152
11/15/78

AD. 727

MASTER

MLM-2419

**An Evaluation of Fuel Resources
and Requirements for the Magnetic
Fusion Energy Program**

T. Ben Rhinehammer and Layton J. Wittenberg

October 31, 1978

Monsanto

MOUND FACILITY
Miamisburg, Ohio 45342

operated by

MONSANTO RESEARCH CORPORATION
a subsidiary of Monsanto Company

for the

U. S. DEPARTMENT OF ENERGY

Contract No. EY-76-C-04-0053

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The following pages are an exact
representation of what is in the original
document folder.

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

PRINTED IN THE UNITED STATES OF AMERICA

Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy \$6.50; Microfiche \$3.00

An Evaluation of Fuel Resources and Requirements for the Magnetic Fusion Energy Program

T. Ben Rhinehammer and Layton J. Wittenberg

Issued: October 31, 1978

MOUND FACILITY

Miamisburg, Ohio 45342

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

U. S. DEPARTMENT OF ENERGY

Contract No. EY-76-C-04-0053

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Contents

	<u>Page</u>
SUMMARIES.	4
INTRODUCTION	8
REQUIREMENTS FOR EXPERIMENTAL FUSION POWER REACTORS	
Tritium Requirements.	9
Lithium Requirements.	11
TRITIUM REQUIREMENTS FOR A FUSION POWER REACTOR	
Background.	13
Energy Yield per Fusion Reaction.	13
Tritium Fuel Reprocessing and Storage	13
Tritium Inventory in the Breeder Blanket.	14
Excess Tritium Required for Start-up.	14
SOURCES OF TRITIUM	15
TRITIUM AVAILABILITY FROM DOE PRODUCTION REACTORS.	17
TRITIUM AVAILABILITY FROM HEAVY-WATER REACTORS	
Background.	18
Projected Tritium Generation.	19
Availability of Tritium	21
TRITIUM AVAILABILITY FROM LIGHT-WATER REACTORS	
Background.	22
Projected Tritium Generation by PWR's	23
Availability of Tritium from PWR's.	23
TRITIUM AVAILABILITY FROM FUEL REPROCESSING PLANTS	
Background.	25
Projected Generation of Tritium	26
Availability of Tritium	26
NATURAL LITHIUM REQUIREMENTS AND AVAILABILITY	
Background.	30
Lithium Reserves and Resources.	30
Projected Commercial Demand and Production Capacities	35
Lithium Demands by a Fusion Reactor Economy	35
Conclusions	40
LITHIUM-6 REQUIREMENTS AND AVAILABILITY	
Background.	48
Potential Lithium-6 Demands	48
Isotopic Separation Facilities and Technology	48
AVAILABILITY OF HELIUM-3 AND HELIUM-4	
Background.	51
Current Inventory of Helium-3 in the U. S.	52
Tritium Production as a Source of Helium-3.	52
Atmosphere as a Source of Helium-3.	52
Natural Gas Fields as a Source of Helium-3.	53
An Appraisal of Helium-4 and Helium-3 Availability.	56
Current Technology for Helium Recovery from Natural Gas	57
Enrichment Technology for Recovery of Helium-3 from Helium-4.	57

	<u>Page</u>
ACKNOWLEDGEMENTS.	59
REFERENCES.	60
APPENDIX A: MODIFICATION OF COMMERCIAL LIGHT-WATER REACTORS FOR TRITIUM PRODUCTION	68
APPENDIX B: HYDROGEN ISOTOPIC SEPARATION PROCESSES	75
APPENDIX C: PROJECTED TRITIUM GENERATION RATES FOR PRESSURIZED WATER REACTORS.	95
APPENDIX D: LITHIUM ISOTOPIC SEPARATION PROCESSES.	97
APPENDIX E: AVAILABILITY OF MERCURY.	100
APPENDIX F: HELIUM-3 RECOVERY AND ENRICHMENT TECHNOLOGY.	102
DISTRIBUTION.	106

Summaries

REQUIREMENTS FOR EXPERIMENTAL FUSION POWER REACTORS

During the developmental phase of experimental fusion power reactors, all tritium fuel must be provided from external sources because tritium breeding will be minimal in the experimental reactors. The tritium requirements for these reactors can only be grossly approximated at this time because several plasma physics scaling relationships remain untested. A recently identified aggressive scenario which leads to the construction of a Tokamak Demonstration Power Reactor (TDPR) by the year 1998 has been used in order to estimate the potential tritium requirements for these experimental reactors. This estimate indicates that 118 kg of tritium will be consumed and an additional 38 kg will be required for start-up inventories. In order to supply this tritium, approximately 42 Mg of natural lithium will be needed to provide the lithium-6 for irradiation in fission reactors. An additional 24 Mg of lithium, perhaps enriched to 90% lithium-6, may be required in the test blanket of the TDPR.

TRITIUM REQUIREMENTS FOR A FUSION POWER REACTOR

In a full-scale, commercial fusion power plant, the required tritium fuel will be supplied from the tritium breeder blanket after an initial loading is supplied from external sources for start-up of the reactor. During operation of the reactor, a steady-state tritium inventory is accumulated. This total tritium inventory has varied widely in the conceptual reactor design studies from less than 2 kg/GW(e) to as high as 20 kg/GW(e).

SOURCES OF TRITIUM

The more important nuclear reactions which generate tritium include the neutron irradiation of lithium, boron, deuterium, and nitrogen. Tritium, although continuously generated in nature, does not exist in sufficient quantities for recovery. Small quantities of tritium are generated by light-water reactors (LWR) and heavy-water reactors (HWR). Most of the tritium formed in LWR's appears in the spent fuel and might be recoverable at the fuel reprocessing plant. Significant quantities of tritium could be extracted from the heavy water of HWR's when technology for detritiation of water is proven.

Large quantities of tritium can only be made available by the neutron irradiation of lithium-6 in fission production reactors or with other neutron sources. Technology has been well developed for tritium production from both lithium-aluminum alloys and lithium aluminates.

TRITIUM AVAILABILITY FROM DOE PRODUCTION REACTORS

Tritium has been produced for thermonuclear weapons and commercial uses in DOE production reactors by irradiation of lithium-aluminum alloys. Five heavy-water-moderated production reactors at the Savannah River Plant (three currently in operation and two shut down) can be assumed to be capable of tritium production.

Studies of tritium production by the irradiation of lithium aluminates in the Hanford N reactor indicate that 6-7 kg of tritium can be produced annually as a coproduct with plutonium production of 815 kg at a reactor power level of 860 MW(e). Additional DOE-owned and operated graphite-moderated reactors at the same site are currently on an inactive status. Alternate means of neutron generation which might be considered for tritium production either are at uncertain stages of development or are at least 15 yr away from application to tritium production.

Elemental tritium is available to commercial users from DOE through the Oak Ridge National Laboratory at a minimum cost of \$0.75/Ci in quantities of 25,000 Ci and larger. Tritium is also available from the Savannah River Plant, but currently only to qualified DOE contractors.

TRITIUM AVAILABILITY FROM HEAVY-WATER REACTORS

The Canadian CANDU heavy-water reactors (HWR), which use deuterium oxide as moderator and coolant, could be a potentially large source of tritium in the long term. As a result of neutron activation of the heavy water, about 190 g/yr of tritium is produced in each 1000-MW(e) reactor. Based on the projected growth of CANDU reactors, tritium generation may be 2 kg annually by 1985, 7 kg by 1990, and 19 kg by the year 2000. Tritium from the CANDU reactors may be available for sale pending development of economical tritium extraction technology. Study of tritium separation and recovery techniques is currently limited to a modest effort in the United States. Detritiation might be expected to maintain the tritium concentration in the heavy water below 2 Ci/liter and recover tritium at a cost of around \$4500/g.

TRITIUM AVAILABILITY FROM LIGHT-WATER REACTORS

Nearly all of the tritium generated by ternary fission in light-water reactors (LWR) is retained in the fuel rods and Zircaloy cladding. Tritium in the amount of 500-1000 Ci/1000 MW(e)-yr is generated by neutron capture reactions, primarily by the boron in the primary coolant of pressurized water reactors. Annual tritium generation rates from these reactions may be 32 g by the year 2000. Tapping this meager supply of tritium requires the development of the same detritiation technology and facilities needed for tritium removal at fuel reprocessing plants and heavy-water reactors. This source of tritium, however, would incur high recovery costs because of the low tritium concentrations (less than 2 μ Ci/ml).

TRITIUM AVAILABILITY FROM FUEL REPROCESSING PLANTS

Fuel reprocessing plants (FRP's) rank third after production reactors and heavy-water reactors as a potential source of tritium. Tritium generated by ternary fission in the fuel of fission power reactors is trapped in the fuel and the Zircaloy cladding but is expelled from the irradiated oxide fuel during fuel reprocessing. If fuel reprocessing is permitted in the U.S., the annual tritium generation rate at FRP's could reach 190 g by 1985, 350 g by 1990, and 850 g in the year 2000.

The availability and quantities of tritium depend upon the development of detritiation methods for use at FRP's, the resumption of fuel reprocessing in the United States, and the effect of the higher power densities on the amount of tritium remaining in the oxide fuel.

The type of headend operation (initial treatment of the fuel) will determine the cost of isotopic separation and recovery. Estimated detritiation costs associated with wastes generated by direct acid dissolution of the oxide fuel (current technique) may exceed \$17,000 per gram of tritium because of the large volumes of liquid at low concentration (up to 0.1 Ci/liter) that must be processed. If plants use the voloxidation process prior to acid dissolution, the cost of recovery from liquid wastes with tritium concentrations of 200 Ci/liter may be under \$2000/g.

NATURAL LITHIUM REQUIREMENTS AND AVAILABILITY

Cumulative natural lithium requirements for experiments and demonstration reactors up to the date of commercialization will be approximately 1×10^6 kg, which is about equal to current U. S. annual exports of lithium.

The demand of the fusion power industry then will be a function of the lithium requirements per reactor and the rate of reactor construction. A typical lithium inventory is projected to be 300 Mg/GW(e) for a reactor using a natural lithium breeding blanket, and 24 Mg/GW(e) with an enriched blanket. Assuming a base growth rate in electrical generating capacity of 1.4% annually, the cumulative lithium requirement to the year 2050 will be 3.7×10^8 kg. Although cumulative requirements of lithium needed for isotopic separation of lithium-6 will be larger for a reactor industry using enriched breeder blankets, 95% of the lithium processed can be returned to the marketplace.

Lithium demand in the United States is chiefly met by two major sources, with two-thirds coming from Carolina pegmatite mineral deposits and the remainder from Nevada brine

fields. U. S. domestic lithium reserves (proven) and resources have been estimated at 4.2×10^8 kg and 3.6×10^9 kg, respectively. These estimates are based upon a National Research Council committee report which is conservative because it does not include undeveloped and unproven sources of lithium, namely, oil field brines, geothermal brines, desert salt brines currently uneconomical to recover, and speculative pegmatite deposits. Potentially vast resources probably exist in Canada and Chile. The conservative total western world resource projection of 1×10^{10} kg includes only one recently discovered salt basin in Chile which makes up 40% of this resource estimate and, in addition, is larger than the total estimated U. S. resources. Because of the large reserves relative to consumption, the small lithium industry has done little exploration to date. Hence, lithium specialists believe the potential is enormous for the discovery of new lithium deposits both in the U. S. and worldwide.

Although future demand for all lithium uses appears large in terms of today's consumption, the cumulative demand up to the year 2050 falls within the limit of domestic resources. Conventional demands are projected to grow at 5% annually to the year 2000 and by 2.5% thereafter. Using the high growth case of 2.5% for fusion power (which might be caused by a massive shift to electrically powered vehicles), the cumulative lithium demands up to the year 2050 for both conventional applications and fusion reactors would require about 65% of the estimated U. S. resources.

The only significant impact on lithium resources appears to come from lithium batteries predicted for utility and vehicular use. Projected commercialization of this battery in mid-1980 has shown the need for production capacity to increase annually by 5% to 1985, 10% to 1990, and 15% to the year 2000.

Cumulative battery demands for lithium dwarf the needs of fusion power because of the enormous number of batteries projected for use prior to the year 2000. The cumulative lithium demands of conventional, battery, and fusion uses, all at annual growth rates of 2.5% between 2000 and 2050, are projected to exceed the current estimated domestic resources only some time after the year 2040. For a reactor industry using enriched breeding blankets, the isotopic extraction of lithium-6 from lithium feedstock obtained from recycled batteries would extend the life of domestic resources. Cumulative consumption for all uses could then be met beyond the year 2050.

LITHIUM-6 REQUIREMENTS AND AVAILABILITY

Up to 3000 kg of lithium-6 for irradiation in production reactors may be needed by the year 2000 to fulfill tritium fueling needs for experimental fusion reactors. Experimental tritium breeding blankets, using up to 90% enriched lithium-6, may also require an additional 24,000 kg. If enriched blankets are chosen for fusion power commercialization, the cumulative needs by 2010 may be 120,000 kg and by 2020, 2,100,000 kg.

No operable commercial or government facilities exist for lithium isotopic separations. Because of an isotopic separation program in the United States in the late 1950's, DOE has classified quantities of lithium-6 reserves. Diversion of any of these reserves to fulfill fusion demands would affect the need or timing for new isotopic separation facilities. One of two facilities built at Oak Ridge for lithium-6 separation work has been dismantled; the other, which had been placed on standby in 1963, cannot be economically renovated.

Construction of lithium-7 enrichment facilities is planned by Eagle-Picher Industries. Design is complete for this plant which will have an annual production capacity of 1000 kg of lithium-7. This \$3-million facility, which will use the basic technology of the Colex lithium-amalgam process developed by Oak Ridge, could be converted to lithium-6 enrichment.

Isotopic separation methods developed for other metals in recent years may be applicable to lithium separation, and perhaps provide more economical enrichment without the potential environmental problems with mercury. If the Colex system were revived, however, adequate mercury reserves appear to exist for supporting any conceivable level of enrichment through the 21st century.

AVAILABILITY OF HELIUM-3 AND HELIUM-4

The $D-^3\text{He}$ fuel cycle which uses the reaction $D + ^3\text{He} \rightarrow ^4\text{He} + p$ has been considered for fusion power reactors. Since this type of reactor would be expected to breed helium-3, a fuel source of helium-3 would only be needed for fusion experiments and initial start-up.

