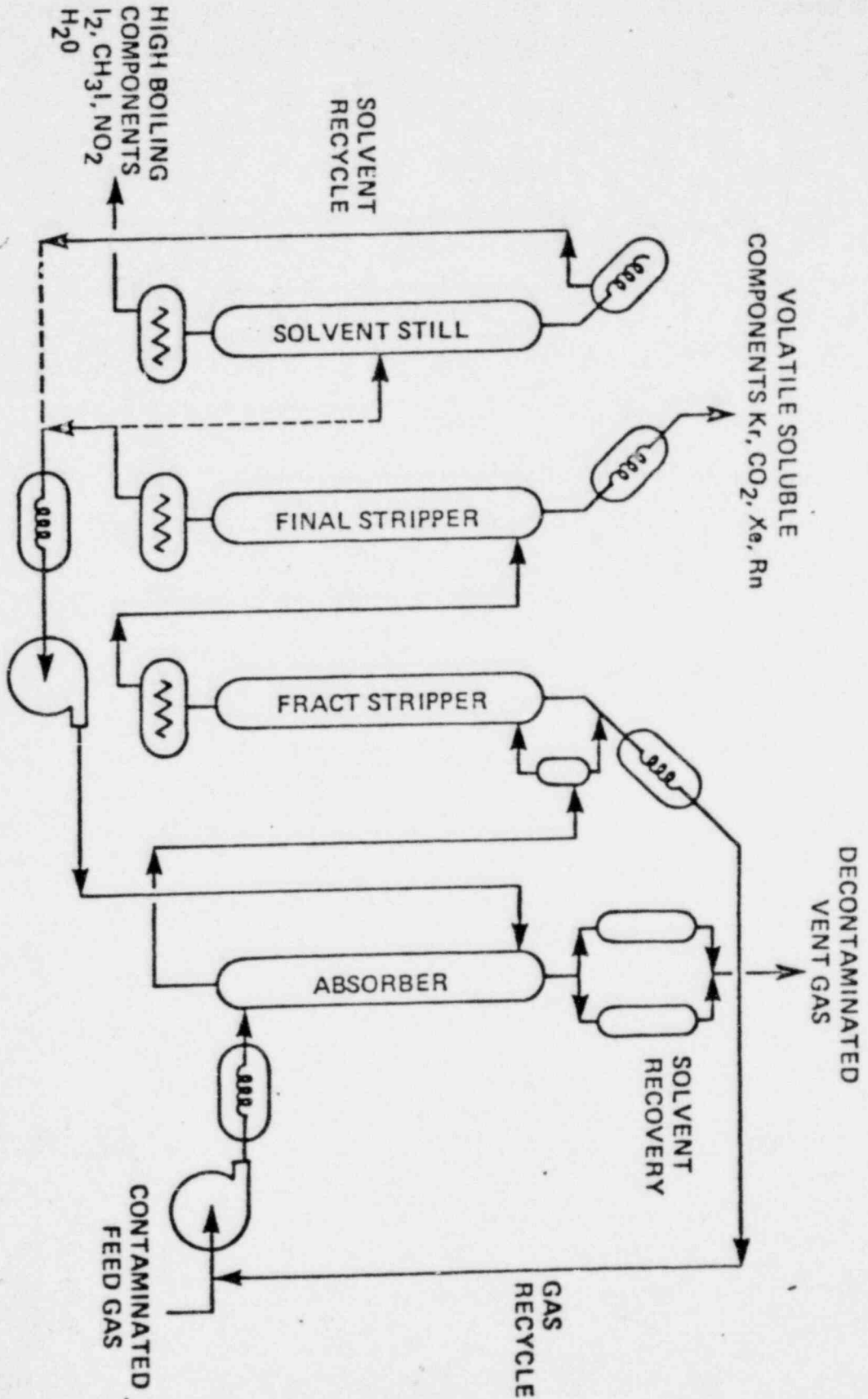
Figure 3 is a schematic of the selective absorption process as it was originally conceived. The process serves to remove volatile radioactive contaminants from various waste gas streams and subsequently concentrate the contaminants for long-term radioactive waste storage. Absorption, intermediate stripping, and final stripping steps must be performed in order to accomplish these two process objectives. Each separation step exploits prevailing gas-liquid solubility differences that are established between the solvent and the various feed gas constituents. The main separation of radioactive components from the bulk gas is effected in the absorber. The intermediate or fractional stripper serves to remove the coabsorbed carrier gas from the solvent, thereby enriching the remaining dissolved gas in the more soluble components. The final stripper removes all remaining gas from the process solvent for collection and regenerates the solvent for recycle back to the absorber. The absorption section consists of only a packed column, reboiler, and overhead condenser. In addition, the intermediate stripper also includes a flash drum. Support equipment items for the basic process include a feed gas heat exchanger, process gas compressor, solvent pump, solvent cooler, storage tanks, and several refrigeration compressors\*. If the feed gas contains significant quantities of high boiling components, i.e., those components that have a vapor pressure less than refrigerant-12, a solvent purification still is available as an in-line option to prevent these materials from building up in the recirculating solvent. A solvent recovery system is necessary to remove solvent vapor from the process off-gas.

Figure 4 shows a photograph of the second generation ORGDP selective absorption pilot plant. This particular plant was put into operation in 1974 and operated for approximately four years. Detailed engineering drawings and descriptions of the facility are given elsewhere [28]. The plant is designed on the basis of handling a nominal 15 scfm of contaminated gas at absorption pressures from 100 to 600 psig and temperatures from minus 45 to plus 25°F. The nominal process solvent flow rate is 1.5 gpm. Approximately 900 to 1000 pounds of solvent is required to charge the pilot plant to normal operating levels.

In the course of the pilot plant operation and analysis, a soluble gas peak was observed in the fractionator column owing to gross internal condensation of the upflowing stripping vapor [31]. Further definition of the internal peaking phenomenon showed that when the internal condensation zone was raised in the column, the magnitude of the soluble gas concentration peak increased dramatically. It became apparent that if sufficient stripping stages were provided below the condensation zone, the final stripping section of the three column process could be eliminated with the product

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\*These equipment items are for a typical plant. An emergency unit might well be different in some respects. For example, an emergency unit would probably use a direct cooling scheme, e.g., via liquid nitrogen, instead of a mechanical system.



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Figure 3  
SCHEMATIC OF THE CONVENTIONAL FLUOROCARBON PROCESS

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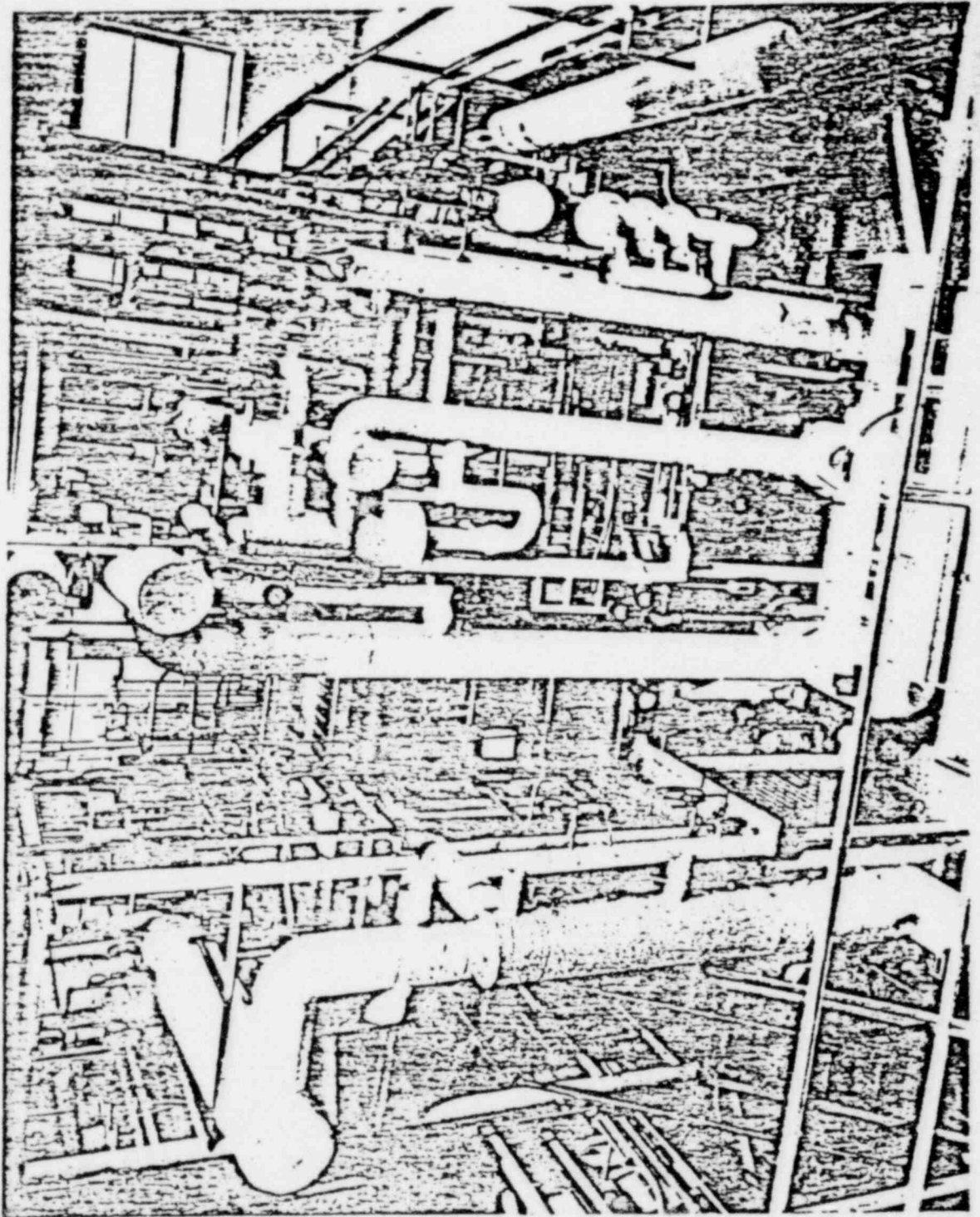