Helium-3 and helium-4 could be recovered from both the atmosphere and natural gas. The latter is a potentially large source of fairly high concentration whose availability depends upon the conservation measures adopted for the recovery of helium from natural gas before its consumption. Helium-4 occurs in natural gas in concentrations ranging from traces to 8%; helium-3 is found in helium-4 at nominally 0.2 ppm. Helium-3 reserves are projected to be a minimum of 29 kg recoverable from 38 billion cubic feet (Bcf) of helium-4 currently held in storage by the Bureau of Mines. Unfortunately, most additional helium contained in natural gas is expected to be lost as the gas is consumed for fuel. The amount of helium-3 that is potentially recoverable over the period of 1978-2000 is less than 100 kg and would require immediate implementation of a recovery program for natural helium. The recovery of natural helium from the air, at a nominal concentration of 5 ppm, is estimated to increase the cost of helium up to 1000-fold.

The availability of helium-3 by separation from natural-abundance helium will depend upon the development of low-temperature helium isotopic separation technology. Estimated unit separation cost for a production level of 1000 liters/yr is approximately \$150/liter based upon a pilot-scale superleak-distillation process.

Introduction

The successful development of a viable fusion industry utilizing the deuterium-tritium nuclear reaction must consider both the immediate and long-term availability of fuel. The long-term supply of deuterium seems assured when the deuterium oxide content of all the water in the world is considered. By contrast, a naturally occurring tritium resource is not available. A successful fusion energy program must include, therefore, the breeding of tritium within the reactor in order to supply this fuel for sustained operation of the reactor and, additionally, to supply tritium for the start-up of new power plants.

In the near-term, however, the development of a fully operational fusion power system requires the progressive construction and operation of large plasma physics experiments, experimental power reactors, and one or more demonstration power reactors. The fuel requirements for these experimental reactors can become appreciable. During this period of development, all tritium will need to be provided from external sources because breeding with the experimental reactors will be trivial. This report assesses the potential tritium requirements in the presently formulated development plan and identifies possible sources for the required tritium.

Only rough estimates of the tritium demands can be made at this time because this experimental field represents a rapidly changing technology. Periodic revisions of these projected demands will be necessary. During CY-1976 several scenarios were prepared to help identify

the next step and beyond in fusion reactor experiments which would lead to a demonstration power reactor. These compilations were reviewed in order to scope the magnitude of the potential tritium demand.

Tritium sources identified and surveyed included:

- DOE Production Facilities
- Light-Water Power Reactors
- Heavy-Water Power Reactors
- Nuclear Fuel Reprocessing Plants

The availability of lithium was surveyed also because the only practical production method for tritium is the neutron irradiation of lithium. The lithium survey is divided into two parts: (1) lithium requirements for fission reactors to produce the tritium needed during the experimental program, and (2) lithium requirements for fusion reactor breeder blankets needed to sustain a fusion reactor industry to the year 2050. The estimates of world-wide resources of lithium available to supply such an industry are reviewed. Additionally, the isotopic separation techniques for lithium-6 enrichment are discussed. The resources and requirements for mercury are included because of its potential use in a lithium isotopic separation technique.

The availability of helium-3 and helium-4 is briefly discussed. Helium-3 has potential usefulness as an advanced fusion fuel component, while large quantities of helium-4 will be required for various cryogenic systems in all fusion reactor facilities.

Requirements for Experimental Fusion Power Reactors

Tritium Requirements

Tritium requirements to the year 2000 for various test and experimental power reactors can only be grossly approximated at this time. Such uncertainty exists chiefly because several plasma physics scaling relationships which would define the number, size, duty cycle, and construction schedule for the test reactors required remain untested. Also unresolved are the types of plasma fueling and exhaust devices and the fuel re-processing plants. These latter considerations will affect the tritium inventory in the test reactor facilities. Several alternative paths to the construction of a Tokamak Demonstration Power Reactor (TDPR) have been identified (ERDA-76/110) [1]. An intermediately ambitious schedule, called Logic III, has been selected to aid in the identification of the potential tritium requirements for the development of fusion power.

The development plan (identified in Logic III) proposes the construction and operation of the following test facilities in advance of the Tokamak Demonstration Reactor: three Prototype Experimental Power Reactor/Ignition Test Reactors (PEPR/ITR), two Experimental Power Reactors (EPR-1 and EPR-2), and one Fusion Engineering Research Facility/Tokamak Engineering Test Reactor (FERF/TETR). The tritium requirements for these experiments (both the start-up inventories and the burnup quantities per year) have been estimated based, whenever possible, upon preliminary designs of these experimental facilities. Some tritium requirements also exist for the operation of the TFTR and several neutron irradiation facilities in advance of the FERG/TETR; however, the requirements for these facilities are small compared with the major experimental facilities. The assumptions (listed below) for the calculations of the tritium requirements were based upon reviews of a number of conceptual facility design studies [2,3,4] (see also Table 1).

a) Tokamak PEPR/ITR

Initial Operation - CY 1986

Intermittent operation about 100 shots per day (1 g tritium burnup per day, 200 g/yr) increasing to 250 shots/day in 5 yr; 8-yr life.

Tritium Inventory: 200 g, based upon 1 day of operation at a low burnup fraction of 0.5%.

b) Mirror PEPR/ITR

Initial Operation - CY 1990 - same operational assumptions as the Tokamak PEPR.

c) Theta-Pinch PEPR/ITR

Initial Operation - CY 1992 - same operational assumptions as the Tokamak PEPR.

d) Tokamak Experimental Power Reactor

Initial Operation - CY 1992

Operation: 500-MW thermonuclear power during burn
10% duty cycle first year;
25% second year; 50% 3rd-6th years.

Tritium Inventory: 6.4 kg - based upon 1 day of operation at 1% burnup fraction.

Tritium Breeding: Test modules only, not available for fueling.

e) Mirror Experimental Power Reactor

Initial Operation - CY 1997
- same operational assumptions as Tokamak EPR.

f) Tokamak Demonstration Power Reactor

Initial Operation - CY 1998

Operation: 500-MW thermonuclear power peak during burn, goal of approximately 85% duty cycle with sustained operation.

Table 1

TRITIUM REQUIREMENTS FOR EXPERIMENTAL REACTORS

CY	PEPR/ITR						EPR						DEMO	Total Burnup per Year
	Tokamak		Mirror		Pinch		TETR		Tokamak		Mirror		Tokomak	
	Start- up	Burn- up	Start- up	Burn- up	Start- up	Burn- up	Start- up	Burn- up	Start- up	Burn- up	Start- up	Burn- up	Start- up	
1985	0.2 ^a													
86		0.2												0.2
87		0.3												0.3
88		0.3												0.3
89		0.4	0.2				5.8							0.4
90		0.5		0.2				0.5						1.2
91		0.3		0.3	0.2		3.2	1.9	6.4					2.5
92		0.2		0.3		0.2	3.2	3.4		2.3				6.4
93				0.4		0.3		3.4		6.4				10.5
94				0.5		0.3		3.4		11.7				15.9
95				0.3		0.4		3.4		11.7				15.8
96				0.2		0.5		3.4		11.7	6.4			15.8
97						0.3		3.4		11.7		2.3		17.7
98						0.2		3.4		6.0		6.4	12.8	16.0
99								3.4				11.7		15.1
	0.2	2.2	0.2	2.2	0.2	2.2	12.2	29.6	6.4	61.5	6.4	20.4	12.8	118.1

Total Burnup = 118.1

Startup = 38.4

Total Requirement = 156.5

^aAll values are in kilograms.

Tritium Breeding: Complete blanket with tritium extraction; breeding ratio >1.00; sustained fueling operation to be supplied from blanket.

Tritium Inventory: 12.8 kg - based upon 2 days of operation at a 1% burnup fraction, permits 1-day delay in fuel recycle; also allows for increase of tritium concentration in blanket to its equilibrium value (approximately 1 kg).

g) FERF/TETR - Neutron Irradiation Facility

Initial Operation - CY-1990

Operation: Tritium plasma interacting with energetic deuterium neutral beam; 246-MW thermonuclear power average over burn cycle; 100 full days operation per year.

Startup Schedule: 10% 1st year; 50% 2nd year; 100% 3rd-10th years.

Tritium Inventory: 12.2 kg - based upon 1 day of operation at 0.28% burnup fraction. Gradual inventory buildup possible (i.e., 5.8 kg 1st year plus 3.2 kg 2nd and 3rd years).

Tritium Breeding - Test modules only, none available for fueling.

Based upon the previously described assumptions, the tritium burnup in the experimental fusion projects (Table 1) will not exceed 1 kg/yr until CY 1990 and gradually increases to a peak consumption of 17.7 kg/yr in CY 1997. The total tritium consumed up to operation of the Tokamak Demonstration Reactor would be approximately 118 kg. At the present cost of \$7500/g, the tritium cost would be \$885M, or approximately \$1 billion, for this Logic III route.

The tritium inventory required for startup of the experimental facilities is more difficult to define because of such poorly defined parameters, at this time, as the burn fraction per confinement time and the tritium holdup in the plasma fueling and exhaust systems as well as in the purification system. The first major tritium inventory buildup occurs during CY 1989-90 when 5.8 kg will be required for start-up of the TETR. Nearly 38.4 kg of tritium will be required for the inventories in all the experimental reactors including the Tokamak Demonstration Reactor to the year 2000. Not

all of this fuel may need to be supplied from external sources because it may be possible to shift the inventory from an early experiment being deactivated to a facility being newly activated. These scheduling options will need to be examined more closely as the experiments become better defined.

Lithium Requirements

The previously described tritium requirements for the test and experimental reactors can be met only by the neutronic irradiation of lithium-6 in a fission reactor. In addition, the testing of lithium breeder blankets in some of the experimental reactors is anticipated. The availability of lithium must be assured, therefore, in order to keep the fusion reactor program on schedule. An estimate of the lithium requirements is made based upon the previously described fusion energy development plan.

Approximately 312 kg of lithium-6 will be consumed to produce the 156 kg of tritium required in the fusion reactor development plan by the year 2000. If the lithium-6 burnup is permitted to proceed to 10 at. %, then 4.2×10^4 kg of natural lithium will be utilized in the irradiation program. Natural lithium will probably not be utilized in the fission reactor; instead, a lithium-6 enriched feed will be irradiated. The specific lithium-6 enrichment will vary with the type of reactor utilized and will depend upon such parameters as the neutron flux, energy spectrum, location of the lithium targets, etc. Consideration must be made also for the lead time needed in advance of the tritium requirement. Such lead time is necessary to prepare the lithium targets, irradiate the targets, remove the targets from the reactor, and extract the tritium. The chemical form of the lithium in the targets may also vary with the type of irradiation facility.

Some small amounts of lithium will be required for breeder blanket test modules in the FERF/TETR and TEPR experimental facilities. The first complete breeder blanket assembly will probably be scheduled for the Tokamak Demonstration Reactor. Such a reactor with a major radius of 6 m, a minor radius of 2 m, and a lithium blanket thickness of 10 cm will require 2.4×10^4 kg of lithium. It may be necessary to enrich this lithium to 90% lithium-6 in order to reduce the thickness of the blanket. Increasingly larger amounts of enriched lithium may be

required for fabrication of the breeder blankets in the commercial reactors.

In summary, the total lithium requirements for the fusion reactor program through the year 2000 can be assessed; however, specific information such as lead times, chemical form, isotopic enrichment required, etc., cannot be addressed until the fission re-

actor irradiation facility is defined. These subjects deserve consideration because some new technologies may need to be developed. For instance, lithium ore is a commercially available commodity, but no commercial facility is available to produce enriched lithium-6 (see section "Lithium-6 Requirements and Availability" and Appendix D).

Tritium Requirements for a Fusion Power Reactor

Background

In the previous section, estimates were made regarding the tritium requirements during the experimental and demonstration phases of fusion power development. Consideration will be given here to the tritium requirements in a full-scale, commercial power plant. The factors which affect these tritium requirements are the energy produced per fusion reaction, the tritium "hold-up" in the fuel reprocessing system, the residual tritium in the breeder blanket, the additional tritium required for start-up of the reactor, and the reserve amount desired in storage. The estimated total tritium inventories at a fusion reactor plant have varied widely in the reactor design studies, thus far, from as low as 2 kg/GW(e) to as high as 20 kg/GW(e) [5-19]. The factors which affect this total tritium inventory will be briefly reviewed and rough estimates will be made as to their effects upon the tritium requirements.

Energy Yield per Fusion Reaction

The primary fusion reaction in the plasma, ${}^3\text{H}({}^2\text{H}, n)\alpha$, with an energy release of approximately 17.5 MeV, imparts kinetic energy to the neutron (14 MeV) and the alpha-particle (3.5 MeV). In order to obtain useful power from the energetic neutron, the designers have provided a surrounding blanket in which the energetic neutron moderates its energy by multiple collisions with the blanket materials and is eventually captured by one of the blanket or shielding components. In addition, new tritium fuel must be produced by a nuclear reaction in order to supply fuel for the plasma. Both of these objectives are accomplished by the use of lithium in the blanket. Because natural lithium is composed of two isotopes (7.42% lithium-6 and 92.58% lithium-7), two nuclear reactions occur. At low neutron energies the reaction ${}^6\text{Li}(n, \alpha){}^3\text{H}$ predominates with an exothermic energy release of 4.785 MeV. At higher neutron energies the reaction ${}^7\text{Li}(n, n'\alpha){}^3\text{H}$ increases in importance but has an endothermic Q-value of -2.467 MeV. Additional nuclear reactions, principally the (n, γ) type which may be exothermic, occur with the structural materials in the blanket. In order to assess these multiple exothermic and endothermic reactions, Abdou and Maynard [20] have

analyzed a variety of potential blanket configurations and concluded that the energy released per primary fusion reaction can be as high as 16-17 MeV in the blanket.

The thermal energy from the nuclear reactions in the blanket and the alpha particle heating of the plasma are eventually converted into electrical power with an efficiency of 30-40%. Based upon these efficiencies, the tritium fuel requirements range from 340 to 470 g/GW(e)-day. Because of this large tritium requirement, fusion power reactor economics require that the tritium fuel be co-produced with the power.

Greater energy multiplication and, consequently, less tritium requirements per GW(e), can be achieved by the insertion of materials in the blanket which increase the exothermic nuclear reactions. Such materials as beryllium and the fissionable elements have been studied for this purpose. For instance, in the design study of the Mirror Reactor [16], an energy multiplication of 1.7 was obtained by the use of a large amount of beryllium along with the lithium in the blanket region. An energy multiplication of up to 10 times was obtained with uranium in the blanket region. Design studies of these blankets are continuing although the apparently limited world-wide resource of beryllium may curtail its use.

Tritium Fuel Reprocessing and Storage

The quantity of fuel which must be supplied to the plasma is much larger, however, than the amount which is consumed by nuclear fusion, because only a fraction of the fuel reacts during its residence time in the plasma. Based upon optimistic forecasts of particle confinement times, the present magnetically confined reactor design studies project from less than 1% up to 10% "burn-fraction" for the fuel, with somewhat higher values for the inertially confined reactors. As a result of this low "burn-fraction" a number of studies [21] have been made regarding the necessity to provide for the rapid recirculation of unburned fuel for reinjection into the plasma.

Recirculation of the fuel requires a series of chemical and physical processing steps, such as: evacuation of the plasma chamber,

removal of impurities, adjustment of the deuterium-tritium ratio and removal of protium by a hydrogen isotopic separation technique and, finally, interim storage before reinjection of the fuel to the plasma. Each of these steps usually involves some tritium inventory, or "hold-up" in the processing equipment. Estimates of the tritium inventory in these reprocessing procedures have ranged from less than 1 to 4 kg/GW(e).

An additional quantity of tritium fuel in storage has been included in most of the fusion reactor designs in order to maintain the plant operations during temporary malfunctions of the fuel or blanket reprocessing systems. If the tritium fuel consumption is 0.34-0.47 kg/GW(e)-day, and the fraction of fuel consumed is only 1 to 10%, then the tritium fuel requirements in storage would vary from 3.4 to 47 kg/GW(e) in order to supply a day's fuel supply without reprocessing. Because such inventories may be unacceptably large, storage for only 6-hr operation is recommended by some designers.

Tritium Inventory in the Breeder Blanket

All of the fusion reactor designs propose the generation of new tritium fuel by the nuclear reaction of the neutrons originating in the plasma with lithium-bearing materials in the blanket. The lithium-bearing materials suggested have been liquid metal, metal alloys, fused salts and ceramic compounds (these materials are reviewed in Appendix A). Each of these lithium-bearing materials retains some tritium, either by chemical solubility or physical entrapment, which contributes to the tritium inventory in the total fusion power plant.

Liquid lithium has been proposed as both the breeder material and the heat transfer fluid; however, it does have a high affinity for tritium. Several chemical reprocessing systems have been proposed in order to permit extraction of tritium from lithium to a very low concentration (approximately 1 ppm); however, because the quantity of liquid lithium is usually large, the total tritium inventory may range from less than 1 to 4 kg/GW(e). Conversely, the solubility of tritium in the fused salt, LiBeF_3 , is very low and the tritium can probably be removed by gas sparging; therefore, the total tritium in such a fused salt breeder blanket has been estimated [22] to be as low as 5 g/GW(e).

The tritium solubility in the lithium ceramic compounds proposed as breeder materials is low at the high operating temperatures of the blanket. It is proposed that this tritium would continuously diffuse from the ceramic and be removed in a stream of inert gas. The diffusion of tritium, either as the chemical species T_2 or as T_2O , through the ceramic materials is very slow; consequently, the particle size must be kept small or the tritium "hold-up" may be excessive. An estimate of the total tritium retention in an oxide ceramic blanket indicates that it may be on the order of 25 g/GW(e) for a large fusion power plant [23].

Excess Tritium Required for Start-up

Because of the residual tritium inventory remaining in the blanket, as previously discussed, an excess amount of tritium must be supplied during start-up of the reactor in order to build up this blanket inventory. This excess tritium inventory (ΔI), can be calculated, based upon the relationship described by Vogelsang [24]:

$$\Delta I = \frac{I_B}{BR} \left[1 - (BR - 1) \ln \frac{BR}{(BR - 1)} \right]$$

where: I_B = the blanket inventory

BR = the breeding ratio

For a nominal breeding ratio of 1.1 the amount of excess tritium can be calculated for the two extreme values of I_B . For liquid lithium, the value of I_B may be 4 kg/GW(e), in which case $\Delta I = 2.76$ kg. For a ceramic compound in which $I_B = 25$ g/GW(e), the value of ΔI is only a trivial 17 g, although slow kinetics of release may make it slightly larger. In either case, the value of ΔI is less than that amount of tritium normally in storage.

The tritium requirements and inventory for a commercial fusion power plant are summarized in Table 2.

Table 2
TRITIUM REQUIREMENTS FOR A
COMMERCIAL FUSION POWER PLANT

Function	Tritium [kg/GW(e)]	
	Min.	Max.
Fuel Burn-up (Daily)	0.34	0.47
Excess for Start-up	0.02	2.8
Inventory (Total)	<2.0	20.0
Consisting of:		
Reprocessing	<1.0	4.0
Equipment		
Blanket Materials	0.03	4.0
Storage	<1.0	12.0

Sources of Tritium

Tritium is produced by numerous types of nuclear reactions. The more important reactions which generate tritium are ternary fission and the neutron irradiation of lithium, boron, and deuterium. Tritium can also be generated by deuteron bombardment of beryllium, thermal-neutron reactions with helium-3, and fast-neutron irradiation of nitrogen [25].

Naturally occurring tritium, thought to result from primary cosmic-ray interaction with nitrogen of the atmosphere, is generated at the rate of 4 to 8 MCi annually. Most of the earth's steady-state tritium inventory, estimated to be 70-140 MCi, is in the form of water [25]. Hence, tritium does not occur in nature in sufficient concentration or quantity for extraction.

Tritium is formed in light-water reactors by the neutron irradiation of deuterium, helium-3, boron, and lithium-6 in the reactor coolant and also by fission of the reactor fuel. Fission produces far more tritium than do all other sources in a light-water reactor (LWR). Availability of fission tritium is discussed in the section "Tritium Availability from Fuel Reprocessing Plants." The yield of tritium from the other sources is insignificant since these elements either occur in low concentrations or are purposely maintained at low levels (e.g., the use of lithium-6-depleted lithium hydroxide for pH adjustment in pressurized-water reactors). The exception is boron which is added as a chemical shim for reactivity control. (See discussion in the section "Tritium Availability from Light-Water Reactors.")

Deuterium is a significant source of tritium in heavy-water reactors where D₂O is used as the moderator and coolant. The concentration of tritium in the heavy water depends chiefly on reactor power level and irradiation time. The potential availability of tritium from this source is reviewed in the section "Tritium Availability from Heavy-Water Reactors."

A review of the various sources of tritium generation quickly shows that large quantities of tritium can be made available only by neutron irradiation of lithium-6 in fission or fusion reactors or in special neutron irradiation sources. Tritium has been produced by the irradiation

of lithium alloys, oxides, or salts according to the reaction:

Helium-3 formed by the radioactive decay of tritium also absorbs neutrons to yield both hydrogen and tritium.

The advantages of irradiating lithium-aluminum alloys rather than lithium salts in heavy-water production reactors, operating near ambient temperature, were revealed in a 1963 patent [26]. These include elimination of target swelling during irradiation, the option of using greater flux densities, and the recovery of elemental tritium in a relatively concentrated form requiring little subsequent purification. Although up to 25% lithium in the alloy target may be used satisfactorily, it is suggested that restricting the lithium content to 4% may provide greater product purity by reducing the protium (H₂O) content. The alloy is normally jacketed by casting the alloy into aluminum cans under vacuum. After irradiation the target may be decanned or treated directly for recovery of the tritium. Tritium can be extracted easily by melting the target under vacuum. The alternative of heating a decanned target to temperatures just below melting is also effective but requires a longer extraction period.

Large-scale tritium production by the irradiation of lithium aluminate (LiAlO₂) has also been accomplished in an operating power reactor [27,28]. Jacketed ceramic targets were irradiated in the graphite-moderated Hanford N reactor to demonstrate the feasibility of a coproduct program (target loading and irradiation for both plutonium and tritium production). In addition, it was desirable to develop a tritium extraction process for ceramic targets compatible with facilities at the Savannah River Plant (SRP). A fuel design was developed for operation within an 860-MW(e) reactor power level which could allow an annual production of 6.25 kg of tritium and 815 kg of plutonium. Both SRP and Battelle Pacific Northwest Laboratory report studies on vacuum extraction of tritium from lithium aluminate either by heating or dissolution in molten sodium tetraborate [27-30]. An extraction efficiency greater than 95% was obtained with both methods.

Several fusion reactor conceptual designs may require ceramic lithium compounds (oxides, silicates, aluminates) in the breeding blanket. These studies of alternate tritium production methods as reported by Battelle provide an excellent base for future production and extraction of tritium if ceramic breeder materials were to be used in fusion power reactors. Evolution rates for tritium from ceramics and the parameters that control the form of tritium that is evolved apparently require study [28].

There is little likelihood of procuring tritium from foreign sources. As a result of weapon programs several European countries have tritium production capabilities. For example, the French Celestin reactors at Marcoule have been producing tritium since 1967 [31]. If tritium could be made available, there would still be complex political, security, and transportation problems to resolve.

A secondary foreign source is tritium extraction from the coolant of heavy-water reactors, especially the CANDU-type reactors (see "Tritium Availability from Heavy-Water Reactors"). With the exception of Canada, few heavy-water reactors have been built or are planned in Europe or other western world countries. France has been extracting 16-18 g of tritium annually from the coolant of the high-flux heavy-water reactor at Grenoble which is reported to produce 6000 Ci/MW(th)-yr [31]. Operating experience with this extraction plant, which employs catalytic exchange processing, has been published [32].

Short reviews on the management of tritium and tritium production alternatives relative to start-up of commercial fusion reactors have been reported [31,33].

Tritium Availability from DOE Production Reactors

Tritium has been produced for thermonuclear weapons and commercial uses in DOE production reactors by the irradiation of lithium-aluminum alloys. Public records show the existence of five heavy-water production reactors at the Savannah River Plant, and one or more can be assumed to be capable of tritium production or coproduction of plutonium and tritium [34]. Three of these reactors are in operation and two are inactive. Information concerning their capabilities and availability is classified.

The graphite-moderated N reactor at Richland, Washington, is capable, with changes in the fuel design, of producing 6-7 kg of tritium annually as a coproduct with plutonium production of 815 kg [28]. This capability was demonstrated with a reactor power level of 860 MW(e). The N reactor is a DOE-owned reactor used for the production of special nuclear materials and also steam that is supplied to an adjacent utility-owned electric generating plant. Although there were reports of placing the reactor on standby in 1977 it is still functioning in a dual-purpose capacity. Additional DOE graphite-type reactors of unlisted size have been operated at the Richland, Washington site in the past but are now on an inactive status [34]. Considerable upgrading and renovation may be necessary to place one or more of these reactors in operation.

The price of tritium is very dependent upon neutron economy since neutrons can account for up to 50% of the costs. If it becomes necessary to increase tritium production for fusion experiments, detailed engineering studies may be necessary to determine whether reactivation of graphite-type or heavy-water reactors is more economical. Because production reactors discharge their power from fission as heat to the environment and only use the excess neutrons for tritium or plutonium production, alternate neutron sources could have an economic advantage.

In addition to production reactors, neutron sources which might be considered for lithium irradiation include commercial light-water reactors (LWR), breeder reactors, high-energy accelerators, hybrid fission-fusion reactors, and fusion reactors. Commercial pressurized-water reactors (PWR) could be considered as a

substitute for heavy-water production reactors if this can be done without interfering with the fuel cycle and the safety of operation. A recent report, which briefly addresses the alternate sources of tritium generation for fusion reactor development, indicates the use of PWR's would require a lead time of at least 7 yr [31]. Although it appears unlikely that PWR's would be used for this purpose, the feasibility of tritium production in LWR's is discussed in Appendix A, "Modification of Commercial Light-Water Reactors for Tritium Production."

Other neutron sources were not considered for further evaluation here because their development is either far in the future or uncertain. Breeder reactor development may suffer delay or termination due to concern over plutonium safeguards and weapon proliferation. At best, commercialization may not occur until 1990.

High-energy accelerators or intense neutron sources are currently receiving considerable attention but their application to produce significant quantities of tritium may be 15 yr away. Furthermore, special target facilities and much higher beam currents, several orders of magnitude greater than now achieved, must be developed.

Elemental tritium, with a radiochemical purity of greater than 99%, is made available to commercial users through the Oak Ridge National Laboratory [35]. For quantities greater than 10 Ci, tritium is shipped in returnable metal cylinders varying in size from 10 cm³ to 16 liters. Small amounts of helium-3 are found in the tritium which is shipped at less than atmospheric pressure. Prices range from \$2/Ci for quantities up to 1000 Ci to \$0.75/Ci for quantities larger than 25,000 Ci.

Tritium is also supplied to DOE sites by the Savannah River Plant in 50-liter stainless steel primary containers (LP-50) sealed within an aluminum vessel (secondary container) and surrounded by insulation in a steel drum [36]. The container is restricted to a maximum tritium pressure of 800 torr. A 12-liter container (LP-12) is also approved for tritium shipments of smaller quantities.

Tritium Availability from Heavy-Water Reactors

Background

Tritium is produced during neutron irradiation of deuterium by the reaction $^2\text{H}(n,\gamma)^3\text{H}$. In light-water reactors (LWR) the amount of deuterium is small (150 ppm in natural water) and the probability of capturing a neutron to form tritium is very low. Consequently, in a 1000-MW(e) power reactor, not more than 10 Ci/yr of tritium would be generated by deuterium activation. The formation of additional deuterium by the neutron bombardment of hydrogen is a minor source when compared with the deuterium naturally existing in ordinary water.

Deuterium, as heavy water (D_2O) of at least 99.75% purity, is used as the moderator and/or coolant in small research and test reactors and also in government production reactors in the United States. Tritium, present in the heavy water as tritiated heavy water (DTO), can exist in concentrations of several hundred up to as much as 20,000 $\mu\text{Ci/ml}$ in large production reactors after years of operation [37]. Heavy-water reactors in the United States are not a significant source of tritium because of their small number and size [about five research/test reactors of less than 75,000 kW(th) and five production reactors, three of which are currently operating] [34].

Commercial pressurized heavy-water power reactors outside of the United States could be a significant source of tritium. In a typical 1000-MW(e) heavy-water-moderated reactor, tritium production is projected by Kouts and Long to be at least 60 g/yr [38]. An additional 1.5 g is generated in the fuel elements. The Canadian heavy-water reactors (CANDU), however, are reported to have a tritium generation rate of 90 mCi/MW(e)-day in the coolant and 6.3 Ci/MW(e)-day in the moderator [39]. These values translate into about 190 g of tritium/1000 MW(e)/yr for an 80% reactor capacity factor.