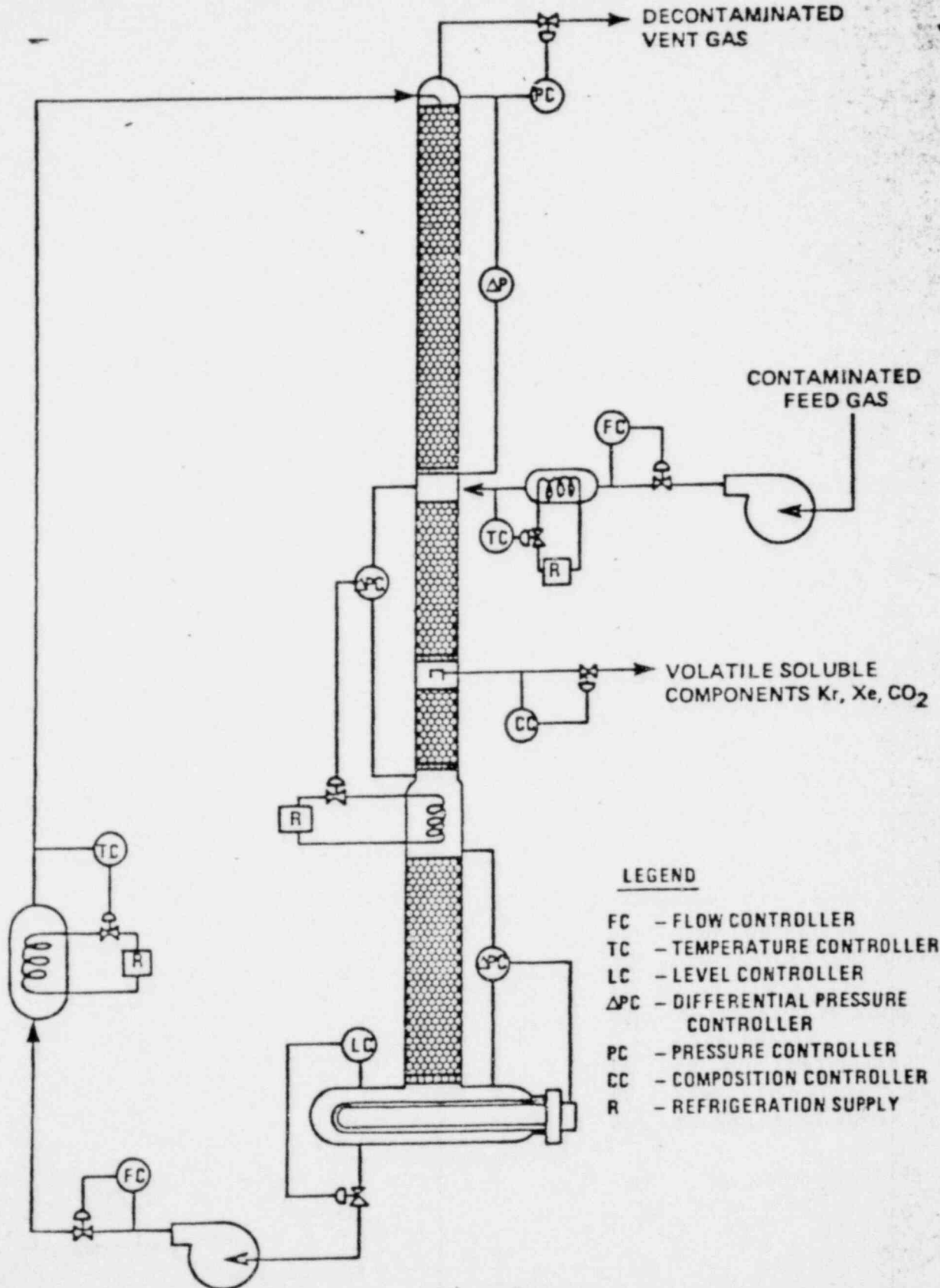
Figure 4  
OVERVIEW OF THE ORGDP PILOT PLANT



being collected as a side stream. Furthermore, it also seemed feasible to place the intermediate section directly below the absorber and operate the entire assembly at a common pressure. Subsequently, a single column was designed that combined the three functional steps of absorption, fractional stripping, and final stripping into a continuous contactor [30]. Figure 5 gives a schematic of this piece of equipment. Decontaminated off-gas flows from the top of the combination column and regenerated solvent from the bottom, while the fission product gases are collected as a side stream. The combination column requires substantially less equipment and control instrumentation than the conventional flow sheet, and because of its greater simplicity, it offers numerous operational and economic advantages. Because of its potential and design uncertainties, a combination column was recently built and installed at the ORGDP for evaluation [29]. Figure 6 is a photograph of the column taken during construction. The column is approximately 24 feet tall and has the same flow capacity and performance capability as the three-column development facility. The absorber and intermediate sections are again 3 inches in diameter, while the final stripper is 6 inches. High efficiency, wire mesh column packing is used in all sections of the column. Pilot plant test results clearly show that scale-up on the column area is direct for this particular packing as long as well designed gas and liquid distributors are employed [9]. Hence, larger flow equipment can be designed with confidence using the same type of column material.

The combination column has been undergoing performance evaluations for almost 1 year. These tests not only established the overall feasibility of the concept, but showed conclusively that the combination column could perform nearly as well as the separate three columns. On the basis of a one-to-one comparison of the two options, the combination column was recently selected as the preferred version of the process for the reprocessing plant application and, similarly, would probably be recommended for the emergency unit.





LEGEND

- FC - FLOW CONTROLLER
- TC - TEMPERATURE CONTROLLER
- LC - LEVEL CONTROLLER
- ΔPC - DIFFERENTIAL PRESSURE CONTROLLER
- PC - PRESSURE CONTROLLER
- CC - COMPOSITION CONTROLLER
- R - REFRIGERATION SUPPLY

Figure 5  
SCHEMATIC OF THE COMBINATION COLUMN

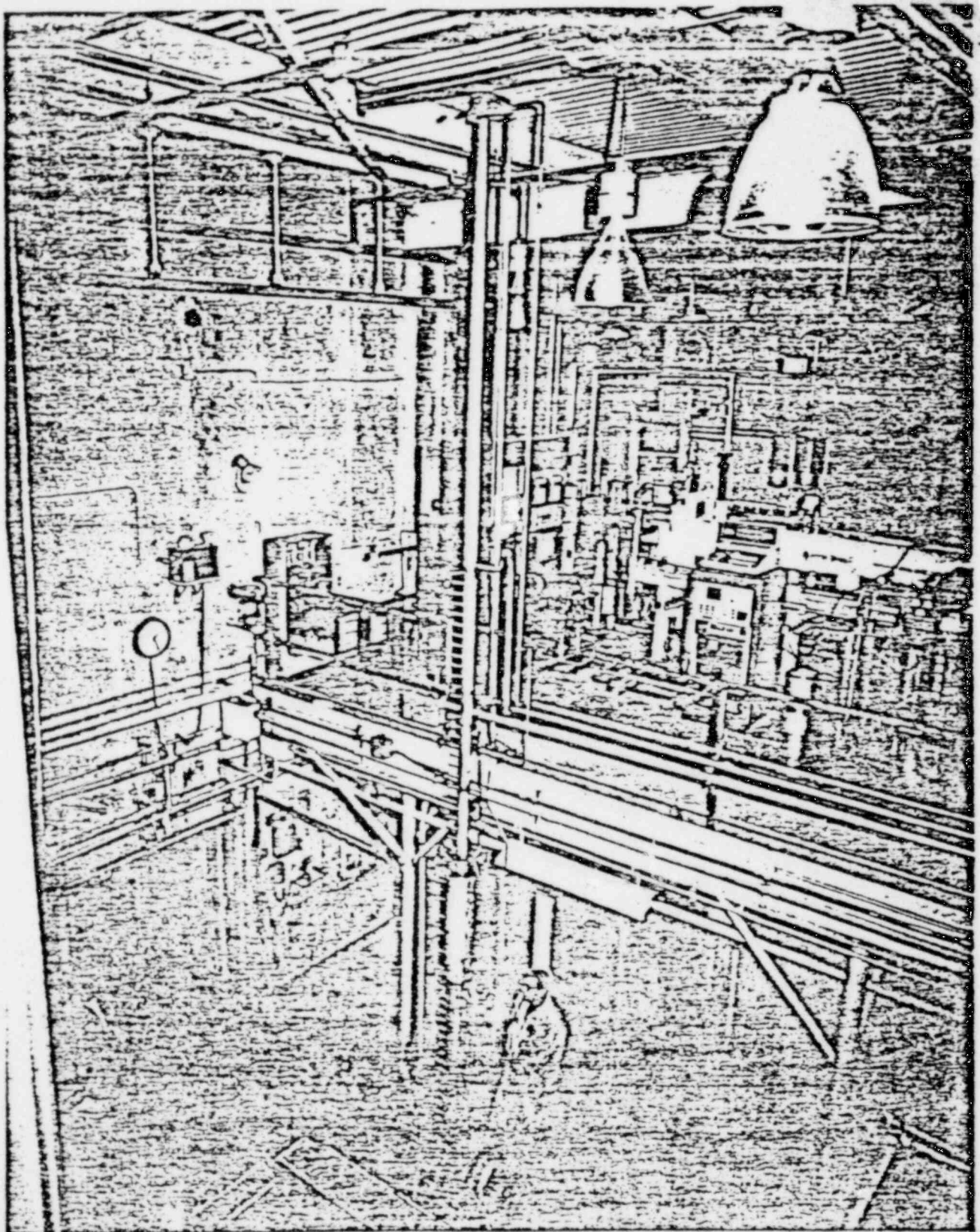


Figure 6  
OVERALL VIEW OF THE COMBINATION COLUMN DURING CONSTRUCTION

## IV. PROCESS DESIGN CRITERIA

The decontamination process throughput, fission product recovery, and radioactive product purity have to be specified before equipment design can be initiated. Usually, an economic balance would be established between the cost of removing the noble gas from the reactor following an accident and the cost of the reactor downtime. In this case, however, there may be overriding safety and social ramifications which dictate that the decontamination process proceed posthaste. The process decontamination factor is contingent upon the particular processing scheme but must at least be high enough to meet applicable federal release regulations. To illustrate some of the trade-offs, if the decontamination process off-gas is recycled back to the reactor containment, lower single pass decontamination factors are permissible. Also, if the concentrated radioactive product is relatively pure, fewer gas cylinders will be generated for long-term radwaste storage.

Figure 7 presents decay curves for krypton-85 and xenon-133 in the containment shell of a 1000 MWe reactor following the total release of the reactor core inventory after full power operation for 500 days. The total activity in the containment shell will be near  $2 \times 10^8$  curies after 1 day of cooling. Most of this radiation will be due to xenon-133. After 42 days, krypton-85 will become the dominant source at  $6.6 \times 10^5$  curies. The amount of krypton-85, unlike the generation patterns of the short-lived isotopes, increases substantially with fuel burnup. After 1100 days of operation, for instance,  $1.1 \times 10^6$  curies will be present[2]. This radiation source will remain at virtually the same level for many years thereafter if the containment volume is not purged.

In the absence of a suitable decontamination system, the containment gases would have to be held for about two months to give the short-lived isotopes sufficient time to decay. The krypton might then be slowly vented if both atmospheric conditions and public relations were favorable. At a discharge rate of  $10^3$  curies per day, over 600 days would be required in this case to vent the reactor inventory. The krypton-85 release, however, would be in violation of EPA standard 40 CFR Part 190 which states that the total quantity of radioactive materials entering the general environment from the entire fuel cycle must contain less than 50,000 curies of krypton-85 per gigawatt-year of electrical energy[6]. Thus, slow venting does not seem to be an acceptable alternative.

Use of an effective noble gas removal process in conjunction with the decay phenomenon will allow rapid removal of the containment activity following an accident. A central sizing issue is the combination of flow rate and single-pass decontamination factor required to reduce the curie loading within the reactor to a specified level in a given time. Figures 8 and 9 show krypton-85 and xenon-133 activity levels as a function of elapsed time after release to the reactor containment and various processing rates. These calculations assume that the radioactivity will be removed simultaneously by radioactive decay and a noble gas recovery facility. The decay mechanism,