Table 3 shows the 1978 and projected 1985 generating capacities of countries reporting the greatest commitments to heavy-water moderated reactors [40].

Canada appears to be the only country in the world dedicated to the heavy-water reactors for power production. This decision was probably due in a large part

Table 3

HWR GENERATING CAPACITIES		
Country	1978 Capacity [MW(e)]	Projected 1985 Capacity [MW(e)]
Canada	3,754	10,817
Argentina	319	919
India	202	1,284
Korea	-	629
Others	125	250-910

to their success in producing heavy water at a moderate cost, the simplicity of fuel fabrication, the flexibility in fuel selection, and the development of a fuel cycle which can burn natural uranium leaving spent fuel with less fissile uranium than is found in the tails from isotope diffusion plants which supply enriched uranium for light-water reactors [41,42]. The reactor design is believed to be readily adaptable to fuel cycles based on plutonium and thorium, in addition to providing the most efficient utilization of uranium and a very high neutron efficiency.

The Canadian heavy-water reactors are referred to as the CANDU reactor system. CANDU (Canada Deuterium Uranium) is an acronym for a family of nuclear power reactors of Canadian design characterized by heavy-water moderation, pressure-tube containment of the coolant, and on-power fueling [42]. The CANDU power reactors have the unique feature of separate coolant and moderator systems which can allow the use of different coolants. However, only the CANDU PHW (Pressurized Heavy Water coolant) is being considered for Canada's current and immediate future electrical needs. Because Canada has large reserves of uranium (estimated to be one quarter of the world's reserves) the current CANDU reactor design is considered to be economical for many years, perhaps into the next century [42-45].

The projected nuclear capacity for CANDU reactors as shown in Table 4 was compiled from Atomic Energy of Canada Limited (AECL) documents published from 1973 to 1976. The higher projections may appear to be

optimistic. As in the United States, availability of capital funds, high interest rates, and apparent reductions in electrical demand growth (which only appears to be temporary) have caused deferment in these plans and sizeable cut-backs. More current estimates in 1976 suggest an operating capacity of about 11,000 MW(e) by 1985 and a more conservative total of 100,000 MW(e) by the year 2000 [40,43]. However, the higher projected generating capacity may prevail since the construction of nuclear plants in Canada primarily for the sale of power to the United States is receiving serious consideration [44]. This would not seem unexpected since Canada has extensive ties with the electrical network in the United States and has been a power exporter for years.

The projected nuclear generating capacity could also be affected in the period beyond 1985 by the availability of natural uranium which in turn would be affected by the world demand and costs for uranium. However, the discovery potential for large reserves of low-cost uranium below \$100/lb of U_3O_8 is high in Canada, and extensive quantities should be available for export, perhaps beyond the year 2000 [42].

Even though Canada appears to have adequate uranium reserves, studies are being made on the use of alternate fuels. Three alternatives to the once-through uranium cycle being considered by AECL include: 1) uranium with plutonium recycle; 2) once-through thorium with uranium-235; and 3) thorium with uranium-235 and uranium recycle [43]. None of these options or variations, however, are expected to result in immediate reductions in uranium consumption. Other possible changes in CANDU design for which technology is well

advanced are the direct-cycle system cooled with boiling light water (CANDU-BLW) and the organic-cooled CANDU-OCR which operates on an indirect cycle [42].

With these possible options in coolant and fueling two points must be made. First, the basic CANDU system which employs a heavy-water moderator is expected to remain essentially unchanged and the projected tritium generation levels can be assumed to be relatively unaffected by fuel or coolant selections. Second, the Canadians appear to be completely dedicated to the CANDU concept stating that since the CANDU reactor can be modestly changed to make it insensitive to uranium costs, the CANDU concept must be considered a strong competitor of the LMFBR or other breeder reactors in the 21st century [42].

Significant quantities of tritium could also be recovered from spent fuel removed from the CANDU reactors. As a source of tritium, however, spent fuel should not be considered since future plans for reprocessing of the fuel are very uncertain. Current publications show no hint of planned construction of reprocessing plants.

Canadian reactors are expected to be generating plutonium at the rate of 1600 kg/yr by 1980 and 8500 kg/yr by 1990. With this potential of plutonium, a commercial fuel reprocessing plant could be economical after 1985, fostering a fuel fabrication industry and a source of tritium. In the next 10 yr experimental work is expected on fueling some CANDU reactors with plutonium. Depending upon the success with these experiments and the problems of plutonium recovery, the world demand for uranium, and the discovery of new uranium deposits, "radioactive wastes will stay in the spent fuel which will be stored in interim facilities like the water-filled pools or above ground concrete canisters" [46].

Table 4

PROJECTED ELECTRICAL GENERATING
CAPACITY WITH CANADIAN CANDU
HEAVY-WATER REACTORS

Year	Capacity [MW(e)]	Reference
1978	3,754	(40)
1985	10,817	(40)
	15,800	(46)
	17,000	(43)
1990	36,500	(46)
1995	72,500	(46)
2000	100,000	(43)
	131,300	(46)

Projected Tritium Generation

The CANDU reactor system could be a lucrative source of tritium because of its unique design which maintains separate moderator and coolant systems with no interconnection. The major source of tritium is the moderator in which tritium production rates are about 6.3 Ci/MW(e)-day; the generation rate in the coolant is only 90 mCi/MW(e)-day.

Table 5

ELECTRICAL GENERATING CAPACITY AND TRITIUM GENERATION
FOR CANADIAN HEAVY-WATER REACTORS (CANDU)

Year	Capacity [MW(e)]	Tritium Generated in Moderator ^a (g/yr)	Tritium Generated in Coolant ^a (g/yr)	Total Tritium Generated ^a (g/yr)
1978	3,754	690	10	700
1985	10,817	1,990	30	2,020
1990	36,500	6,720	95	6,815
1995	72,500	13,340	190	13,530
2000	131,300	24,150	345	24,495
	100,000 ^b	18,400	260	18,660

^aGeneration of tritium is based on an assumed 80% net capacity factor (a factor calculated by subtracting any losses in electric production; during an outage, a unit is penalized for electricity it consumes; while operating, any energy produced in excess of the declared unit capacity is ignored).

^bRevised 1976 estimate reflecting general reduced funding, higher interest rates, and reduced energy growth.

The generation rate of tritium at various projected electrical generating capacities to the year 2000 is presented in Table 5. As a rule of thumb; one can assume about 190 g/yr of tritium to be produced for each 1000-MW(e) reactor operating at a capacity factor of 80% (see Note "a" in Table 5).

By 1985 the tritium generation rate is expected to reach 2 kg/yr, and by the year 2000 up to 20 kg could be extracted each year from some 100 heavy-water reactors. As shown, more than 95% of the tritium is found in the moderator system or in 60% of the heavy water required for operation of the CANDU reactor. The tritium generation figures appear realistic since the plant capacity factor for HWR's has gradually risen above 80% and indicators point to even higher capacity factors in the future, which is in contrast to the much lower capacity factors to date for light-water reactors.

There is no reason to believe that projected electrical capacity and tritium generation should be lower than shown in Table 5. There appears to be a resurgence in the need for electrical energy as the world economy and the GNP of individual countries increase. Canada is an exporter of power to the United States [44].

Another factor supporting an expanding nuclear power industry is the fact that, although hydroelectric power development sites exist, there are many serious environmental and logistics problems.

Canada has extensive fossil fuels but their location often prevents economic development. In some provinces, such as Ontario, undeveloped hydro sites are not adequate to satisfy their electrical growth needs beyond 1985 and relatively little fossil fuel is available.

The use of light water or organic coolant should have little effect on the moderator system and, hence, the tritium availability figures for a given-size reactor are expected to remain nearly the same. As an indication of the quantities of heavy water requiring detritiation, a typical 645-MW(e) reactor contains 264.5 Mg in the moderator, 183 Mg in the coolant, and 4 Mg in the fuel handling system [43].

The equilibrium concentration of tritium in the moderator and especially the coolant is very dependent upon tritium control actions, heavy-water management, and leak rates. Theoretical equilibrium concentrations of tritium are 1-3 Ci per kilogram of D₂O in the coolant and up to 50 Ci per kilogram of D₂O in the moderator [39]. Based upon an 80% capacity factor, tritium concentrations of 30 Ci per kilogram of D₂O might be expected in the moderator after 10 yr or more of operation. For comparison, the expected equilibrium concentration in the Grenoble (France) High Flux Reactor [57 MW(th)], which has a single heavy-water-cooled and moderated circuit, is reported as 80 Ci/liter and after 10 yr of operation, 30 Ci/liter [32].

Heavy-water leakage affects the equilibrium tritium concentrations more than any other single factor. In a 500-MW(e) reactor the amount of heavy-water coolant loss with the most recent CANDU reactor is less than 0.5 kg/hr and is expected to become even less with improved reactor designs and equipment. There are other leakages which are collected in downgraded form for subsequent recovery and upgrading. Losses from the moderator system are, because of its simpler function, a factor of two or three less than that from the coolant. Make-up of less than 1% of the heavy-water inventory per year is needed to replace these losses.

Availability of Tritium

Heavy water as a viable source of tritium is dependent upon feasible and economical detritiation technology which can be applied at each reactor site. As pointed out elsewhere in this report, technology for recovery of tritium from water is still under development. There are no documents in the open literature on tritium separation or recovery relative to the CANDU reactors. However, heavy water of the High Flux Reactor at the Grenoble Nuclear Center in France is treated for simultaneous extraction of hydrogen and tritium. This extraction plant uses the principle of catalytic exchange between heavy water vapor and deuterium gas at 200°C followed by cryogenic distillation of the hydrogen isotopes [32].

The need for detritiation of heavy water, particularly the coolant, is obvious from the operator's or utilities' standpoint. Cost benefits include reduced personnel exposures, lower health physics costs, and reduced costs of maintenance. These cost savings are difficult to estimate accurately but they must not be discarded lightly when analyzing the impact of costs for detritiation of the coolant and moderator. Cost of detritiation must be compared with not only the value of the tritium recovered but the benefits of reduced operating costs and exposures.

If feasible and economical detritiation methods are developed, the recovered tritium would be available for sale since Canada has no plans in the foreseeable future requiring tritium in quantities other than for research and development work. Tritium would be available for sale, subject of course to Canadian export controls and any safeguards that might be applicable at the time [39].

There are at least two water detritiation methods which are currently receiving detailed study in the United States for application to heavy-water and light-water detritiation. In Appendix B the technology for these two methods is discussed in detail along with cost estimates as applied to detritiation of water containing various tritium concentrations.

Preliminary results from a small-scale pilot plant at the Department of Energy's Mound Facility show that the electrolysis-catalytic exchange process is the most promising method to date for heavy water detritiation [47]. A precious metal hydrophobic catalyst developed by AECL is the key to the DT/D₂O or HT/H₂O isotopic exchange reaction [48]. For many years AECL has been trying to develop a more economical process as a substitute for the standard GS (hydrogen sulfide/water exchange) process used for the production of heavy water. Because of this work by both Canada and the United States, an international cooperative agreement has been reached involving AECL's Chalk River Nuclear Laboratories and DOE's Mound Facility to engage in joint development of this catalytic exchange process [49].

The tritium separation and recovery schemes cannot be appraised accurately for cost since development work has not progressed sufficiently to permit evaluation of all the operating parameters. Estimates, however, indicated the cost of the recovered tritium to be about \$4,500 per gram (See Appendix B). It is reasonable to expect that detritiation would maintain a tritium concentration in the heavy water below 2 Ci/liter.

Tritium Availability from Light-Water Reactors

Background

The design and chemistry of light-water reactors (LWR) are aimed at minimizing tritium generation and its release to the environment. Tritium generated in light-water reactors can be said to be compartmentalized. Relatively large quantities (>95%) will appear in the fuel elements from ternary fission while small quantities are generated in the primary coolant from neutron capture.

Individual fuel tubes are expected to contain up to 2 Ci of tritium at the end of their fuel life or up to 790 Ci/metric ton of heavy metal (MTHM) at time of fuel replacement [50,51]. The ternary fission yield of tritium in a typical large 1000-MW(e) nuclear power reactor may range from about 12,000 to 25,000 Ci/yr. The amount of tritium is dependent upon burn-up achieved. As higher burnups are obtained and as fuel is recycled, the amount of tritium resulting from ternary fission will also increase because of increased amounts of plutonium that will be present in the fuel.

Fission tritium is essentially contained in Zircaloy-2 and Zircaloy-4 clad fuel with releases to the coolant of 0.1% for boiling water reactors (BWR) and less than 1% for pressurized water reactors (PWR) [51,52]. Losses depend upon the type of cladding, temperatures, and integrity of the cladding. The recovery of tritium from spent fuel elements is discussed under the section "Tritium Availability from Fuel Reprocessing Plants."

Tritium is also generated in boron-loaded burnable poison rods or curtains of PWR's and BWR's, and also in boron-filled, permanent control rods of BWR's which are moveable and function to control the power level. The burnable poison elements of both PWR's and BWR's are removed after the first cycle of operation and are not a significant source of tritium [<2000 Ci/1000 MW(e)] [50].

No tritium is generated by the silver-indium-cadmium alloy which is used for permanent control rods in PWR's. The estimated rate of tritium production in the control rods of BWR's varies from 2000 Ci/yr for relatively new rods to

20,000 for well-burned rods [50]. Other estimates indicate a tritium formation rate up to 10,000 Ci/yr in a 1000-MW(e) reactor [51]. The control rods would not be considered as a tritium source because of their life expectancy of 15 yr or more which would result in a significant loss of the tritium by decay before recovery could be initiated. Recovery would also be very costly.

A more accessible source of tritium from the standpoint of recovery is the reactor coolant. In addition to the very small quantities of tritium entering the coolant by leakage from the fuel elements, the principal source of tritium in the coolant is neutron capture reactions with deuterium, lithium, and boron. These elements are present as trace-level impurities or are intentionally added to the coolant. The tritium concentration in the coolant will depend upon two factors: 1) concentration of these elements, and 2) the coolant leak rate and turnover.

Neutron capture by approximately 150 ppm of deuterium which occurs in natural water is expected to generate negligible quantities of tritium, something less than 10 Ci/yr estimated for a 1000-MW(e) light-water reactor.