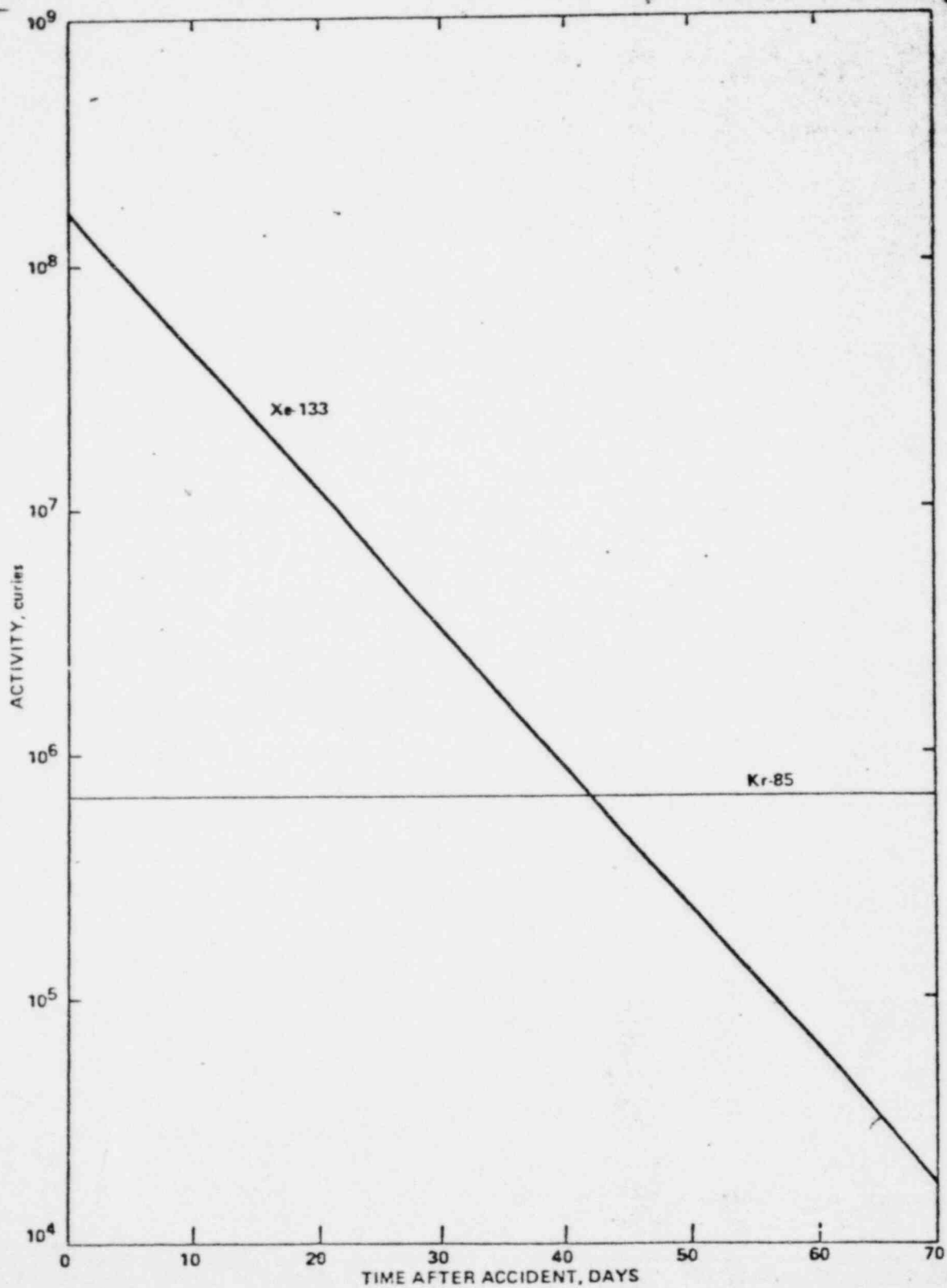


Figure 7

DECAY OF NOBLE GASES FOLLOWING REACTOR ACCIDENT



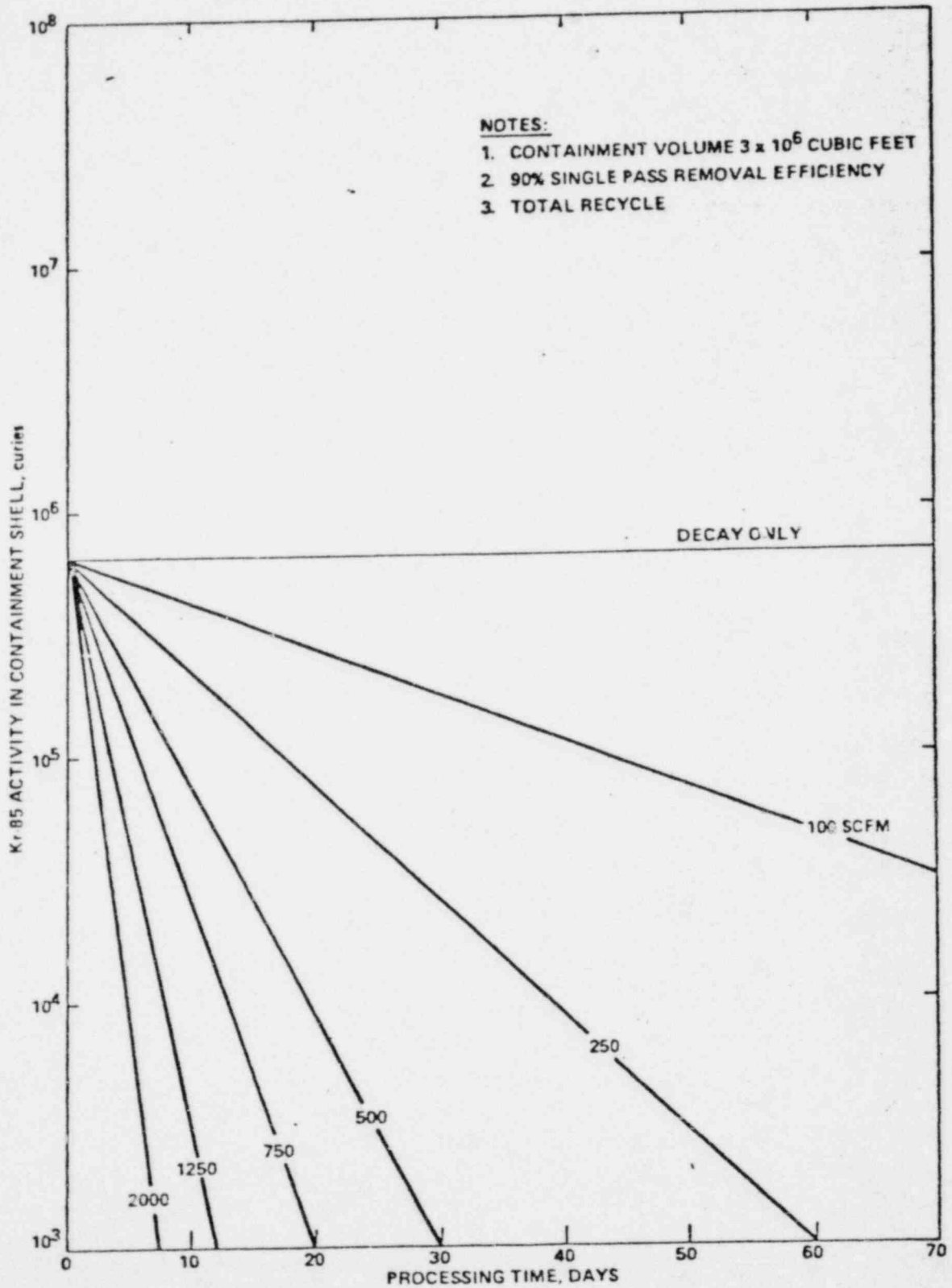


Figure 8  
REMOVAL OF Kr-85 FROM REACTOR CONTAINMENT  
AS A FUNCTION OF PROCESSING TIME AND RATE

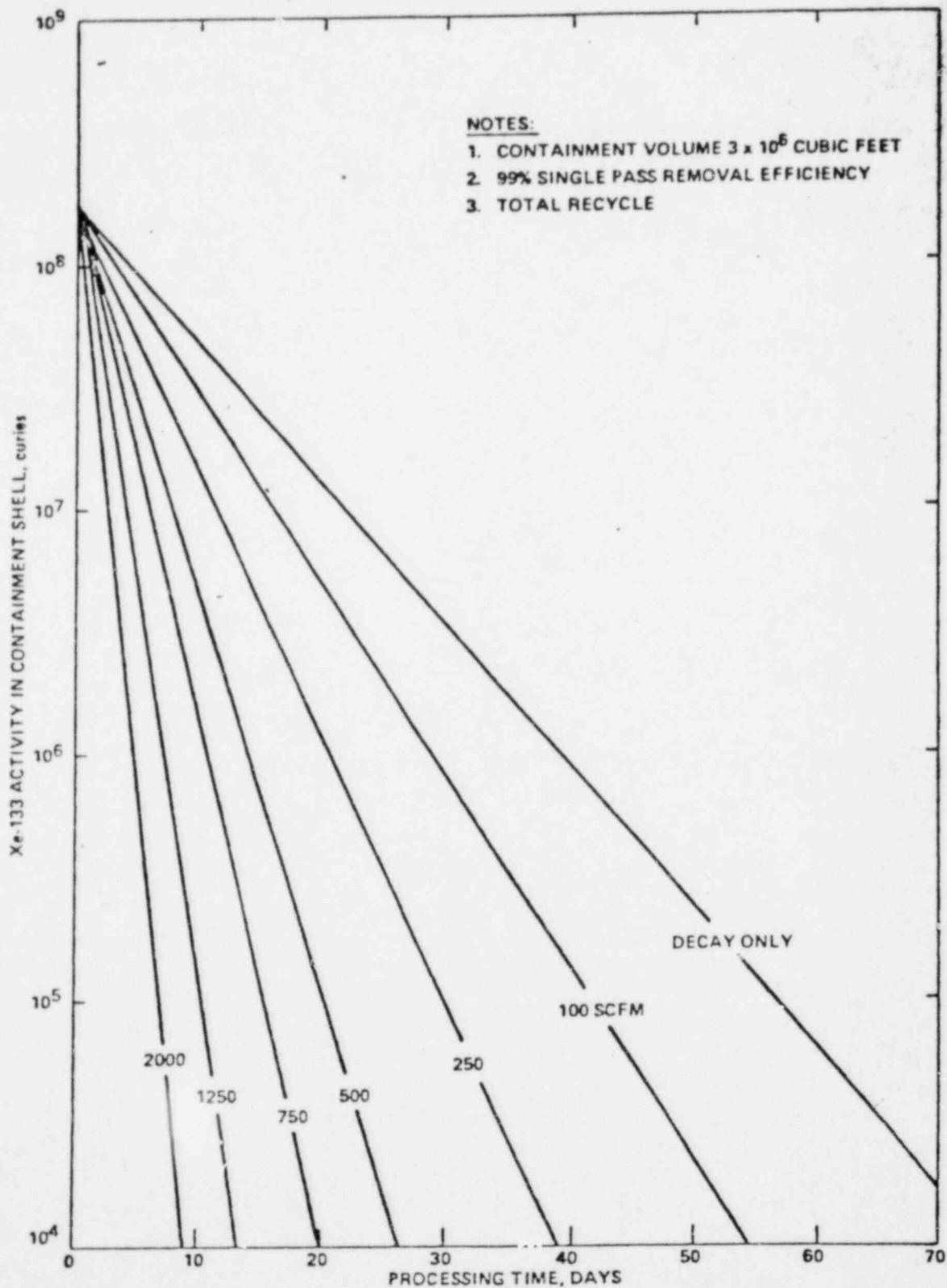


Figure 9

REMOVAL OF Xe-133 FROM REACTOR CONTAINMENT  
AS A FUNCTION OF PROCESSING TIME AND RATE

of course, will have little effect on the removal of krypton-85. The recovery facility, in this case, would recycle the processed gas back to the containment vessel following 90 percent recovery of the krypton and 99 percent of the xenon. At a processing rate of 250 ft<sup>3</sup>/min, about 39 days would be required to get both the krypton-85 and xenon-133 containment activities down to 10<sup>4</sup> curies. Increasing the processing rate to 500 ft<sup>3</sup>/min reduces this time to 19 days for krypton and 26 days for xenon, while 1250 ft<sup>3</sup>/min requires only 8 days and 13 days, respectively. Increasing the single-pass removal efficiency of the recovery process will also reduce the processing time and/or will allow the use of a smaller throughput system. The fluorocarbon process can typically remove 99 percent of the feed gas krypton and 99.9 percent of the xenon.

A preliminary schematic of the proposed processing system is shown in Figure 10. The contaminated gas, withdrawn from the reactor containment, turbine, and/or auxiliary buildings, will first be filtered to remove possible particulates, compressed to approximately 125 psig, and then cooled to near -30°F. The bulk of the reactor airborne tritiated water and iodine will freeze on the heat exchanger surfaces and thereby become immobilized. Trace amounts of water remaining in the feed gas will be adsorbed on 3A molecular sieves. Next, the reactor gas will be fed into the absorption section of the combination column and contacted countercurrently with downflowing solvent. The decontaminated gas leaving the top of the column, containing 5 to 10 percent refrigerant-12, will be passed through a turboexpander and 13X molecular sieve bed for solvent recovery. Alternatively, a low temperature condenser might be used to effect the same separation. The process off-gas can be recycled or vented at this point, depending upon the noble gas concentration. Initially, all gas will be recycled. The solvent containing the dissolved gases will subsequently flow into the intermediate and final stripper sections of the column. Regenerated solvent will be pumped back to the top of the column. If the solvent contains trace quantities of water and iodine, a 4A molecular sieve and/or silver impregnated zeolite will be used to further decontaminate the solvent prior to recycle. At a total pressure of 125 psig, the reboiler will operate at around 104°F. A solvent heat exchanger will be used to cool this stream down to -30°F. Exact equipment arrangements would, of course, be determined as a part of this project.