The water coolant of both PWR's and BWR's contains trace levels of natural lithium which consists of 7.42% lithium-6. The lithium-6 isotope undergoes thermal neutron capture by the reaction ${}^6\text{Li}(n,\alpha){}^3\text{H}$. In addition, LiOH is intentionally added to the water of PWR's to control the pH in the primary coolant system and to limit corrosion of the cladding; lithium cation exchange resins are used for cooling water purification. Tritium generation is controlled by limiting the lithium-6 isotope in the LiOH and also in the lithium of the demineralizers by the use of 99.9 at. % lithium-7. Lithium-6 can be a potentially important source of tritium, but in the trace amounts maintained in LWR's the amounts generated are insignificant.

Data from operation of BWR's indicate that the tritium generated in the coolant is less than 50 Ci/yr and can be accounted for by deuterium activation, lithium impurities, and leakage from fuel elements.

In the case of PWR's a significant source of tritium is that arising from boron which is added to the primary coolant as a chemical "shim" to provide reactivity control. Hence, tritium production is directly proportional to fast and thermal neutron fluxes, boron concentration, and core volume coolant. The generation rate in the coolant from the boron/neutron reaction is predicted to be 500-1000 Ci/1000 MW(e)-yr [50]. A 1976 study of tritium releases from PWR's indicates that the tritium formation rate in the coolant for reactors operating at an 80% capacity factor could be projected at 1000 Ci/1000 MW(e)-yr reactor [53].

Concentrations of tritium expected in the coolant are nominally less than 2 μ Ci/ml and often as low as a few hundredths of a microcurie per milliliter [37]. Concentrations, of course, are very dependent upon leakage and coolant turnover. It is not unusual that the coolant replacement rate corresponds to one or more complete turnovers each year. Increased emphasis on eliminating effluents of any type may mean that plant liquids (primary coolant as well as reactor makeup water and recovered leakage) will be retained and recycled during the reactor's operating life (perhaps 30 yr). If this were done, the estimated maximum tritium content of the coolant in a 430-MW(e) reactor would be 3.3 μ Ci/ml at 580°F (304°C) or 4.5 μ Ci/g, and this concentration would be reached after 32 yr of operation [52]. The concentration after 2 yr of operation would be approximately 1/3 of this. These concentrations should not cause any problems as some PWR's have operated satisfactorily while the tritium concentration in the coolant exceeded 5 μ Ci/g.

Projected Tritium Generation by PWR's

In Table 6 is given a moderately low energy-growth case for nuclear reactors as obtained from recent ERDA (now DOE) projections contained in ERDA-76-43 [54]. These are considered to be conservative numbers in light of a very fluctuating, uncertain energy demand and changeable energy policies. According to trends in projected sales and the ERDA report referenced above, the ratio of PWR's to BWR's in the long term is 2:1.

The tritium available in the coolant from PWR's increases from about 4 g/yr in 1980 to nearly 16 g/yr in 1990 and 32 g/yr in the year 2000 as shown in Table 6.

Table C1 of Appendix C shows projections of nuclear power capacity having a much higher growth rate in the immediate future but a lower total by the year 2000. Those projections are based on Case A, the lowest of four forecasts of nuclear capacity presented in the ERDA Planning Document WASH-1139(74) [55]. With this different growth rate projection, the overall tritium generation is nearly the same. For comparison, Table C2 of Appendix C was prepared referencing Case C, the highest forecast given in WASH-1139(74). With this highest projected growth the tritium generation of 6 g in 1980, 13 g in 1985, 28 g in 1990, and 51 g in the year 2000 is only 50% greater per year than the lowest case.

Oak Ridge National Laboratory under contract to DOE periodically publishes projections on shipments, wastes, capacity, etc., relative to the nuclear fuel cycle [56,57]. Projections of waste water and tritium generated by light-water reactors as prepared by Blomeke et al., have been given [58]. Through these types of documents projections are continuously updated.

Availability of Tritium from PWR's

From the previous section it is readily apparent that recovery of tritium from PWR coolant water cannot provide significant quantities of tritium for energy uses. Not only are the quantities of tritium meager but detritiation techniques must be developed which can economically remove tritium on-site at each of possibly 190 PWR's projected for 1990.

Currently and in the very near future, utilities will probably continue to discharge their primary coolants to available surface waterways as necessary for efficient operation of the facilities and to keep the tritium levels of the coolant at desirable operation levels. However, operating data from several PWR's would seem to indicate that all liquids can be retained and recycled indefinitely within the power plant during the life of each reactor. The elimination of effluents and the retention of plant liquids appear to be the mode of future operation as regulatory guidelines become more restrictive.

The only detritiation method currently under development which might prove economically feasible is photoexcitation isotope separation which is described in detail in Appendix B. Recovery costs, based on limited data, are projected to be in excess of \$35,000 per gram of tritium recovered.

Table 6

PROJECTED TRITIUM GENERATION IN COOLANT OF PWR's

<u>Year</u>	<u>Electrical Generating Capacity^a [GW(e)]</u>	<u>Installed Nuclear Capacity^a [GW(e)]</u>	<u>Installed LWR Capacity^a [GW(e)]</u>	<u>Number of PWR's^b</u>	<u>Available^c Tritium from PWR Coolant (g/yr)</u>
1973	436	18	18	--	--
1980	620	76	75	46	3.8
1985	800	185	179	109	9.0
1990	1040	340	316	191	15.7
1995	--	--	484	293	24.2
2000	1750	800	639	387	31.9

^aCapacities cited are based on data in References 54 and 55.

^bNumber of PWR's is based on the assumption that the average PWR will be 1100 MW(e) and the ratio of PWR's to BWR's is 2:1.

^cCalculations based on a tritium generation rate of 750 Ci/yr/1000 MW(e).

Tritium Availability from Fuel Reprocessing Plants

Background

Fuel elements from nuclear reactor plants must be replaced periodically because of the accumulation of fission products, irradiation damage, and the depletion of fissile material. Equally important is the recovery for recycle of the valuable fuel (uranium and plutonium) remaining. Typically, model fuel would be replaced after generating a nominal 33,000 MW-day of heat per metric ton of heavy metal (MTHM). In current practice, fuel replacement may occur at usage levels as low as 15,000 MW-day, but burnups to 44,000 MW-day may be sought in the future. Hence, tritium is generated and retained in the fuel element at the rate of 12,000-24,000 Ci/1000 MW(e)-yr, the total generation being dependent upon burnup achieved.

More than 99% of the tritium produced by ternary fission in LWR's is retained in the fuel elements. Hence, the largest quantity of tritium which is potentially available for recovery will be released in the waste effluents of fuel reprocessing plants. The quantity of tritium released in reprocessing operations depends upon the fuel type, burnup, and fuel irradiation temperature. For current fuels and irradiation temperatures, 5-15% of the total fission product tritium may appear in the Zircaloy hulls with the remainder as tritiated water in overheads (distillate) of evaporation and calcining operations of liquid waste [59].

Fuel burnup governs the total amount of tritium generated in LWR fuel rods whereas the linear power density (in kW/ft) influences the fraction of tritium in the oxide fuel and the cladding. According to several studies, the fraction of tritium entering the cladding increases with increased linear power density or irradiation temperature [60,61].

In an experiment at an average power density of 4.8 kW/ft. with a UO_2 rod clad with Zircaloy-2, it was found that 7% of the fission tritium was in the cladding [61].

The Zircaloy clad from UO_2 fuel with burnups ranging from 17,000 to 30,000 MW-day/MTHM at linear power densities of 3-5 kW/ft of fuel rod was found to have a tritium content that correlated closely with both burnups and power level, ranging from 2 to 16% [62].

In high-power UO_2 fuel clad with Zircaloy-2 a greater fraction of the tritium would be expected to be released from the fuel and retained in the clad. Two rods were irradiated to obtain burnups of 21,000 MW-day/MTHM and 12,000 MW-day/MTHM. The average linear power densities were 31.4 and 17.6 kW/ft, respectively. The cladding of the first rod contained 80% of the total tritium found in the rod while the cladding of the second rod contained 47% of the tritium recovered [60].

According to Grossman and Hegland, tritium migration from the fuel into the cladding might approach 100% at 30,000 MW-day/MTHM burnup and power levels of 30 kW/ft [60]. Current linear power densities seen by fuel elements in LWR's are much lower than the design levels. Tritium fractions in the cladding for high power densities have not been confirmed by actual large-scale fuel reprocessing. Hence, future power levels may significantly change the ratio of tritium in Zircaloy hulls and the amount of tritium available for recovery and recycle.

All three commercial fuel reprocessing plants originally planned for operation in the late 1970's were to have similar processing operations: shearing of the rods into short segments, dissolution of the fuel in aqueous nitric acid, and treatment of the product solution by a Purex-type solvent extraction process. Tritium in the fuel would be released during the dissolution of the fuel in aqueous nitric acid. In general, tritium from the shearing operation is combined with the gases from the dissolver and all the gases are treated by an off-gas clean-up system. Tritium from dissolution appears mainly as tritiated water with a small fraction appearing as elemental tritium. Nearly all of the tritium entering the dissolver solution will enter the Purex co-extraction process and finally appear as dilute tritiated water either from the nitric acid recovery stream or from evaporation of aqueous wastes.

The volume of tritiated water waste from plants employing the acid dissolution-Purex process may vary from 4×10^4 to 60×10^4 gal/1000 MW(e)-yr [59]. The concentrations of tritium in aqueous wastes at the planned commercial FRP's were expected to range from 5 to 50 $\mu\text{Ci/ml}$ and 10 to 80 $\mu\text{Ci/ml}$ [59,37].

Projected Generation of Tritium

The U.S. Energy Research and Development Administration Office of Planning and Analysis (now under DOE) prepares reference cases forecasting nuclear power growth in the United States, for example, planning document WASH-1139 [55]. These cases are based upon various assumptions such as power consumption trends, technology development, current operational experience, and construction and planning of nuclear power plants. Several major documents by Blomeke et al. in 1974, referencing these forecasts, give projections for radioactive wastes including tritium to be generated by the nuclear power industry [56,57]. Several revisions of these projections have appeared as a result of rapid changes in economic conditions, energy supplies, and the demand for electrical power [54,58,63].

Tables 7 and 8 give projected nuclear generating capacities, fuel reprocessing loads, tritium generation rates, and tritium accumulation to the year 2000. The projected quantities of tritium expected to be discharged from the fuel reprocessing operation in the United States each year are: 1980, 80-130 g; 1985, 190-200 g; 1990, 350-450 g; and 2000, 850-1000 g.

Table 9 gives detailed year-by-year projections of LWR fuel reprocessing requirements, expected reprocessing levels, tritium annual additions, and tritium accumulated up through the year 2000.

Table 7 is a summary of data from ERDA document ERDA-76-43 published in 1976 [54]. ERDA-76-43 was prepared referencing previous energy requirement projections but was based on a revised moderately low-energy-growth case from WASH-1139. The premises for this case included a moderately low growth of electrical energy, the delay of spent fuel reprocessing until late calendar 1978, the delay of plutonium recycle until calendar year 1981, and a kilowatt-hour production growth of 6% per year through 1985 followed by a decline to 5.4% per year growth through the year 2000. According to ERDA-76-43, projection assumptions included reactor plant factors of 40% during the pre-operational period between fuel loading and commercial operation, 65% during the first 2 yr of commercial operation, 70% for years 3 through 15, and thereafter a decline of 2% per year to a minimum of 40%. The ratio of PWR's to BWR's is 2:1.

Table 8 is based on slightly older, perhaps more optimistic projections [58];

it is a revision of Case A, the lowest of four forecasts of nuclear capacity presented in 1974 in WASH-1139. More detailed assumptions for the projections in Tables 7 and 8 are described elsewhere [57].

Both Tables 7 and 8 reflect reduced growth of the LWR industry over that shown in the WASH-1139 planning document. If the highest growth case of WASH-1139 were used, which assumes an electrical consumption growth continuing at the rate of the period prior to 1972 and no conservation efforts to reduce electrical consumption, the increased tritium generated would not be greater than 20% above the values given in Table 8.

Availability of Tritium

The availability of tritium from fuel reprocessing plants is dependent upon three factors: (1) fuel reprocessing of some type will be approved for use in the United States, (2) the concentration of tritium in the fuel oxide will remain relatively high compared to that migrating into the cladding, and (3) detritiation techniques will be developed to extract tritium from the waste water effluent generated at the reprocessing plants.

The future of fuel reprocessing is very unpredictable since severe economic, processing, regulatory, and safeguards problems face this industry. Some doubts as to reprocessing spent fuel at all had been raised in late 1976 by the 13-agency Nuclear Policy Review Group because of the spread of reprocessing plants worldwide and because the recovery of plutonium constitutes an unacceptable risk of proliferation of nuclear weapons. It suggests the one option that the "U.S. should take a marked public posture favoring non-reprocessing alternatives to the fuel cycle."

Current (1978) U.S. nuclear policy indicates an indefinite delay in fuel reprocessing and plutonium recycle. Various proliferation-resistant fuel reprocessing technologies are currently being studied. Decisions on acceptable technology and management control options must await completion of these various studies, particularly the International Nuclear Fuel Cycle Evaluation (INFCE) and the Nonproliferation Alternative Systems Assessment Program (NASAP).

Table 10 is a summary of the predicted distribution of LWR spent fuel reprocessing up through 1987, the last year of the projection as taken from ERDA-76-43 [54].

Table 7

SUMMARY OF PROJECTED U.S. NUCLEAR ELECTRICAL CAPACITY, FUEL
REPROCESSING REQUIREMENTS AND TRITIUM GENERATION BY FUEL REPROCESSING PLANTS^a

Year	Total Electric Generating Capacity [GW(e)]	Total Installed Nuclear Capacity [GW(e)]	Nuclear LWR Operating Capacity [GW(e)]	LWR Fuel Reprocess- ing Load (MTHM)	LWR Fuel Reprocessed (MTHM)	Projected Tritium from LWR Fuel	
						Annual Addition (g/yr)	Accumulation Through End of Year (g)
1973	436	18.4	-	-	-	-	-
1975	-	-	38.0	495	0	-	-
1980	620	76.0	75.5	1435	1800	83	155
1985	800	185.0	179.4	3284	3100	189	760
1990	1040	340.0	315.6	6250	6250	347	1846
1995	-	-	483.9	10154	10154	587	3592
2000	1750	800.0	638.6	14045	14045	844	6066

^aBased on Reference 54 which uses a moderately low energy growth case.

Table 8

SUMMARY OF TRITIUM GENERATION BY FUEL REPROCESSING PLANTS^a

Year	Nuclear Generating Capacity [GW(e)]	Number of Reactors	LWR Generating Capacity [GW(e)]	Fuel Reprocess- ing Loads (MTHM)	Tritium Genera- tion (g/yr)	Accumu- lated Tritium (g)	Volume of Water Waste (liter/yr)	
							Acid Leach	Voloxi- dation
1975	35 ^b	51 ^b	-	None				
1980	78 ^c 85 ^d	95 ^c	84 ^e	2180 ^e	130 ^e	300 ^e	8x10 ^{7h} 19x10 ⁷ⁱ	
1985	180 ^c 231 ^d	186 ^c	222 ^d	4110 ^e	200 ^e	890 ^e	8x10 ^{7h} 19x10 ⁷ⁱ	5x10 ^{3g}
1990	410 ^d	395 ^f	375 ^e	7810 ^e	440 ^e	2200 ^e	8x10 ^{7h} 19x10 ⁷ⁱ	1.7x10 ^{4g}
2000	850 ^d	795 ^e	715 ^e	16680 ^e	1000 ^e	7500 ^e		5x10 ^{4g}

^aBased on Case A, Low Growth Rate, references "d" and "e" below.

^bIn operation 8/1/75, Nuclear News, 18:10, 69-74 (August 1975).

^cNuclear News, 19:10, 73-78 (August 1976).

^dSee Reference 55.

^eSee Reference 58.

^fCalculations based on references "c" and "d" assuming new reactors will average 1.1 GW(e) each.

^gCalculations based on tritium concentration of 200 Ci/liter for voloxidation-type reprocessing plants as assumed in reference "e".

^hCalculations based on acid-leaching plants (AGNS and NFS) in operation at combined capacity of 2150 MT/yr.

ⁱSee Reference 59.

Table 9.

FUEL REPROCESSING REQUIREMENTS, REPROCESSING LEVELS, AND PROJECTED ACCUMULATION OF FISSION-PRODUCT TRITIUM FROM LWR FUEL^a

Year	LWR Fuel Reprocessing Load (MTHM)	LWR Fuel Reprocessed (MTHM)	Tritium (g)	Tritium Accumulation Through End of Year (g)
1975	494.7			
1976	712.9			
1977	900.3	500.0	0	0
1978	1,075.2	1,000.0	25	25
1979	1,259.5	1,500.0	53	76
1980	1,435.2	1,800.0	83	155
1981	1,631.5	2,100.0	104	250
1982	1,910.0	2,100.0	125	362
1983	2,298.4	2,600.0	128	470
1984	2,762.0	3,100.0	160	603
1985	3,284.0	3,100.0	189	760
1986	3,840.2	4,100.0	189	906
1987	4,397.3	5,027.5	251	1,107
1988	4,965.4	4,965.4	307	1,353
1989	5,577.8	5,577.8	307	1,586
1990	6,250.3	6,250.3	347	1,846
1991	6,691.0	6,961.0	390	2,135
1992	7,719.4	7,719.4	435	2,452
1993	8,515.0	8,515.0	483	2,800
1994	9,314.4	9,314.4	534	3,180
1995	10,153.8	10,153.8	587	3,592
1996	10,975.9	10,975.9	641	4,036
1997	11,744.9	11,744.9	695	4,509
1998	12,515.3	12,515.3	745	5,006
1999	13,267.7	13,267.7	795	5,526
2000	14,044.8	14,044.8	844	6,066

^aReference 54.

Three commercial reprocessing plants were planned for processing spent fuel in the last half of the 1970's: Allied General Nuclear Services (AGNS) [Barnwell Nuclear Fuel Plant (BNFP)], Nuclear Fuel Services (NFS), and General Electric Midwest Fuel Recovery Plant. Only BNFP, the newest reprocessing plant, has survived the technological problems, cost escalation, and new design and regulatory requirements. With that survival has come an indefinite delay in startup. The G.E. Midwest plant will not go into operation due to the almost insurmountable problems of operation and maintenance experienced in initial process checkout of the plant. Hence, it is not listed in Table 10. The NFS plant, which operated successfully until shutdown in 1972 for modifications and expansion, is not expected to go back into operation because of additional design changes and expenditures necessary to bring the plant into compliance with Nuclear Regulatory Commission requirements.

Exxon, a 1500-MT/yr plant to be built near Oak Ridge, is shown in Table 10 to have a startup date of 1983. The date and fate of that proposed plant is currently uncertain.

Variations in the headend processing step prior to dissolution of the fuel are expected to change the concentration of tritium recoverable from the waste stream but not the total quantities. Currently, at least two headend modifications to the Purex process are being examined for future FRP's.

The most promising method, which was developed at the Oak Ridge National Laboratory for liquid-metal fast-breeder reactor (LMFBR) fuel treatment, is voloxidation [64,65]. It involves the heating of sheared fuels in dry air or oxygen at temperatures of 450-550°C. This technique allows easy isolation of gaseous fission products (³H, Xe, Kr, I) before dissolution

Table 10

PREDICTED DISTRIBUTION OF LWR SPENT
FUEL REPROCESSING AMONG U.S. FACILITIES^a

Year	BNFP	NFS	Exxon	New Capacity	Total
1977	500 ^b				500
1978	1000				1000
1979	1500				1500
1980	1500	300			1800
1981	1500	600			2100
1982	1500	600			2100
1983	1500	600	500		2600
1984	1500	600	1000		3100
1985	1500	600	1500		3600
1986	1500	600	1500	1000	4600
1987	1500	600	1500	1000	4600

^aFrom Reference 54.

^bValues are in metric tons of heavy metal per year (MTHM/yr).

of the fuel. The elemental tritium, by conversion to HTO in the headend high-temperature oxidation process, can be collected as a separate low-volume waste on molecular sieves.

The volume range of effluents from a voloxidizer is expected to be 10-1000 liters/day from a 5-MT/day FRP. Most projections use a 5-MT/day plant capacity (1500 MT/yr) and assume 400-600 Ci of T₂/MT, yielding 2000 to 3000 Ci/day. Developers of the process hope that the liquid waste volume can be limited to 100 liters/day, and predict a tritium concentration with a maximum of 300 Ci/liter in the future FRP's.

The proposed Exxon plant may employ voloxidation, which is projected to yield a liquid waste having a nominal tritium concentration of 200 Ci/liter, an assumption used by Blomeke et al. in waste generation projections [58].

Another possible change in fuel processing is the "pyro-chemical headend" process which has been investigated on a laboratory scale at Argonne National Laboratory [66]. In this process the fuel is separated from the cladding by dissolving the cladding in molten zinc. The fuel is then reduced to the elemental state and the zinc is removed by distillation. The control and recovery of tritium is made easy by the absence of water and the small volume of waste gas. Elemental tritium is collected and stored as a hydride or converted to water for collection on molecular sieves. Both collection methods of this relatively high tritium concentra-

tion would be amenable to economical shipment and recycle of the tritium.

For reprocessing plants employing nitric acid dissolution of the fuel elements, which was expected in the first three plants (NFS, BNFP, and GE Midwest), up to 85% of the tritium generated in the fuel matrix is expected to appear in the aqueous effluent. However, as discussed in the background portion of this section, several investigators suggest that the tritium migration from the fuel matrix into the cladding might run 50-100% at high power densities. Although only low power levels have been used to date, high levels may be achieved in the future. Consequently, this puts considerable doubt on the tritium availability figures normally projected by various forecasters.

A factor which may increase the total tritium generated in irradiated fuel is allowable impurities. If the impurity content of fuel is allowed to increase (e.g., several parts-per-million of lithium in UO₂), the concentration of tritium in the fuel may become much higher than current experience indicates.

The projected quantities of tritium generated by fuel reprocessing differ somewhat in Tables 7 and 8. This is due only to different assumptions made in nuclear power growth, particularly by the year 2000.

Assuming that fuel reprocessing resumes in the United States, the number of reprocessing plants in operation by the year 2000 is estimated at 6-10 units. Tritium recovery at each site should be relatively easy and inexpensive because of the limited number of plants, the high concentrations of tritium (up to 200 Ci/liter), and the large quantities (kilograms) of tritium per site.

For tritium from FRP's to become available for recycle and use in fusion experiments, detritiation processing of liquid wastes must become available within 5-10 yr. Two techniques and their costs, currently under study as applicable to FRP waste effluents, are described in detail in Appendix B. A preliminary cost estimate for recovery of tritium from FRP's which use acid dissolution-Purex processing is \$17,000/g. If voloxidation processing were used, the cost of separation would drop to less than \$2000/g. Feasibility and economics of recovery must still be proven.

Natural Lithium Requirements and Availability

Background

The availability of natural lithium is one of the controlling factors in the development of a fusion power economy based on the D-T reaction. When commercialization of fusion reactors is achieved, tritium fuel needs will be met by the tritium breeding within the lithium-bearing materials of the fusion reactor blanket. The blanket-breeder concept finally selected will strongly affect the cumulative quantities of lithium required. Quantities of needed lithium must still be considered speculative until data are accumulated from operation of the first experimental power reactor (EPR) in 1986-1988 and subsequent demonstration reactors.

During the period of fusion test experiments and demonstration reactors (1985-2005), the total tritium requirements have been estimated at 156 kg. About 40,000 kg of natural lithium will be needed to provide the lithium-6 isotope used for this tritium production. These figures assume the achievement of a minimum lithium-6 burnup of 10 at. % when the material is irradiated in a heavy-water production reactor. Higher burnup, of course, could be achieved depending upon the production reactor and the parameters of irradiation. Subsequent recovery efficiencies will also influence the tritium yield. Tritium generation by fusion breeding blankets is expected to be minimal during this period.

Breeder blanket experiments can be expected with the EPR-2 and the Tokamak Demonstration Power Reactor (TDPR), also called Demonstration Fusion Power Plant (DEMO) some time in the period of 1990-2005. If a natural lithium breeder concept is selected, a maximum of 1×10^5 kg may be needed in that time frame. This quantity is nearly equal to U.S. lithium exports in 1976. If it is necessary to reduce the thickness of the breeding blanket for engineering reasons or if the solid blanket concept is chosen, lithium-6 enriched up to 90% may be required. The lithium inventory requirements may then decrease by an order of magnitude or more.

The ability of the U.S. to meet future lithium demands of a fusion power industry has been questioned by spokesmen from various government agencies. Concern has

arisen because of the high potential lithium demands projected for high-specific-energy storage batteries. The lithium industry, on the other hand, has taken a very optimistic position. Widely differing opinions over the potential lithium resources in the United States surfaced at the 1976 lithium symposium "Lithium Resources and Requirements by the Year 2000" [67]. This symposium prompted a special review article [68].

These divergent points of view appeared to moderate somewhat at the more recent lithium symposium held in October 1977 at Corning, New York. This conference revealed a special lithium study made by the National Research Council. In 1975, the Department of Energy (then ERDA) requested the National Academies of Sciences and Engineering to report on the role of nuclear power relative to alternate energy sources for the period 1985 through 2010. A National Research Council Committee on Nuclear and Alternative Energy Systems was organized. A lithium sub-panel of this group reported on lithium resources and availability. The panel's findings were summarized at the 1977 lithium symposium by R. K. Evans and references to this study were made by I. A. Kunasz and others at the same meeting [69-71].

In the following sections the potential lithium resources in the United States are reviewed. Lithium demands are projected for fusion reactors and other commercial products to the year 2050. Finally, lithium demands are compared with the potential resources over this 70-yr time frame.

Lithium Reserves and Resources

Table 11 summarizes the lithium reserves and resources in the United States and the western world as determined by the lithium sub-panel and reported by Evans [69]. The U.S. reserves and resources are estimated to be 4.2×10^8 kg and 3.6×10^9 kg, respectively. The total resources of the western world are listed as 1.1×10^{10} kg.

Unlike previously published estimates involving category titles such as economic, sub-economic, recoverable, proved, possible, and conditional, the lithium sub-panel has tried to simplify the classification and nomenclature. Four classes shown in Table 11 were developed: Class A, reserves proved by systematic exploration; Class

Table 11

LITHIUM RESERVES AND RESOURCES ESTIMATED FOR THE WESTERN WORLD^a

Classes and Sources ^b	Quantities (10 ⁶ kg)	
	United States	Others
Class A		
Pegmatites	329	366
Brines	41	1,290
Government Stockpile (Available to Industry)	6	--
	376	1,656
Class B		
Pegmatites	47	457
Brines	--	--
	47	457
Class C		
Pegmatites	2,781	1,969
Brines	77	3,000
	2,858	4,969
Class D		
Brines	284	--
Total, Class A	376	1,656
Total, Classes A and B	423	2,113
Total, Classes A, B, and C	3,281	7,082
Total, Classes A, B, C, and D	3,565	7,082

^aFrom the NRC Lithium Sub-Panel findings as reported by Evans [69].

^bClassification definitions:

- A. Reserves proved by systematic exploration.
- B. Reserves indicated by limited exposures and/or exploration.
- C. Resources inferred on geological evidence.
- D. Quantities largely known but economic lithium extraction probably dependent upon marketing of co-products (Searles Lakes and Great Salt Lake).

B, reserves indicated by limited exposures and/or exploration; Class C, resources inferred by geological evidence; and Class D, quantities largely known but economic recovery dependent upon marketing of co-products. According to Evans, Class C material, in the case of pegmatites, represents a conservative estimate of the ore grade potential outside current mining limits and depths in the Carolina pegmatite belt.

The Department of Energy (DOE) has in stockpile more than 80 million lb of lithium hydroxide monohydrate (6×10^6 kg of lithium) with very low lithium-6 content [72]. These lithium-7 tails remaining from the lithium-6 isotopic separation processing of the 1950-60's are now on sale to industry for conventional

applications. This stockpile is shown as a part of the Class A reserves in Table 11.

The word "reserves" is generally misused, often referring to all material that can be mined and brought to the marketplace. Reserves by definition, however, refers to material that can be economically mined or recovered today with current technology. Enough information is available from exploration and development that the extent of the deposits and their recovery can be virtually guaranteed. Resources, on the other hand, may have two meanings: 1) a term to identify material that is believed to exist by geological evidence or very limited exploration and/or is currently unprofitable for recovery (e.g., Class C and D of Table 11),

and 2) a term to include all material discovered and undiscovered, profitable and currently unprofitable, which seems likely to become a source of that commodity [73]. The second usage, therefore, includes reserves. For example, the total resources of the western hemisphere listed at 1.1×10^{10} kg includes both reserves and resources, whereas Class C material listed in Table 11 refers only to the first definition given for resources.