The amount of noble gas present in the reactor will depend upon the fuel exposure and the reactor specific operating power level. Figure 11 presents calculated PWR krypton and xenon generation rates for a power level of 30.0 MW/MTU[2]. Most of the krypton and xenon will be stable and isotopic decay will have little effect on the bulk concentrations. After 500 days of operation, 180 standard cubic feet (4900 liters) of krypton and 1400 standard cubic feet (40,000 liters) of xenon will be present. If all of the core gases are released into a 3 x 10<sup>6</sup> cubic foot reactor containment shell, the resulting volume will contain 60 ppm krypton and 470 ppm xenon. The noble gas product will be pulled as a combination column side stream. Solvent removal will be achieved by adsorption on 13X molecular sieves. The product flow rate will be less than 0.1 percent of the process feed rate. Provisions will have to be made for long-term storage of about

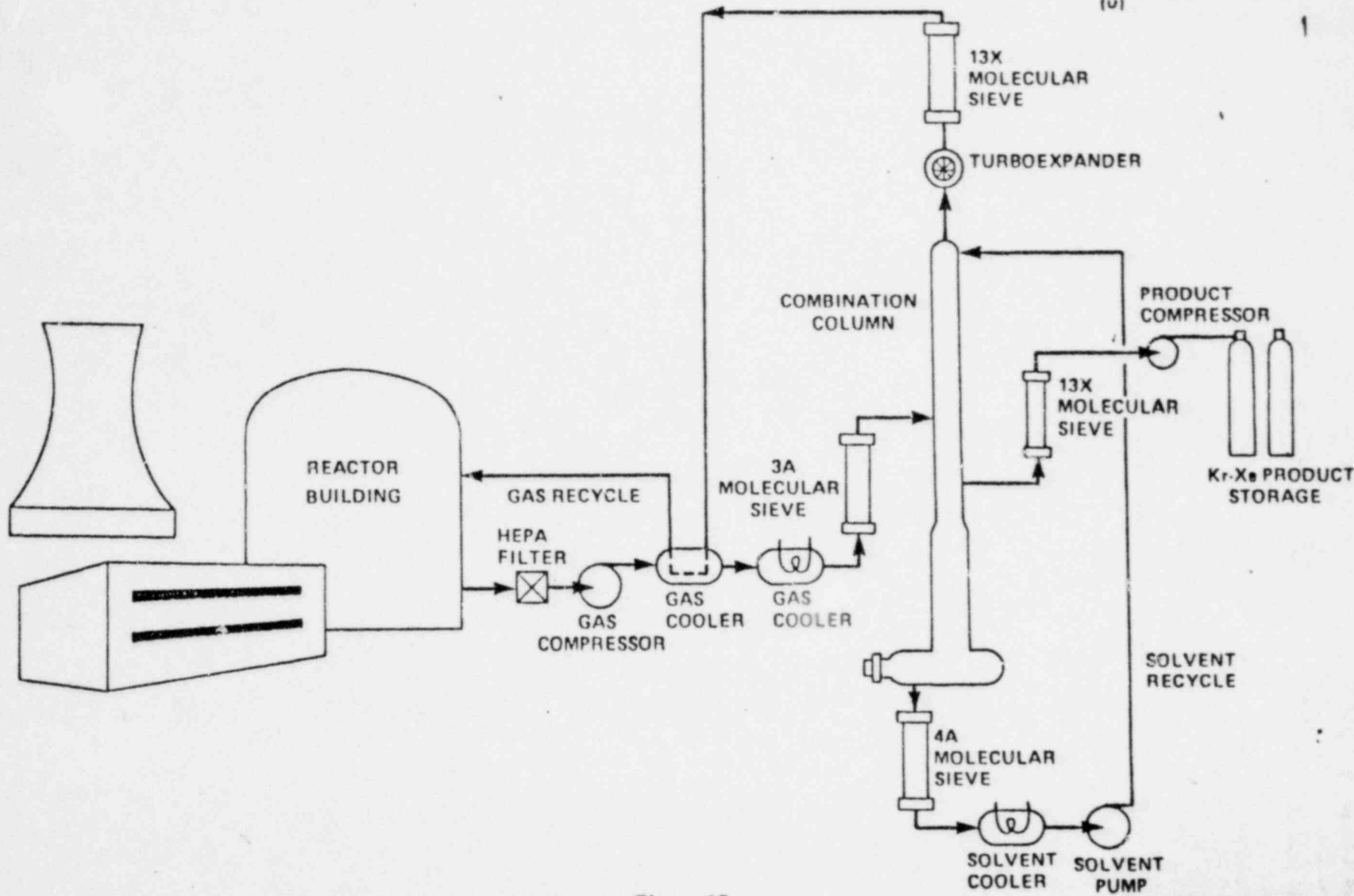


Figure 10  
SCHEMATIC OF THE FLUOROCARBON REACTOR DECONTAMINATION PROCESS

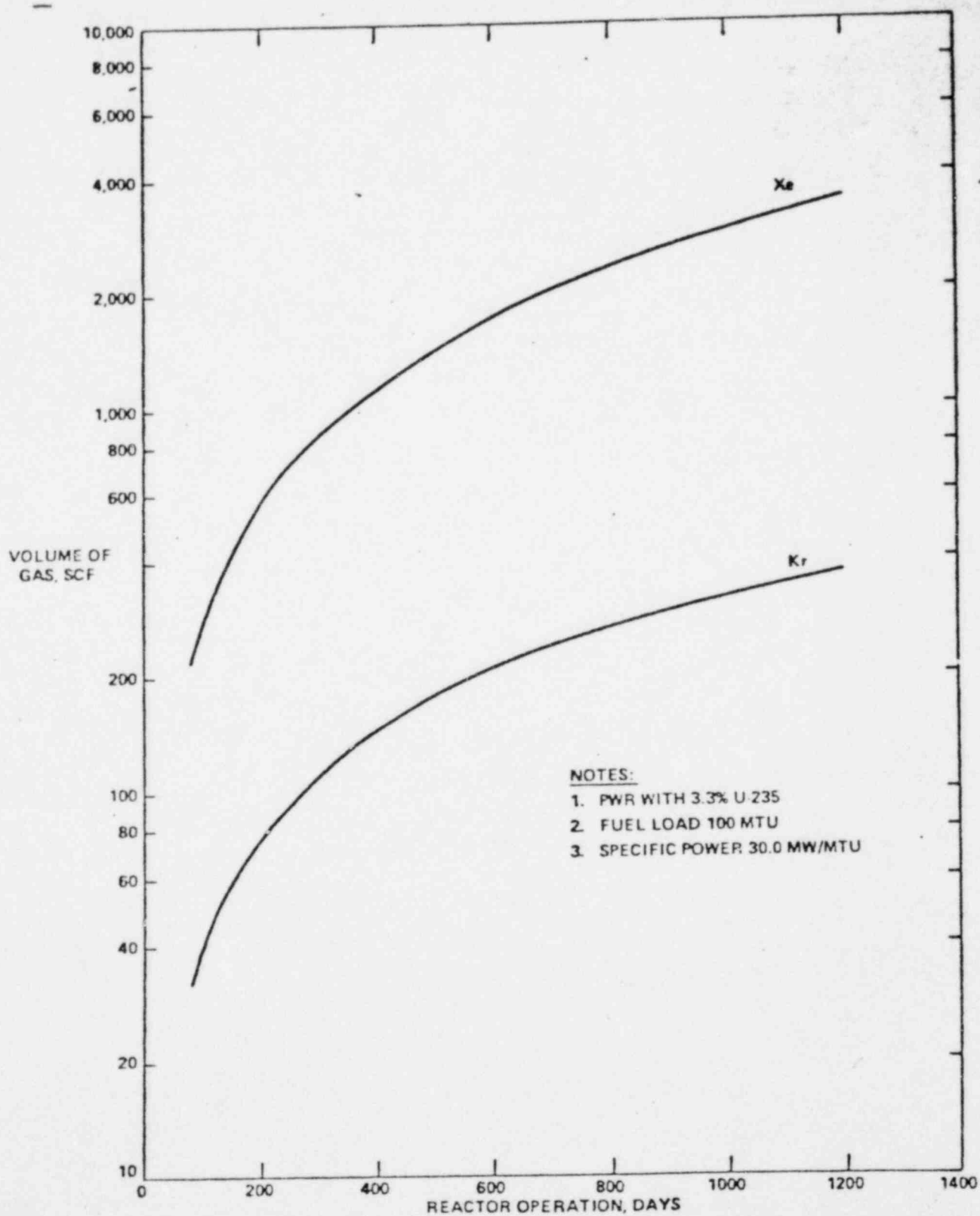


Figure 11  
QUANTITY OF NOBLE GAS GENERATED IN A PWR  
AS A FUNCTION OF REACTOR OPERATING TIME



1600 ft<sup>3</sup> of radioactive product gas. A generally applicable and acceptable method for management of the gaseous waste is encapsulation in high-pressure cylinders and storage in a suitable repository<sup>[1,3]</sup>. In this case, the noble gas will be held in standard 1A high-pressure gas cylinders, 9 inches in diameter by 52 inches high. This type of cylinder has an internal volume of 1.54 cubic feet (43.8 liters) and is normally filled to a pressure of around 2000 psig. Xenon is fairly compressible at 150°F, with a compressibility factor ( $z = PV/nRT$ ) reaching a minimum of 0.50 at 2000 psig. Figure 12 gives the number of cylinders required to contain the noble gas generated by a PWR after full power operation for 100, 500, and 1000 days as a function of cylinder pressure. For example, 5 cylinders will be required if the reactor has been in operation for 500 days prior to the core release and the gas is stored at a pressure of 2000 psig and temperature of 150°F.

The amount of radioactivity contained in the cylinders will decrease rapidly as the xenon and short-lived krypton isotopes decay, until the krypton-85 source is left. Then, a total of  $6.6 \times 10^5$  curies will be present in the example case. Nearly 1 inch of lead would be required to reduce the external Kr-85 dose rate to 10 mrem/year at 1 meter from the surface. Correspondingly, the krypton-85 activity will result in a heat load of near 700 Btu/hr/cylinder of the noble gas mixture.

Biological shielding and heat dissipation will necessitate the use of water-filled storage and shipping casks. Blomeke and Perona<sup>[3]</sup> present the details of such a cask in Figure 13. The cask is 5 feet in diameter and is fabricated from 1-inch-thick, type 304 stainless steel. The water provides shielding and serves as a heat transfer medium. External fins enhance heat dissipation. The design meets applicable impact, puncture, and fire resistance specifications for shipping capsules for curium oxides. A 200 psig rupture disc is provided as a safety measure in addition to 16 fusible plugs, which are designed to allow steam to escape in case of fire. In addition, a vapor space is provided sufficiently large to hold the contents of a leaky cylinder without exceeding the cask pressure limits. Each cask can accommodate about 5 cylinders of krypton-xenon mixture. A loaded assembly would weigh about 7 tons.

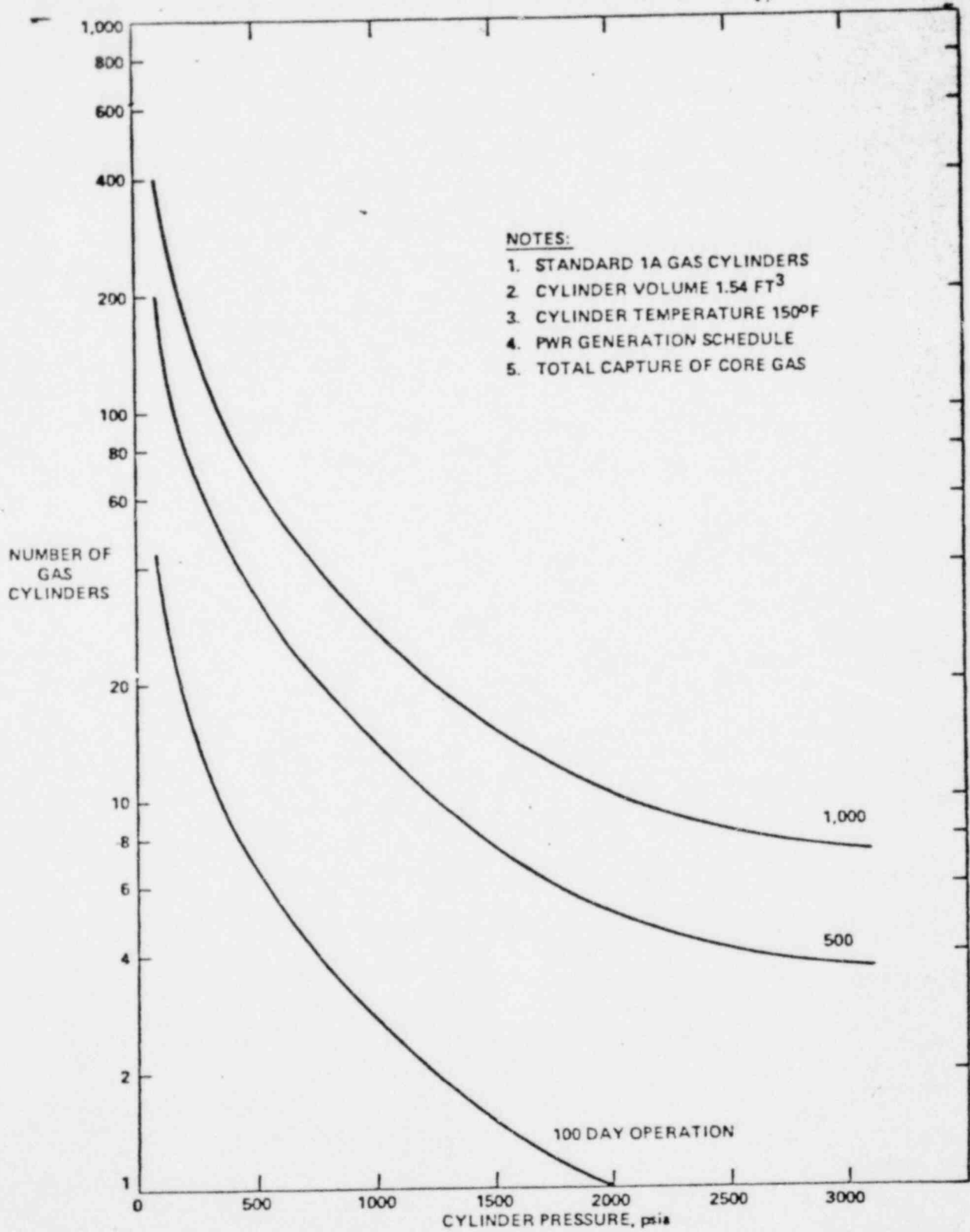


Figure 12

NUMBER OF GAS CYLINDERS REQUIRED TO STORE PWR NOBLE GAS AS A  
FUNCTION OF REACTOR OPERATING TIME AND CYLINDER STORAGE PRESSURE

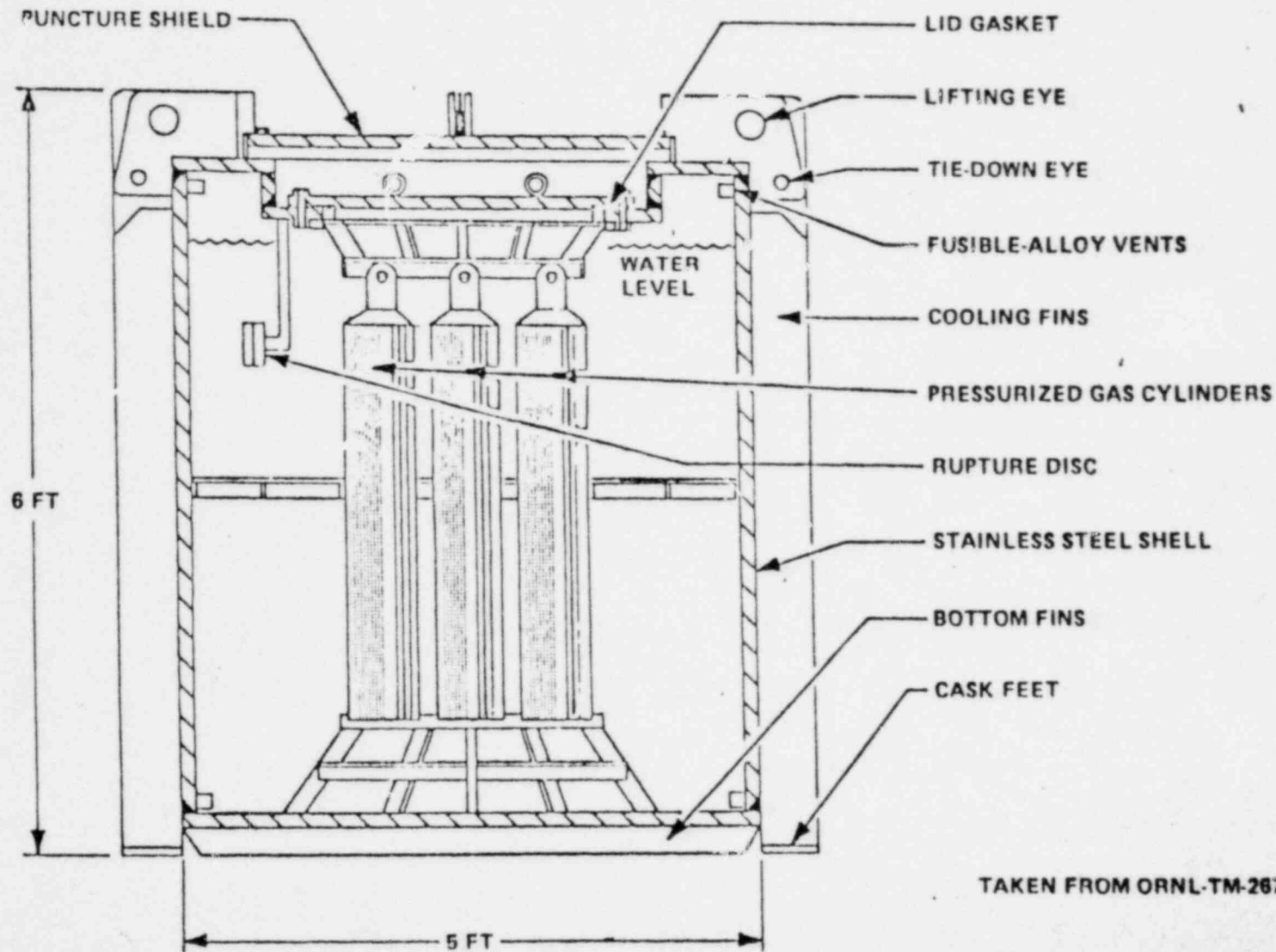


Figure 13  
CONCEPTUAL DESIGN OF SHIPPING CASK FOR CYLINDERS OF COMPRESSED  
FISSION-PRODUCT GASES

## V. WORK PROPOSAL

A fluorocarbon-based process has been developed that is capable of efficiently removing krypton and xenon from various nuclear off-gases. The process can also remove carbon-14, as carbon dioxide, and iodine. Several process applications have been made during the past several years. Extensive pilot plant testing has been performed and rigorous design models have been developed. Sufficient process performance and operational information now exists to allow detailed design of an emergency reactor decontamination process with high confidence of reliable, efficient operation.

The program outlined here encompasses four main phases: conceptual studies, detailed design, system construction, and system validation testing. There are logical "go-no-go" opportunities after the first two. The conceptual study phase is considered particularly important. In addition to the normal conceptual design work related to the krypton-xenon unit itself and the associated trade-off studies (size, decontamination factor, location, etc.), this phase will provide an opportunity to place the post-accident krypton-xenon problem in clearer perspective and secure a better understanding of the desired solution.

As regards the approach to this project, it is anticipated that:

1. UCC-ND will provide:

- a. Criteria and technical requirements for an emergency reactor decontamination system.
- b. Technical management for the design, procurement, and erection of the prototype system.
- c. Operating contractor procurement services, quality assurance, and quality control services during system fabrication and erection.
- d. Required environmental and safety assessments and analyses.
- e. Preliminary testing and certification of prototype system performance.
- f. Definition of the operating philosophy and applicable operating procedures and guidelines for ultimate emergency operations.
- g. Requirements definition for the continued performance testing, maintenance, staffing, and operator training that will be needed in the actual deployment of the system.
- h. Preparation of the actual system for its ultimate deployment.
- i. Systems engineering analysis.



2. An architect-engineer will:
  - a. Produce a conceptual design and preliminary cost estimate in cooperation with UCC-ND.
  - b. Assume the major evaluation role in assessing the required interfaces with the reactor types that might be serviced by the system.
  - c. Prepare the Title II design drawings and design documentation.
  - d. In cooperation with UCC-ND, prepare a procurement package for the commercial fabrication of the system.
  - e. In cooperation with UCC-ND, prepare a cost estimate for the system.
  - f. Assist UCC-ND in the preparation of required quality assurance assessment and planning.
3. The Oak Ridge CPAF construction contractor will provide any required erection services and procurement related to those services, as appropriate.
4. A vendor, selected by competitive bidding, will fabricate the system in transportable modules.

During the conceptual design phase, two alternative concepts will be evaluated; one will be based on the mobile or "fire wagon" approach, while the other will be a stationary unit that could become an integral part of each reactor's emergency equipment. One of these concepts will then be selected for detailed design. The single-pass removal capability of the plant assumed in the baseline design will be 90% of the krypton and 99% of the xenon. Corresponding iodine and tritium removals will be in excess of 99.99%. A prototype will then be fabricated and installed at the ORGDP. The design and construction phases will proceed under the scrutiny of an approved quality assurance program and will conform to the codes and standards specified by the customer. Overall system reliability and availability will be emphasized. Once the prototype has been fabricated, operability and performance of the unit will be thoroughly established. Appropriate reactor interfaces will be determined. Optimum or preferred operating conditions and formal procedures will be provided. The requirements for maintenance, operator staffing, and necessary staff training will be specified.

## VI. SCHEDULE AND COST

This program will produce an emergency reactor decontamination system, ready for deployment. This objective will be accomplished in four phases. The first phase will define the system criteria and requirements, provide the preliminary safety and environmental assessments and analyses as required, and produce a conceptual design and cost estimate. The second phase will produce the definitive design documents, the procurement package(s), and the final safety analysis (FSAR). The third phase will include the vendor fabrication and subsequent erection of the system at a test site at the ORGDP. The fourth phase will include operational testing, performance certification, and the necessary actions to make the system ready for deployment.

The schedule, as depicted in Figure 14, is quite tight in spite of a 4-1/2-year space. Some compression might be possible by overlapping phases so that procurement could proceed during the latter phases of design; however, this would compromise the concept of placing a clearly defined contract with a fixed-price vendor. Such an action might reduce the total time to 4 years. Other reductions might be made if certain standard requirements are waived.

The costs for the system are based on extrapolations of earlier estimates produced by UCC-ND and others [18,19]. They are believed to be reasonably conservative; however, they could be altered dramatically by unanticipated customer or regulatory requirements. It should be noted that the schedule does not include gaps or intervals for review and approvals. It is anticipated that these actions will occur on a continuing, concurrent basis during the course of this important project.