Very conservative assumptions were made in developing the estimates in Table 11 since recovery efficiency from mining, beneficiation, and processing is highly proprietary. The assumptions made for mining losses alone were generous enough to account for nearly all processing losses [69]. Hence the quantities shown in Table 11 reflect a conservative estimate of the recoverable lithium that can be brought to the marketplace.

A number of potential lithium sources, however, were not included in these projections made by the lithium sub-panel. These were:

- 1) Pegmatite resources, defined as hypothetical and speculative resources.
- 2) Brines currently considered uneconomical to recover until lithium prices rise significantly.
- 3) Oil field brines.
- 4) Geothermal brines.

Because of the conservative nature of the resource projections in Table 11, it appears appropriate to tabulate these other unlisted potential resources along with earlier published resource estimates by several lithium specialists. This compilation as shown in Table 12 is primarily for comparison purposes. Two of the listed lithium specialists (I. A. Kunasz and J. D. Vine) served on the NRC lithium sub-panel.

A degree of liberty has been taken in comparing the data appearing in Table 12 since differing terminology and definitions have been used by the various lithium specialists. The differences in these projections appear to result from assumption variables and the manner of handling data (e.g., criteria used in the categorization of lithium, optimism of lithium deposits, differing number of categories).

Major differences in resource projections appear in both the Clayton Valley brine

and in the speculative or hypothetical resources primarily connected with the Clayton Valley brines and Imperial Valley geothermal brines. The almost 10-fold larger pegmatite resources estimated by the lithium sub-panel probably include more recent data and inclusion of some resources formerly considered speculative. With the exception of conservative estimates by Vine, the disagreement of the total resources (third line from the bottom, Table 12) is relatively small considering the nature of the lithium industry and the limited geological exploration experience accumulated over the years.

To gain a realistic perspective of the long-term lithium availability, more detail about these resources is necessary. Currently, there are two primary types of lithium raw materials: spodumene-bearing pegmatite ore and brines. Nearly two-thirds of the lithium produced in the United States is open-pit mined as spodumene ore in North Carolina by two corporations [78]. This form of lithium finds its use directly in the ceramics industry.

For decades, the Carolina deposits have been the major source of lithium for the western world. According to the lithium sub-panel study, geological conditions indicate prospects of perhaps an order of magnitude greater than resources reported by the two major companies. In addition, undeveloped parts of this lithium belt constitute 30 times the area of current mining operations. Although ore deposits are found elsewhere such as Maine and South Dakota, none are thought to be significant.

The remaining part of the current lithium demand in the United States is met primarily from a brine field which is found beneath the surface of a closed dry desert basin in Clayton Valley, Nevada. These brines, with lithium concentrations up to 300 ppm, are pumped to the surface and allowed to evaporate. The resulting lithium carbonate can be readily converted to the metal.

Although the lithium sub-panel reports only 1.2×10^8 kg of reserves in the Clayton Valley brines, it has been calculated that the total lithium content to a depth of 360 m is at least six-fold greater [69]. Because it does not appear that the price of lithium will be a significant factor in fusion energy production costs, and if other sources proved to be inadequate in meeting both commercial and fusion demands, it is very likely that all of the brine deposits (as calculated) would be recovered.

Table 12

U.S. LITHIUM SOURCES, CONCENTRATIONS, AND RESOURCES

Source	Lithium Content (ppm)	Resources (Economic and Subeconomic) (kg)				
		Norton ^a	Vine ^b	Kunasz ^c	Steinberg and Dang ^d	Lithium Sub-Panel ^e
Subsurface Brine (Clayton Valley, Nev.)	300	2.3×10^9	1×10^8	7×10^8	--	1.18×10^8
Searles Lake (Calif.)	50-80	3.6×10^7	8×10^6	--	--	2.4×10^7
Great Salt Lake (Utah)	60	--	1×10^7	4.8×10^8	--	2.6×10^8
Imperial Valley (Calif.)	Up to 250	1×10^9	1×10^7	--	--	--
Spodumene-Containing Pegmatites (N.C.)	7000	4.4×10^8	3.85×10^8	4.3×10^8	--	3.16×10^9
Sea Water	0.17	--	--	--	2.5×10^{14}	--
Others (e.g., oil field brine)	Up to 500	9×10^6	1.7×10^7	--	--	--
Total Resources		3.8×10^9	5.3×10^8	1.6×10^9	--	3.56×10^9
Speculative and Hypothetical Resources	--	3.2×10^9	4.7×10^8	--	--	--
Total, All Resources	--	7×10^9	1×10^9	1.6×10^9	--	--

^aEstimates under Resources (economic and subeconomic) for Norton include identified proved reserves that can be mined economically plus possible and conditional resources, identified but not profitably recoverable with existing technology [74].

^bEstimates under Resources (economic and subeconomic) for Vine include probable yields of identified reserves which are economic at current prices and technology plus provable yields of identified low-grade resources which may become economic at a later time and with improved technology [75].

^cEstimates under Resources (economic and subeconomic) for Kunasz are data originally listed as major identified resources [76].

^dEstimates for sea water by Steinberg and Dang [77].

^eFindings of Lithium Sub-Panel of the National Research Council Committee on Nuclear and Alternative Energy Systems (1976) [69].

Lesser amounts of lithium are recovered as a by-product in the extraction of potash and borate from brines in Searles Lake, California. The latter resource is included in the Class D category by the lithium sub-panel (see Table 11).

Geothermal brines in the Imperial Valley, California, are considered a large potential resource [74, 79, 80]. Recent studies by Berthold and Baker indicate that the lithium resource of the Imperial Valley, Salton Sea KGRA (Known Geothermal Resource Area) may be comparable in magnitude to the lithium brine reserves of Clayton Valley, Nevada. Lithium has been found in concentrations up to 240 ppm in geothermal fluids pumped from 5000 ft below the surface. However, these brines may range from low concentrations to high concentrations (10-250 ppm), varying with location and depth of the producing zone. Unlike other simple brine deposits, these high-temperature, very-saline fluids would probably require removal of silica and numerous minerals before recovery of lithium is attempted. These new discoveries must still be considered speculative and unproven. Commercial development is doubtful at current lithium prices unless associated minerals of the brine or the potential thermal energy are recovered.

Enormous quantities of lithium can be found in saline lakes such as Great Salt Lake, Utah, which is estimated by Whelan and Petersen to contain 5.3×10^8 kg [81]. Most lithium specialists are convinced that only one-half of the lithium could ever be recovered from this source without destruction of the lake. With concentrations of 35 ppm (low average), probable extraction would be as a by-product of a magnesium and/or primary salt industry. Concentrations within the lake vary up to 60 ppm depending upon the depth and location. According to the lithium sub-panel, the available lithium (Table 12) was calculated based on a low average figure of 35 ppm and at a recovery cutoff value of 17 ppm as dilution of the feed water occurs.

Preliminary studies have been initiated on the feasibility of extracting lithium from sea water [77]. From this work supported by DOE (formerly ERDA), production cost estimates are at least double the current lithium selling price. Processing technology must yet be proven. There are others who believe economic recovery may not be possible from this vast, almost limitless, lithium resource containing nominally 0.2 ppm.

It should be noted that "cut off" levels selected by the lithium sub-panel for terminating recovery of lithium from brines and salt lakes are at least 100 times greater than the concentration in the ocean. Hence, it would appear that there are enormous quantities, not currently shown as reserves or resources, that would be found economically recoverable before recovery from sea water would be attempted. Table 12 gives the range of lithium concentrations to be expected with the various sources.

Little is known about lithium resources worldwide (particularly the eastern hemisphere) since there has been little exploration, production, or demand. What little is known, however, would indicate worldwide deposits to be very large. The United States has been and probably will continue for some time to be the largest producer, consumer, and exporter.

Although the United States is thought to have two-thirds of the world's economically recoverable reserves, it has "less than 20% of the world's identified lithium resources" [74, 82]. Other western world countries are known to have two to three times the identified deposits of the United States, according to the lithium sub-panel report.

Large undetermined deposits are forecasted for Canada and Chile. A high discovery rate is predicted in Canada if demand increases [69]. Known resources as open-pit and underground pegmatite deposits are shown to be 2.7×10^8 kg. Chile, on the other hand, possesses many salt basins which are remote and almost inaccessible but promise large deposits of lithium. The most important find to date has been the Salar de Atacama which is a closed structural depression containing salt some 400 m thick. The lithium concentration, reported to be 5000 ppm, is the highest known to exist in any natural evaporated salt basin in the world [71].

It appears then that this one salt basin in Chile may equal the known recoverable resources in the U.S. as estimated by the lithium sub-panel. Although transportation and access to these deposits may add significantly to the cost of recovery, plans to produce potassium sulfate and possibly other chemicals would help offset the higher costs of production.

Projected Commercial Demand and Production Capacities

Dependable data are lacking on both the consumption of and production capacity for natural lithium [72]. A small U. S. industry of three producers, lack of standardized terminology, large reserves versus demand, and past economic hardships from huge changes in (government) demand are all contributing factors.

The United States accounted for about 70% of the world production during the period 1970-1977. Production capacity is currently given as 4.7×10^6 kg/yr [69]. An expected 50% increase in capacity of Lithium Corporation of America in 1978 will bring the overall capacity to about 6×10^6 kg/yr [71].

The total U.S. yearly production of lithium, however, was about 3.5×10^6 kg in 1976 [69]; with about 20-25% of that quantity being exported annually [72]. Based solely on conventional uses, U.S. demand is projected to grow at a conservative 5% per year. Cumulative industrial consumption up to the year 2000 is calculated to approach 1.6×10^8 kg. Hence, by the year 2000 the conventional needs would use less than 5% of domestic resources as estimated by the lithium sub-panel (see Figure 1).

A new commercial use of lithium may possibly impact on this industry in the mid-1980's. Lithium-aluminum/iron sulfide batteries may find widespread use in powering electric automobiles and also as load-leveling devices for energy storage by the electric utility companies.

The program for high-specific-energy battery development has received high priority from DOE because the use of such batteries could provide significant savings in oil resources as well as benefits to the environment. A multitude of storage battery systems is currently under study including metal/halogen, sodium/sulfur, metal/air, and metal/metal sulfide. The lithium-aluminum/iron sulfide system is now well enough developed and tested that forecasts have already been projected for lithium needs over the time period 1985-2000 [83, 84]. Commercialization studies have been started, with pilot-plant operation projected in 1982 and automated plant operation in 1987.

About two million vehicles may be equipped annually with lithium batteries in the year 2000. First projections (1976) showed upward of 18 million battery-powered vehicles in operation by the

beginning of the 21st century [84]. The average amount of lithium required per automobile may be 15 kg. Cumulative demands projected for utilities could run even higher than that for vehicles. Extensive usage by the utilities, however, is still uncertain, and also alternative, more effective means of energy storage may be found. Recycling of the lithium can be expected at the end of the battery life which is estimated at 10 yr. Recycling measurably reduces the demand for new lithium.

Projections for both utility and vehicular use of batteries were revised downward in 1977. Figure 1, showing projected annual and cumulative demands for conventional and battery applications, is taken from 1977 data of Evans, Kunasz, and Chilenskas [69, 71, 83]. Cumulative lithium needs (conventional and battery) up to the year 2000 will be 15% of the estimated U.S. resources or about 5×10^8 kg. The effect of battery (lithium) recycle on annual and cumulative demands should be noted for the period after the year 2000 (see Figure 1 and discussion in the Conclusions section).

Production capacity must be increased ten-fold by the year 2000 to meet the projected annual demand. Kunasz has developed a dynamic model to show how the lithium industry must react to a rapid growth in demand. Applying progressively larger growth rates every 5 yr, starting with 5% annually up to 1985, 10% beginning in 1985, and 15% annually from 1990 to 2000, the industry capacity would be able to meet projected conventional and battery requirements through the year 2000. These increases in production capacity would appear attainable.

Lithium Demands by a Fusion Reactor Economy

A fusion power economy can only be sustained by the breeding of tritium in a lithium blanket surrounding the reactor vessel. The potential amount of lithium required by a large-scale fusion power industry must be appraised, therefore, and compared with the potential resources. The lithium demand will be a function of the lithium requirements per reactor and the rate of construction of fusion power plants for electrical power generation, as previously described by Bogart [85] and Gore and Hendrickson [86] and discussed in the following sections.

Lithium Requirements per Reactor

In order to assess the lithium requirements per reactor, various conceptual

FIGURE 1 - Projected lithium supply, conventional demand and battery demand in the United States up through 2010.

designs for demonstration and commercial fusion reactors must be reviewed as shown in Table 13. In nearly all cases, the designers made no attempt to minimize the lithium requirements which would occur if lithium supplies became scarce. Although many of the reactor designs are only sketchy at this time, some factors which affect the potential lithium requirements are becoming clear. These requirements are composed of the initial inventory plus the quantity required for replenishing the lithium consumed.

In regard to the initial inventory, designers have chosen several different strategies for the breeder blankets. In several designs, liquid lithium, lithium oxide particles, or fused salt are used as the breeder and also as the heat transfer medium. The lithium requirements for these designs are high, ranging from 210 to 1180 Mg/GW(e) (Table 13) while the amount of lithium in the blanket region is much less. This difference is especially evident for the Theta-Pinch reactors where extensive piping was required outside of the blanket. In a recent Tokamak design (UWMAK-III) the liquid lithium breeder is utilized only in the outboard section of the torus and the reactor is more compact because an increased neutron flux is permitted. Hence, the lithium inventory is nominal [240 Mg/GW(e)], and only 17% of the lithium is external to the blanket. This type of design probably represents an advanced trend in reactor designs and in lithium inventory is similar to the recent ORNL-Tokamak DEMO design; therefore, the lithium inventory of 300 Mg/GW(e) was selected as a typical value for such natural lithium breeder designs and was used for preparation of Table 14. The Tandem Mirror and the Field Reverse Mirror designs may require twice as much lithium; however, their blanket designs have not been optimized.

A different breeder blanket design philosophy uses stationary, high-melting lithium compounds in the reactor and extracts heat and tritium with a recirculating gas. The compounds suggested have been ceramics such as LiAlO_2 , $\text{Li}_2\text{Be}_2\text{O}_3$, and Li_4SiO_4 , or intermetallic compounds such as LiAl or Li_7Pb_2 . In most of these designs, in order to obtain a tritium breeding ratio greater than 1.0 it has been necessary to use a neutron multiplier (beryllium or lead) and to enrich the lithium-6 isotope to approximately 90%.