The estimates anticipate that (1) the project will be performed under the normal DOE cost accounting rules (not full cost recovery); (2) the preliminary environmental assessment will validate the assumption that an environmental impact statement is not required; (3) the program does not include the cost of the facilities required for the long-term support of the system (a reference design and description will be provided); (4) a generic assessment of reactor interfaces will be adequate (rather than a detailed reactor-by-reactor design definition); (5) the system will not be required to become a part of the reactor containment; (6) no program-supported facilities will be provided for the disposal of radioactive materials resulting from the emergency operation of the system; and (7) close, mutually supportive cooperation, of the type normally maintained in the DOE system, can be carried out between the customer, the operating contractor, the architect-engineer, the system fabricator, and the system erector. As summarized in Table III, the definition phase is estimated to cost \$500,000; the total UCC-ND and A-E engineering package \$2 million; the fabrication and erection phase \$5 million; the verification phase \$500,000; and total cost \$8 million (all in FY 1979, second quarter dollars). The total cost, escalated to the year of expenditure, will increase to nearly \$11 million.

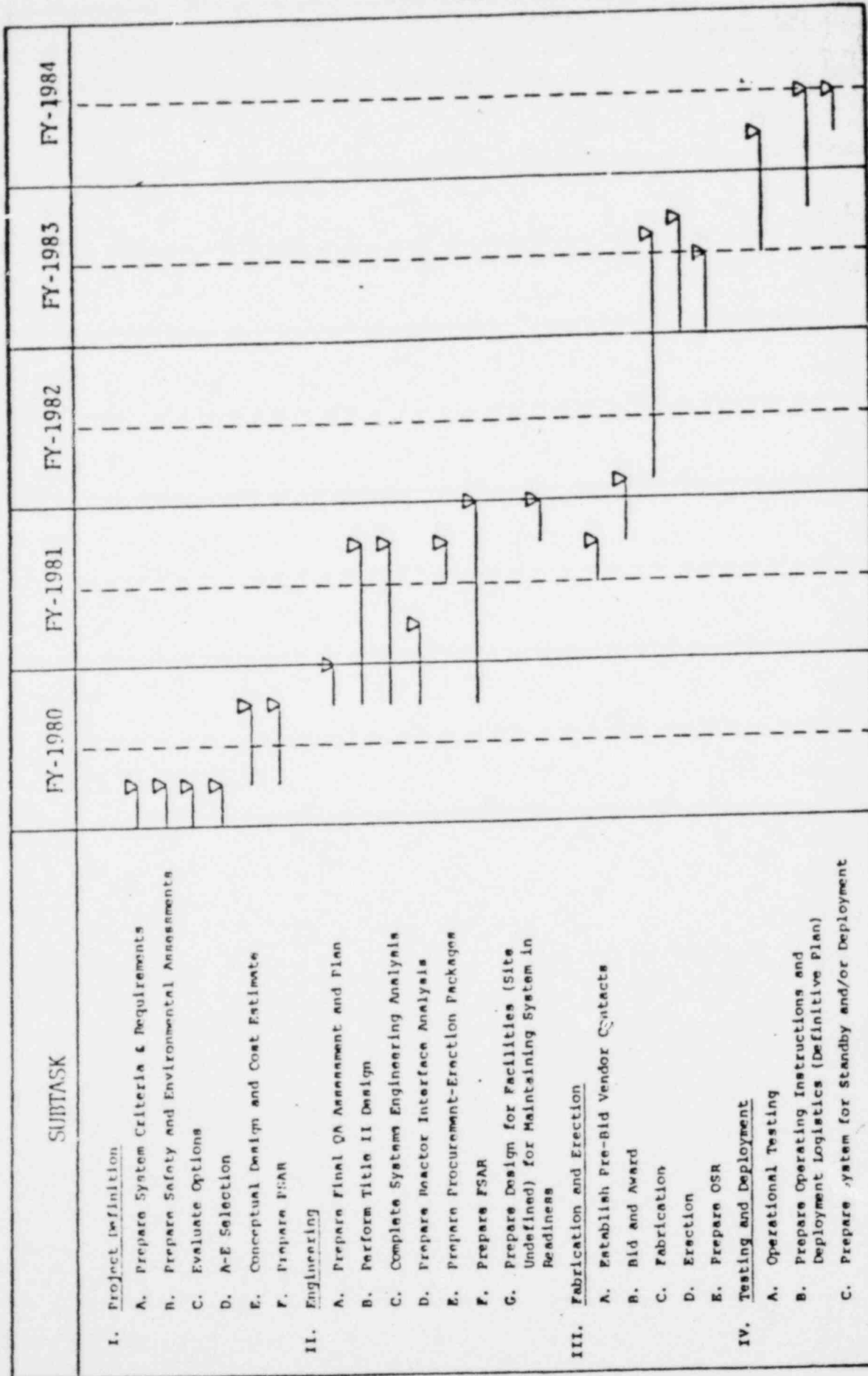


Figure 14  
SUBTASK SCHEDULE

Table III

## ANTICIPATED PROGRAM COSTS BY ACTIVITY AND YEAR (\$1000)

	FY-80	FY-81	FY-82	FY-83	FY-84	TOTAL
I. Project Definition (Criteria, Conceptual Design)	500	-	-	-	-	500
II. Engineering Design, Documentation, Title II	300	1000	400	250	50	2000
III. Fabrication and Erection	-	-	2000	3000	-	5000
IV. Testing and Deployment Preparation	-	-	-	250	250	500
Total \$, FY-79 (2nd Quarter)	800	1000	2400	3500	300	8000
Escalated to year of expenditure	900	1200	3200	5000	500	10800



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Iny du

March 28, 1980

not coded

General Public Utilities  
100 Interpace Parkway  
Passippany, NJ 07054

Attention: Mr. Herman Dieckamp

Dear Mr. Dieckamp:

I offer my humble solution to the removal of the so called 40,000 curies of krypton gas from the Three Mile Island vessel. I feel certain this can be removed inexpensively with the least amount of objections by citizens or environmentalists and above all the most safe yet suggested.

- 1) The use of large balloons capable of travel to the stratosphere and large enough to transport a containment vessel capable of carrying an appreciable amount of the gas under pressure.
- 2) After the balloon reaches a high enough altitude, relief valves on the containment vessel can be released by radio control, and later the balloon can be destroyed by explosives.

This can further solve the apparent transportation problem if an effort is made to transport the gas by land. ie. (citizens objecting to or accidental discharge).

I needn't explain the further repercussions or costs connected with release of the gas in the atmosphere directly above the Three Mile Island plant.

Perhaps this could be the only safe solution and certainly should be considered.

Sincerely,

Albert B. Snizik

ABS/ds

cc: N. R. C. - Attn: Harold Denton

Governor Richard Thornburgh

Robert Arnold - Executive Vice President, N. R. C.



J. A. Van Vechten  
R. J. Gambino  
J. J. Cuomo

Not coded

## Encapsulation of Radioactive Noble Gas Waste in Amorphous Alloy

*Public demand for the containment and safe storage of radioactive waste materials has caused the U.S. Government to require that, beginning in January 1983, most of the  $^{85}\text{Kr}$ , which until now has been vented to the atmosphere during the reprocessing of nuclear fission fuel rods, will have to be captured and retained for several decades. The cost of accomplishing this with present compressed-gas technology is enough to increase the cost of nuclear generated electricity by an estimated 0.3%. However, materials developed for amorphous magnetic bubble memory devices have been found to be capable of storing large quantities of Kr (30 atomic percent) with great stability up to temperatures above 1070 K. The cost of  $^{85}\text{Kr}$  storage in the magnetic bubble memory material appears to be less than 1% of that for present compressed-gas technology.*

### Introduction

The problem of safe disposal of radioactive wastes from nuclear fission power plants is a major obstacle to the continued and expanded use of fission reactors. Perhaps the most difficult radioactive fission product to capture and contain is an isotope of the noble gas Kr,  $^{85}\text{Kr}$ , which has a half-life of 10.7 years and emits  $\beta$ -particles at energies up to 0.67 MeV and  $\gamma$ -rays at 0.5 MeV [1, 2]. Unlike most other fission products, it is neither solid (above 121 K) in its elemental form nor can it be reacted to a stable solid compound. Although heavier than air, it mixes thoroughly in the atmosphere; if released even in a deep mine shaft, it would quickly diffuse into the atmosphere. It also diffuses rapidly through water and earth. It is produced in about 0.3% of all  $^{235}\text{U}$  fission events. This is about 6% of the Kr and 0.8% of the noble gas produced by fission of  $^{235}\text{U}$ . (The other major noble gas produced is Xe.) Almost all processors of nuclear fuel around the world have allowed these radioactive gases to escape to the atmosphere. (It should be noted that essentially all the Kr is released in reprocessing; less than 1% is released from the reactor [3].) One exception is the Chemical Processing Plant at the Idaho National Engineering Laboratory, Idaho Falls, which is operated by Allied Chemical

Corp. and which has developed several methods [1] to capture  $^{85}\text{Kr}$ . The National Engineering Laboratory reprocesses only U.S. Navy nuclear fuels; there are no commercial reprocessing plants at present.

Figure 1 shows the increase in atmospheric  $^{85}\text{Kr}$  measured at various geographic locations up to 1968, at which time there were about 56 million curies (56 MCi) or about  $10^{27}$  atoms of  $^{85}\text{Kr}$  in the atmosphere worldwide [4]. Almost all  $^{85}\text{Kr}$  is introduced by man; of this only 5% is due to nuclear weapons testing. If the rate of expansion of nuclear power along with the concomitant increases in atmospheric  $^{85}\text{Kr}$  experienced up to 1968 had continued, there would now be about 0.6 GCi or about  $10^{28}$  atoms of  $^{85}\text{Kr}$  in the atmosphere [4]. (The medical consequences of this dose are argued [4] to be slight.) The actual amount is much less due to slowed progress in bringing on nuclear fission power as a replacement for fossil fuels. The rate of release has also been limited by the fact that spent fuel from power reactors is not being reprocessed at present. Spent fuel is stored on-site in deep pools, an unsatisfactory procedure for long-term storage. If nuclear fission power were to provide the projected fraction of our en-

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ergy needs and if simple venting were to continue, the atmospheric burden would level out at well over 1 GCi. It might also be noted that 1 GCi of  $^{85}\text{Kr}$  produces 4 MW of power, which might be put to some practical use if it could be safely handled; admittedly, this is an almost negligible amount compared to the total power that would be produced by the reactors.

To give perspective to the quantities involved, let us note that the fission of  $^{235}\text{U}$  produces 200 MeV of thermal energy directly and, depending on design, approximately another 200 MeV of thermal energy by emitting neutrons that produce other fissionable isotopes, principally  $^{239}\text{Pu}$  and  $^{233}\text{U}$ , by transmutation. Thus, the complete fission of one gram of  $^{235}\text{U}$  in a typical reactor would produce about  $5.2 \times 10^3$  watt-years of heat. As nuclear power plants are about 32% efficient in converting heat to electricity, this one gram of  $^{235}\text{U}$  would provide about 1.7 kW of electricity for a year. A typical nuclear power plant generates 1 GW of electricity. To run such a plant continuously for a year requires the complete fissioning of 0.6 Mg of  $^{235}\text{U}$ . In a typical fueling cycle, 3% of the initial charge and 1% of the spent fuel is  $^{235}\text{U}$ , so that fifty times as much material must be processed as is fissioned. At this rate of production, the alternative of storing spent-fuel bundles on-site is untenable. Thus a typical plant would require 30 Mg of fuel to be reprocessed each year of continuous operation. Of this mass, about 390 g would be  $^{85}\text{Kr}$ , about  $5 \times 10^{24}$  atoms or  $2.8 \times 10^5$  Ci. If we project to the year 2000 and assume that each of  $3 \times 10^8$  Americans is to be provided electric energy totally supplied by nuclear fission at the present average consumption rate of 2 kW, i.e., 600 GW for the nation, then 600 standard 1-GW plants would be required for the U.S. alone. These would produce 2.3 Mg or  $1.7 \times 10^6$  Ci of  $^{85}\text{Kr}$  annually. If nuclear power were to provide only a fraction of this energy need or if the average electric consumption were to decrease, the  $^{85}\text{Kr}$  release would be correspondingly reduced. World production of  $^{85}\text{Kr}$  would be at least three times this figure.

U.S. Federal regulations to take effect January 1983 [5] will limit the amount of  $^{85}\text{Kr}$  that may be vented to  $5 \times 10^4$  Ci/GW of electricity generated for one year, for fuel irradiated in 1983 or thereafter. [Editor's note: The global body dose rate per capita from the release of all of the  $^{85}\text{Kr}$  generated in continuous operation of a 1-GW (electricity) reactor is  $\approx 2 \times 10^{-5}$  mrem/year (rem = roentgen equivalent man). This dose rate is about  $2 \times 10^{-7}$  times the average background dose rate; see Reference [3].] Reprocessing with unrestricted venting would result in a release rate about seven times higher than this. The fuel reprocessing plants would be responsible for keeping the  $^{85}\text{Kr}$  release down to this level. (A standard reprocessing plant handles about 2 Gg of spent fuel per year, which is

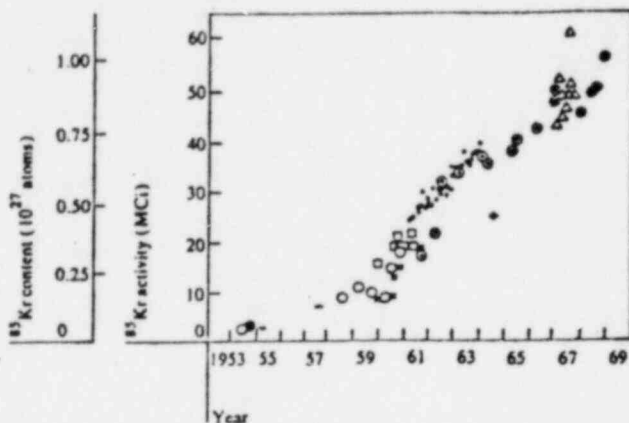


Figure 1 Atmospheric  $^{85}\text{Kr}$  as a function of time up to 1968. Data taken from Ref. [3].

the amount produced by 67 standard nuclear power plants, each producing 1 GW of electricity [2].)

Where the Kr has been captured, the only technology available for storing it is to compress it into cylinders [2]; 133 cylinders 23 cm in diameter would be required to contain the noble gas released each year at each fuel reprocessing plant. There are several problems with this method of containment. Rubidium, the decay product of  $^{85}\text{Kr}$ , causes a deterioration of ferrous alloys; so there is doubt about the long-term integrity of the cylinders. There is also the danger that the cylinders might burst due to some accident in handling and transport or due to corrosion- and radiation-induced damage over long periods of time. Because the radioactive gas is present in large quantity and under pressure, such an accident could easily be fatal to those nearby unless some means of secondary confinement of the gas is provided. The cost of meeting federally imposed safety standards with the compressed gas technology is rather high [2]. The estimated cost of a facility to contain on a 40-year cycle the compressed gas produced by a single reprocessing plant is \$208.5 million. For a 30-year loan at an 11.5% interest rate, this would require an annual payment of more than \$24 million. The cost of compressing the gas, of purchasing and transporting the cylinders, and of salaries and energy would be additional. The warehouse cost alone would run to more than \$200 million per year for the U.S. by the year 2000. In other terms, this would add \$0.00006 to the cost of generating a kWh of electricity, which would be an increase of about 0.3%.

Proposed alternate methods of storage have included incorporation into zeolite lattice pores by high temperature-pressure diffusion and by incorporation into crystalline [2a] and amorphous [2b] metals. The zeolite method

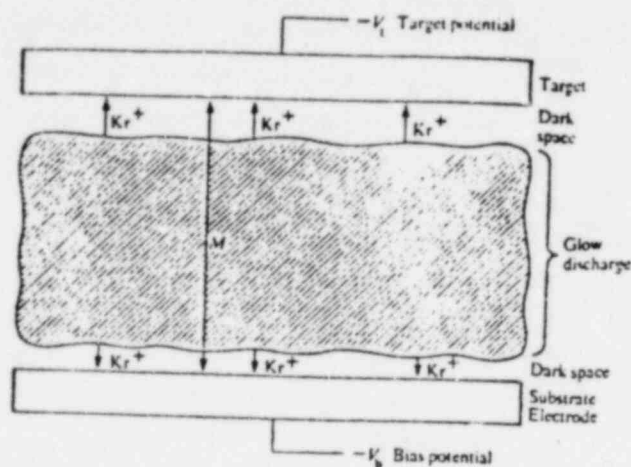


Figure 2 Schematic representation of the bias sputtering process.

suffers from the fact that if water gets to the material, it reacts and rapidly releases the gas. In crystalline metals the Kr forms small bubbles. At high concentration the pressure in these bubbles is sufficient to cause mechanical failure, a phenomenon known as blistering, in which the gas escapes. Furthermore, these bubbles tend to collect at grain boundaries and microcracks along which they diffuse at significant rates even at room temperature. Moreover, due to the power produced by the decay of the  $^{85}\text{Kr}$ , the containment material will be self-heated to a temperature dependent on the size of the individual container; the larger the container, the larger the maximal temperature and the more severe the thermal diffusion and degradation. For most storage schemes the volumes of containment material required are substantial. Each reprocessing plant would require [2] the following volumes per year for the various proposed methods: compressed gas cylinders,  $6.5 \text{ m}^3$ ; zeolite,  $7.3 \text{ m}^3$ ; Ni,  $1.3 \text{ m}^3$ ; Al,  $1.6 \text{ m}^3$ ; glass,  $>190 \text{ m}^3$ .

#### Storage in bias-sputtered amorphous metallic alloy

In the course of development of amorphous materials for magnetic bubble memory devices [6], we have come upon a method for the storage of Kr, Xe and other noble gases, whether or not radioactive, which seems capable of containing the radioactive waste from one of these reprocessing plants in just  $0.2 \text{ m}^3$  of material, and of retaining it stably up to temperatures as high as  $1070 \text{ K}$ . We estimate the cost of storing the  $^{85}\text{Kr}$  by this method as well under 1% that of storage in the compressed-gas cylinders, *i.e.*, less than \$0.24 million per reprocessing plant.

The containment materials in question are formed by bias-sputter deposition [7]. This process is illustrated in

Fig. 2. A low-pressure discharge is established in a sputtering gas between two electrodes, one of which is known as the target and the other as the substrate electrode. The sputtering gas is normally chosen to be one of the noble gases, He, Ne, Ar, Kr, or Xe, to avoid chemical reactions with the target and substrate materials. In practice, Ar is usually chosen on the basis of cost and sputtering rate. The Kr and Xe sputter as rapidly in most applications but are more expensive. The discharge converts the noble gas to a positive ionization state, *e.g.*,  $\text{Kr}^+$ . These ions are accelerated toward the target electrode, which is biased negative with respect to the plasma by the *target potential*. The plasma is in turn biased from ground by a small *plasma potential*. When the noble gas ions reach the target surface they penetrate several atomic layers, producing a process known as a collision cascade in which the energy of an incident ion is transferred to many atoms of the target material. Several of these atoms are subsequently emitted from the target surface in a manner similar to the "break" at the start of a game of billiards. The target atoms are generally neutral and travel by virtue of their kinetic energy through the intervening space between the target and the substrate, perhaps suffering a few collisions with the sputtering gas on the way. For normal choices of substrate temperature and materials, virtually all of the target atoms reaching the substrate stick there. As normally practiced, this results in the growth of a polycrystalline film on the substrate. However, Nowick and Mader [8] discovered that when two or more elements are deposited simultaneously and the radii of their atoms are sufficiently different, the resultant films are not polycrystalline but amorphous. (This means that they are microscopically disordered but macroscopically homogeneous as contrasted to the polycrystalline films, which are microscopically ordered but macroscopically disordered.) It is also possible to obtain amorphous films with atoms all the same size if one deposits faster than a critical rate, this rate being a function of substrate temperature [9].

In bias sputtering, a *substrate bias* is also applied between the plasma and the substrate. This has the effect of accelerating noble gas ions toward the surface of the growing film as well as toward the target. The ion bombardment of the film during growth has a number of useful effects. In the first place, it introduces anisotropies in the properties of the film. In the development of amorphous magnetic bubble materials, it was necessary to use this effect to induce a perpendicular easy axis of magnetization. In the second place, it allows one to eliminate many types of impurities that are not as well bound as host atoms. This is done by inducing a collision cascade in the substrate that is not sufficiently violent to remove host atoms. A third effect, which was discovered by



590 K. The authors associate these peaks with mechanisms having activation energies of 1.31, 1.74, 2.21, and 2.78 eV, respectively.

Rantanen *et al.* [13a] also studied the thermal re-emission spectra of Kr from polycrystalline Ni. They reported activation energies of 1.18, 1.36, 1.50, and 1.71 eV for this case. They also pointed out that these activation energies are probably associated with interstitial migration (1.03–1.09 eV), vacancy formation (1.35 eV), vacancy migration (1.55 eV), and surface diffusion (1.68 eV).

The above results for Kr in polycrystalline Ni should be compared with the thermal release of Kr from amorphous GdCo and GdCoMo alloy films by Frisch and Reuter [14]; see Fig. 3(b). The method used to study the amorphous film was similar to that of Rantanen *et al.*, except that the heating rate was 10 K/min and a high-sensitivity mass spectrometer was used. Extensive measurements have been made on a large number of these bias-sputtered amorphous GdCo and GdCoMo alloy films. All of the thermal re-emission spectra for unoxidized films have the character shown in Fig. 3(b). Oxidation lowers the temperature at which Kr release occurs [14b]. In the amorphous alloy films no detectable rate of noble gas evolution was observed until the film began to crystallize [14a]. At the crystallization temperature the gas was evolved very rapidly. In this case the kinetics of gas liberation are determined by the kinetics of the crystallization, which is a nucleation-and-growth process. An activation energy of 4 eV has been estimated for the migration of Kr in amorphous GdCo alloy [14a]. This implies that the mean time to diffuse one atomic site would be about  $10^{14}$  years at 570 K; at 1070 K, the Kr would diffuse about 10 nm in the 40 years required for the radioactivity to decay to 3% of its original value.

A further benefit of an amorphous structure for a material to contain  $^{85}\text{Kr}$  is that the disorder improves the ability of the material to tolerate radiation damage and impurities. Even if the containment material were pure to begin with, it would not remain so because the  $^{85}\text{Kr}$  transmutes to Rb by radioactive decay. The stability of a crystalline host material would be adversely affected by the simultaneous effects of irradiation, which generally enhances atomic diffusion, and of the incorporation of the daughter isotope, which is chemically incompatible with the crystal lattice of the proposed host materials. This would cause embrittlement of a crystalline host material and would accelerate mechanical failure by such mechanisms as blistering. However, those amorphous alloys which are stabilized by atomic size mismatch and a highly disordered drphs structure are much less sensitive to the

chemical nature of minor impurity constituents and can exist over a broad range of composition. The amorphous alloys in question will contain about 30 at% Kr or Xe, but, as noted above, only 6% of the total Kr released at the reprocessing plant would be radioactive  $^{85}\text{Kr}$ . Let us assume that the Xe is separated out by distillation so that only Kr is stored. This would seem to be economically desirable, although one could also easily store the Xe by expanding the size of the sputtering unit. Eventually, 1.8 at% Rb will be contained in the storage material. This would be enough to affect many crystalline hosts substantially but would have a negligible effect on a drphs-amorphous host. Such host materials are also less susceptible to radiation damage because the currents produced by ionizing radiation do not persist as long and because the resultant atomic diffusion does not have as much effect on a structure that is already disordered.

The selection of the most practical composition from which to form the encapsulating host material requires the consideration of four factors: gas-incorporation capacity, thermal stability, chemical stability, and cost. Let us start with the amorphous magnetic bubble memory material, GdCoMo, for which the incorporation of large quantities of noble gas was first discovered. This material can incorporate more than 50 at% Ar and more than 30 at% Kr and Xe when the three bias voltages of the system are adjusted properly. This large noble gas incorporation capacity occurs because the rare earth element Gd has an atomic radius much larger than the first-series transition element Co. The second-series transition element Mo is intermediate in size and serves to further disorder the drphs structure so that these mixtures will condense in an amorphous phase over a wide range of compositions and will have a relatively large number of interstitial spaces large enough to accommodate a Kr or Xe atom. However, the GdCoMo composition of the magnetic bubble memory would not be an attractive choice from the point of view of cost. Because the rare-earth elements (which in fact are not that rare) are all very similar in their chemical behavior, they are expensive in their pure elemental form. A typical price for pure Gd would be \$500/kg. If one instead purchases the rare earth elements in an unseparated form, called mischmetal or RMM [15], the price is much less, typically \$10/kg, and the chemical behavior as it affects Kr storage in amorphous alloys is no worse. One can also replace Co with Fe without affecting the containment properties significantly. With respect to thermal stability, it has been shown that GdCoMo and GdCoCr ternary alloys are much more stable than binary alloys like GdCo or even ternary alloys containing Au or Cu, e.g., GdCoAu or GdCoCu. For example, 15 to 20 at% Mo increases the crystallization temperature from 770 K for GdCo to more



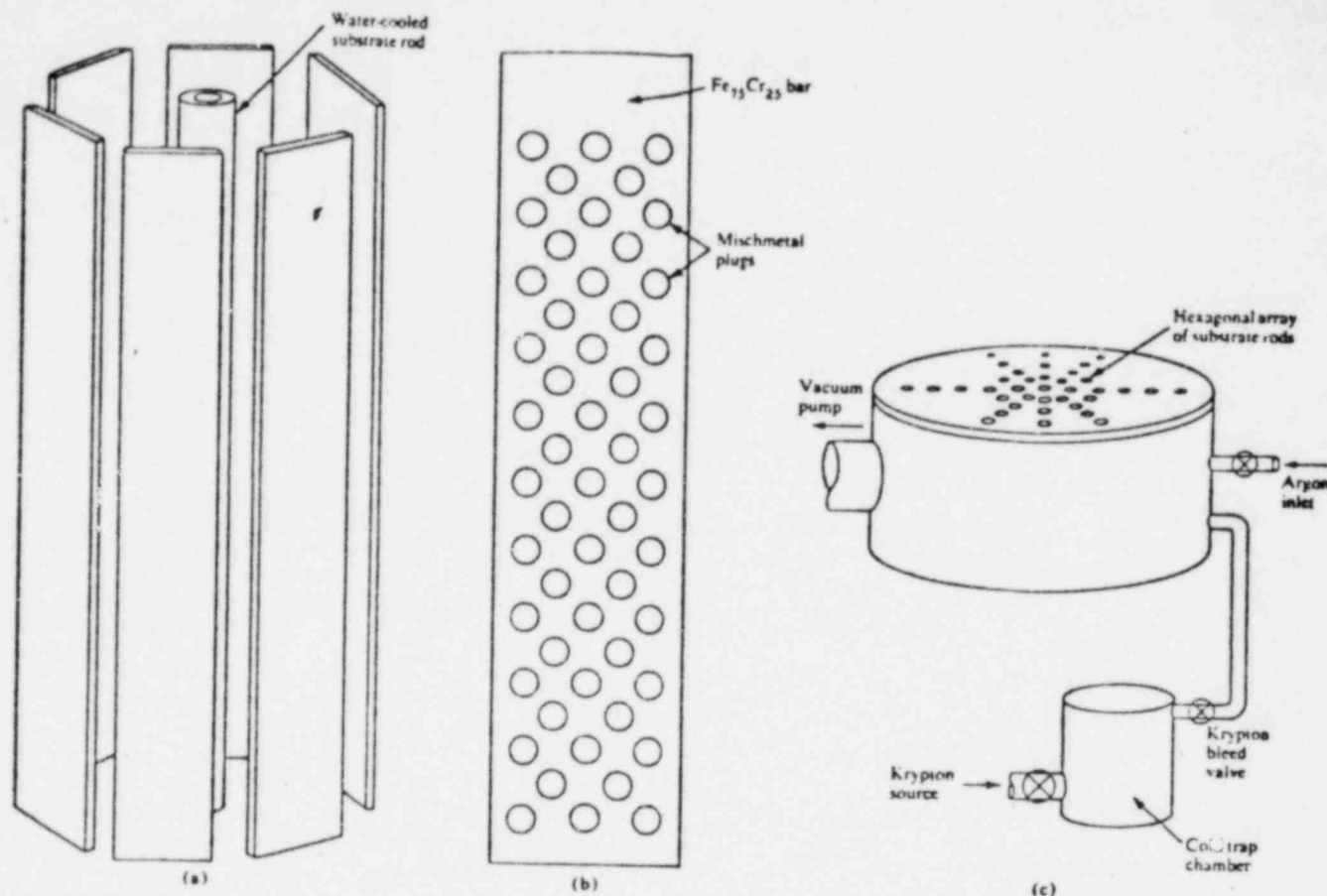


Figure 4 Proposed sputtering apparatus for incorporation of Kr into the amorphous alloy on a production scale. (a) Modular sputtering unit, (b) target bar assembly, and (c) sputtering chamber.

than 1070 K for the ternary alloys. From the point of view of chemical stability, the rare earth concentrations should be kept low because these materials oxidize (as well as cost more than the other constituents). Chromium, on the other hand, significantly improves the oxidation resistance and should be added at a concentration consistent with its cost. Therefore, an appropriate composition for the containment application would be (in atomic percent): RMM 20%, Fe 60%, and Cr 20%. The 2.1 Mg, or about 0.2 m<sup>3</sup>, of this composition that would be required to store the Kr retrieved at each 2-Gg/year reprocessing plant would cost about \$10 thousand. Of course, this material could be recovered and recycled every century or so as the level of Kr radioactivity from each charge decreases.

#### The process

At the reprocessing plant, spent fuel elements containing UO<sub>2</sub> ceramic pellets encased in metal are dissolved in nitric acid. At this point the Kr and Xe are released and bubble out of solution together with several other volatile species. The various volatile species can be separated and

trapped in a cryogenic distillation tower [1]. The Kr and Xe would be trapped at the end of the distillation sequence in cold traps or on charcoal cooled to 77 K with liquid nitrogen.

The liquified noble gas is maintained at 77 K and transferred to the sputtering station for incorporation into the amorphous alloy; see Fig. 4. The vapor pressure of the Kr at this temperature is about 10<sup>2</sup> Pa (10<sup>-3</sup> atm), which is enough to bleed through valving into the sputtering chamber but low enough that the danger of excessive leaks would be easily managed. The gas pressure in the sputtering chamber is about 10<sup>-7</sup> Pa (10<sup>-7</sup> atm). [Compare this situation with that of the compressed gas cylinders, which handle the gas at a pressure of about 10<sup>7</sup> Pa (10<sup>2</sup> atm).]

The rate at which material may be deposited by bias-sputter deposition varies from 1 μm/h for very simple diode systems to 30 μm/h for systems that use electron-injection or magnetic-field confinement of the plasma. We feel that the most practical arrangement would be modular and would consist of a hexagonal array of water-

cooled substrate rods surrounded by bar-shaped target electrodes. With this arrangement a continuous deposition rate of  $10 \mu\text{m/h}$  would be practical. In order to deposit the  $0.2 \text{ m}^3$  of material per year required to contain the Kr retrieved at each 2-Gg/year reprocessing plant, the volume deposition rate will have to be  $2.3 \times 10^{-3} \text{ m}^3/\text{h}$ , so that  $2.3 \text{ m}^2$  of deposition area are needed. This can be accommodated with a system of 232 rods 2 cm in diameter and 30 cm long arrayed honeycomb fashion in a cylindrical vacuum chamber 1.5 m in diameter and 0.5 m high. Such sputtering systems sell commercially for about \$80 thousand [16].

About  $200 \text{ kW/m}^2$  input power would be required to sputter at the proposed rate of  $10 \mu\text{m/h}$  [17]. Therefore, the sputtering station would consume about 460 kW of electrical power in order to capture the Kr retrieved at a 2-Gg/year fuel reprocessing plant. At  $\$0.04/\text{kWh}$  the cost of this power would be \$160 thousand per year. Perhaps another \$10 thousand per year of electricity would be consumed running the vacuum, cooling and control systems.

Due to the inherent simplicity of the sputtering process itself, this could easily be automated or remotely controlled. The cost of special control equipment for the radioactive environment automated operation should not exceed \$100 thousand. However, the deposited rods would have to be removed and replaced periodically. This could be accomplished by valving off the source of  $^{85}\text{Kr}$  and of the cooling water, breaking the vacuum of the system, and pulling the top flange of the vacuum chamber with all the rods and the remains of the target electrodes attached to it out of the body of the vacuum chamber and removing it from the sputtering station. Operators could then attach a new top flange with substrate-rod assembly and target electrodes to the vacuum and cooling systems. This should be done about once a month after about 7 mm of material has been deposited on the rods.

The configuration of the target electrodes shown in Fig. 4 indicates that these consist of  $\text{Fe}_{75}\text{Cr}_{25}$  bars with mischmetal plugs inserted into drilled holes. This configuration is recommended for easy handling of the mischmetal, which is hard and brittle. With this configuration one could also arrange to coat the deposited layer of amorphous metal with crystalline stainless steel in order to provide further protection from corrosion and abrasion, and to contain the beta particles emitted by the Kr. This would be done by continuing to sputter after the Kr source had been turned off and the mischmetal plugs nearly consumed, and the bias voltage would be increased to 250 V in order to increase the fraction of Fe and Cr in the deposited mixture.

For final storage one might wish to pot the entire top flange, rod and target remains assembly in cement and wrap it in lead. However, we feel that the amorphous alloy is so stable a method of storage that the material could be released for several practical applications (ranging from nuclear batteries to fire detectors, cold-cathode stabilizers, thickness monitors, and simple sources of heat) rather than simply putting it away in a deep salt mine.

### Conclusion

The materials developed for the amorphous magnetic bubble memory system have been shown to provide a very stable medium for the long-term/high-temperature storage of the noble gases Kr and Xe. The radioactive isotope  $^{85}\text{Kr}$ , produced in  $^{235}\text{U}$  fission reactors, is difficult and expensive to contain by other means. Compared to the present technology of compressed-gas cylinder storage, which is estimated to cost \$24 million per year per reprocessing plant for warehouse amortization alone, our process would cost approximately \$180 thousand for capital equipment, which would be amortized at less than \$40 thousand per year, plus \$10 thousand per year for materials and \$170 thousand per year for electricity. In our economic analysis we have not considered the cost of the building to contain the process; but since the process runs at high vacuum instead of at high pressure and since the product is quite stable to high temperatures, we feel the cost of this building should be minimal. In the high-pressure cylinder technology the cost of the building is a major part of the total expense. With our process the radioactive material is present only in small quantities before it is incorporated into the solid, and because of the stability of that solid, can be dispersed in practical applications afterwards.

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The release of the contaminated water from the reactor poses the same type of long-term risk to public health. In fact, it is more of a threat to public health because the Susquehanna River provides the drinking water for southeast Pennsylvania and northeast Maryland residents. It is a major tributary to the Chesapeake Bay -- one of the U.S.'s most fragile and productive ecosystems -- thus, further radiation contamination can result by the incorporation of long-lived radionuclides in the food chain. Should the Chesapeake be contaminated by the TMI radioactive wastes the economic and environmental repercussions would be devastating.

The federal government has consistently maintained that TMI radiation releases are not harmful to the public. It has not been able to determine, however, what is causing the increased incidence of spontaneous abortions, stillbirths, and illnesses among TMI residents. Radiation may not be the only reason for this increase but it is unlikely that it has not at least contributed to it.

Because releasing the wastes will create the potential for additional health problems among a larger population and contaminate the environment, the Environmental Policy Center proposes that (1) the NRC adopt an alternative to releasing the radiation into the environment, such as entombment; (2) the Environmental Protection Agency increase its on-site and off-site monitoring capability; (3) the Pennsylvania and Maryland Health Departments monitor vegetables, fruit, and dairy products grown down stream from TMI for strontium; (4) independent monitoring systems be implemented; (5) the NRC, EPA, state, and independent monitoring data be analyzed by independent researchers; and (6) the cost/benefit analyses include the long-term health costs created by TMI.