In some designs, as given in Table 13, both natural lithium and enriched lithium-6 are used in the blanket because of either nucleonic or heat transfer

considerations. Two of the designs, the BNL-Tokamak and the Mirror Machine reactor, require a very small amount of lithium-6; however, this is accomplished by the use of a large amount of beryllium, which is questionable practice because of the potential limited supply of beryllium. The remaining designs use lithium-6 in quantities ranging from 12 to 105 Mg/GW(e). The UWMAK-II design [24 Mg/GW(e)], in which a deliberate attempt was made to minimize the lithium inventory, is typical of these reactors; consequently, its inventory was used for calculations in Table 14.

In addition to the lithium in the blanket inventory, some lithium is needed each year for tritium breeding and replacement of losses. The amount of lithium consumed was determined by the approximations of one lithium-6 atom consumed per D-T fusion, an 80% duty cycle, and a 33% efficiency for electrical power production from thermal power. Lithium losses were estimated based upon blanket module replacements which may occur approximately every 10 yr with an 80% recovery of the lithium (20% of the lithium in the blanket is unrecoverable). Although radiation damage of the first-wall suggests its replacement may be required as early as every 2 yr at the present time, replacement of a complete blanket module not sooner than every 10 yr would be anticipated by the time economically commercial reactors are built. The combined amounts (breeding plus losses) of lithium consumed each year as estimated and used in Table 14 were: 10 Mg/GW(e)-yr in the natural lithium breeder blankets and 0.73 Mg/GW(e)-yr in the enriched lithium (90% lithium-6) breeder blankets.

Projected Fusion Reactor Construction Rate

The principal demand for fusion reactors was assumed to be created by the demand for increased electrical power generation. The construction of fusion power reactors for this purpose was assumed to begin in the year 2008 and asymptotically approach 82% of the total newly constructed electrical power capacity after 20 yr, as previously described by Bogart [85]. Two scenarios were considered for the growth rate of installed electrical generating capacity during the half-century 2000-2050 (Table 14): a Base Case (1.4% Annual Growth Rate), and a High Electrical Growth Case (2.5% Annual Growth), which might be caused, for instance, by a massive shift to electrically powered vehicles.

The lithium requirements (Table 14) were considered separately for the natural lithium breeder blankets and the lithium-6 (90%) enriched breeder blankets; the

Table 13

LITHIUM REQUIREMENTS FOR FUSION REACTOR DESIGNS

System	Reactor Power		Breeder Material	Total Reactor				Blanket Only			
	GW(th)	GW(e)		Li	Li	⁶ Li	⁶ Li	Li	Li	⁶ Li	⁶ Li
				(Mg)	[Mg/GW(e)]	(Mg)	[Mg/GW(e)]	(Mg)	[Mg/GW(e)]	(Mg)	[Mg/GW(e)]
Tokamaks											
UWMAK-I ^a	5.0	1.5	Li	1760	1180	--	--	1400	933	--	--
BNL-UWMAK-I ^b	5.0	1.6	LiAl+LiAlO ₂	--	--	*	*	--	--	5.46	3.6
UWMAK-II ^c	5.0	1.7	LiAlO ₂	--	--	*	*	--	--	41	24
UWMAK-III ^d	5.0	2.0	Li	480	240	--	--	395	200	--	--
PPPL ^e	5.3	2.0	FLiBe	*	*	--	--	250	125	--	--
ORNL-DEMO ^f	2.2	0.75	Li	*	*	--	--	150	200	--	--
GA-DEMO ^g	1.3	0.31	Li ₇ Pb ₂ (Zone I)	*	*	*	*	23.6	76	--	--
			Li ₄ SiO ₄ (Zone II)	*	*	*	*	--	--	20	65
Pinches											
Toroidal Theta-Pinch ^h	3.6	1.7	Li	864	508	49	29	48	28	49	29
Toroidal Theta-Pinch	12.0	4.1	Li	864	210	49	12	48	12	49	12
Linear Reactor ⁱ	2.6	0.84	Li	570	800	88	105	38	45	88	105
Reversed Field Reactor ^j	3.2	1.1	Li	480	440	59	54	27	25	59	54
Fast Imploding Liner Reactor ^k	0.68	0.21	Li ₂ O	*	*	--	--	35	170	--	--
Mirrors											
Mirror Machine Reactor ^m	3.1	0.450	Li ₂ Be ₂ O ₃	--	--	*	*	--	--	2.2	4.9
Tandem Mirror ⁿ	3.1	1.0	Li	*	*	--	--	464	464	--	--
Field Reversed Mirror ^o	0.3	0.074	Li	*	*	--	--	49	662	--	--
Inertial Confinement											
UW-Solase ^p	3.34	1.0	Li ₂ O	1000	1000	--	--	337	337	--	--

^aSee Reference 5^bSee Reference 6^cSee Reference 7^dSee Reference 8^eSee Reference 9^fSee Reference 10^gSee Reference 11^hSee Reference 12ⁱSee Reference 13^jSee Reference 14^kSee Reference 15^mSee Reference 16ⁿSee Reference 17^oSee Reference 18^pSee Reference 19

*Same as blanket.

Table 14

PROJECTED CUMULATIVE LITHIUM DEMAND FOR COMMERCIAL FUSION POWER

Year	Installed Electrical Capacity		Natural Lithium Blankets			Enriched Lithium-6 Blankets			Natural Lithium Processed (Gg)	Tails ^C Available (Gg)
	Total	Fusion	Inventory	Consumed	Total	Inventory	Consumed	Total		
	[GW(e)]	[GW(e)]	(Gg)	(Gg)	(Gg)	(Gg)	(Gg)	(Gg)		
<u>Base Case (~1.4% Annual Growth)^a</u>										
2000	1260 ^b	-0-								
2005	1350	-0-								
2010	1450	5	1.5	0.1	1.6	0.12	0.01	0.13	2.3	2.2
2015	1555	31	9.3	1.1	10.4	0.74	0.08	0.82	14.6	13.8
2020	1670	88	26.4	4.3	30.7	2.11	0.32	2.43	43.2	40.8
2025	1790	178	53.4	11.4	64.8	4.27	0.83	5.10	90.7	85.6
2030	1920	285	85.5	23.5	109.0	6.64	1.71	8.35	146.6	138.2
2035	2060	400	120.0	41.2	161.2	9.60	3.00	12.60	224.1	211.5
2040	2210	523	156.9	64.8	221.7	12.55	4.73	17.28	307.3	290.0
2045	2370	654	196.2	94.9	291.1	15.70	6.92	22.62	402.2	379.6
2050	2540	793	237.9	131.7	369.6	19.03	9.62	28.65	509.5	480.8
<u>High Electrical Growth (~2.5% Annual Growth)^a</u>										
2000	1520 ^b	-0-								
2005	1720	-0-								
2010	1950	12	3.6	0.2	3.8	0.29	0.02	0.31	5.4	5.1
2015	2210	77	23.1	2.8	25.9	1.85	0.10	1.95	34.7	32.9
2020	2500	208	62.4	10.5	72.9	5.45	0.71	6.16	109.6	103.4
2025	2830	423	126.9	27.4	154.3	11.40	2.08	13.48	239.7	226.2
2030	3200	726	217.8	57.5	275.3	18.89	4.49	23.38	415.8	392.4
2035	3620	1070	321.0	104.1	425.1	25.68	7.90	33.58	597.1	563.5
2040	4100	1464	439.2	169.4	608.6	35.14	12.66	47.80	850.1	802.3
2045	4640	1907	572.1	255.9	828.0	45.77	18.97	64.74	1,151.4	1,086.7
2050	5250	2407	722.1	366.3	1,088.4	57.77	27.03	84.80	1,508.1	1,423.3

^a"Project INDEPENDENCE Report", Federal Energy Administration, PB-248 492 (November 1974), pp. 430-435.

^b"Supply 77", EPRI Supply Analysis Special Report (1978).

^cTails composition = 2.5 mole % lithium-6.

latter blankets required that approximately 40% more lithium must be processed, if the tails contain 2.5 at. % of lithium-6. Based only upon economic considerations, the natural lithium breeder blankets would be preferred because less lithium is required and the cost of isotopic enrichment is unnecessary; however, the lithium demands for either blanket design represent a significant impact upon the domestic lithium resources by 2050 and the requirements for fusion reactors may become strongly competitive with other energy uses for lithium, as previously discussed in this chapter. If these competitive market forces materialize, then it would become advantageous to shift to the enriched lithium-6 breeder blankets in which the tails from isotopic enrichment plants, representing nearly 95% of the lithium processed, would be available for resale. In this case only the cost of isotopic separation, estimated at \$0.60/g in Appendix D, would need to be added to the electrical power costs. For instance, when this enrichment cost for the Base Case in the year 2050 (Table 14) is considered with an annual interest charge of 15% for the amount of lithium-6 in the inventory of the breeder blankets, the additional cost is only \$0.0013/kW(e)-hr (in 1978 dollars), a small 4% increase in the total electrical generation costs.

Conclusions

Resources

U.S. resources projected at approximately 3.6×10^9 kg by the special NRC lithium sub-panel should be considered conservative since the estimates do not take into account undeveloped or unproven sources of lithium, namely: oil field brines, geothermal brines, brines of the Clayton Valley currently considered uneconomical to recover, and hypothetical and speculative resources in the Carolina pegmatite belt. The fact that sizable undetermined quantities of lithium exist in these areas is not disputed. The demand and pricing of lithium has not induced exploration and development to allow a determination of the real magnitude of the deposits.

Because of the low commercial demand for lithium relative to recoverable reserves, the lithium industry to date has had little incentive to undertake systematic exploration for lithium. Most deposits in the past were found in surface exposures while some were discovered by accident [73]. Disagreements on estimates

of the Nevada brine field, which is fulfilling one-third of current domestic needs, demonstrate our lack of knowledge concerning brine fields and the geological conditions and geochemistry associated with their formation and discovery. Because exploration has been negligible to date and also limited to a few geological environments, Vine indicates that the discovery of "previously unrecognized lithium resources" is very promising [75]. Discovery may be rather slim for new pegmatite deposits. However, the extent of existing pegmatite deposits is considered large since current operations involve an area which is only 1/30 of the pegmatite belt.

The lithium cornucopia appears to be in brine deposits both in the U.S. and abroad. Lithium-rich brines can be expected to be found in several geological environments. These include oil field brines, closed active desert basins, deposits below the surface of closed dry desert basins, and geothermal brines [73, 87].

The U.S. Geological Survey, due to the long-range concern over the development of energy-related uses of lithium, has already initiated a modest program of exploration, particularly for brine fields [75]. Energy companies and producers of metals and salts from brine-field areas are showing an increased interest in lithium and the use of the energy from geothermal fluids.

If partial dependence upon lithium from abroad is economically and politically acceptable, the lithium resources in Canada and Chile, for example, could satisfy expanding demands of the 21st century. The western world total lithium resource projection of 1×10^{10} kg includes only one salar (salt basin) of Chile which makes up 40% of this resource estimate. Salar are common to the Andean region of Chile, Bolivia, and parts of Argentina. Although lithium cannot be expected in every salar, "preliminary indications are that resources are vast" [69]. An American lithium producer has already entered into a joint agreement with the Chilean government to develop this first lithium field.

One lithium specialist states "the reserve-resource figures presented at this symposium (Corning, N.Y., 1977) must be multiplied by a large factor in order to reach a correct understanding of future availability of lithium" [71].

Intensified lithium exploration would probably meet with some resistance because

private industry cannot be assured that the exploration costs would ever be returned. However, as cited by some of the lithium specialists, historical experience with other commodities indicates that lithium can be expected to be found and produced in a timely manner to meet unusually large increases in demand.

Since the lithium industry is small and relatively young, the incentive of an assured market and profit should guarantee that needs of the future will be met. The development of an orderly demand can also be expected due to better communications and the cooperation now being demonstrated by government agencies, the lithium industry, and energy scientists.

Production Capacity

Current production capacity of 4.7×10^6 kg annually is expected to increase to about 6×10^6 kg by the end of 1978. With current demand under 4×10^6 kg, the imbalance of capacity and demand is readily apparent. Nevertheless, both major producers have expanded or are in the process of expanding, demonstrating their confidence in developing markets.

Historically, the lithium industry has demonstrated its ability to respond quickly to enormous demand changes. Such a demand was the AEC program of the late 1950's to produce lithium-6 for thermonuclear weapons. In the end the industry was left with a 500% over-capacity [69]. Apparently in satisfactory economic condition today, the industry believes firmly in the long-term growth of lithium uses. The consensus of lithium specialists indicates that quantum jumps in processing capacity will be easily achieved, needing only the incentive of a stable, long-term demand.

An annual capacity growth rate of 5% will keep well ahead of the projected conventional demand to the year 2000. In his 1977 projections of battery demand, Chilenskas shows annual consumption of about 5.5×10^7 kg by the year 2000 [83]. Figure 1 illustrates both the annual and cumulative needs of battery commercialization. It appears, however, that time is available for an orderly growth in production. There also appears to be significant communication of these lithium needs. Kunasz's modeling has shown that an annual production growth rate scheme of 5% to 1985, 10% to 1990, and 15% to the year 2000 will provide the capacity to meet both battery and conventional demands [71].

Technology is currently available or can be easily developed which will allow the industry to meet these anticipated production demands. According to Evans, new lithium capacity would not experience delays from environmental restrictions since lithium processing is nonpolluting [69].

Projections beyond the year 2000 are not available although it is suggested that the demand for batteries may stabilize shortly thereafter [71]. Chilenskas has indicated a possible 10-yr life time for these batteries and suggested that lithium may be recycled at a 90% recovery level [84]. Recycling, however, would not be significant until the turn of the century because significant amounts of lithium would not have been used until after 1990. The need for new lithium would decrease rapidly by 2010, perhaps by 50%, as recycling becomes important in the lithium supply picture (see discussion in the next section).

No increase in processing capacity appears necessary after the year 2000. Assuming an annual demand growth of 2.5% after the year 2000 and battery recycling, the need for new lithium might be expected to decrease and bottom out around the year 2010. Hence, manufacturers could expect to continue building batteries at a lithium consumption growth rate of 2.5% annually. Lithium producers would appear to have fallen into an over-production dilemma. However, assuming that demand from all sources developed as projected, the timing of the reduction in lithium demand for batteries and fusion power commercialization would allow this production capacity to be turned toward the needs of the fusion power industry.

Demand Versus Resources

Figures 2 and 3 show the cumulative lithium demand to the year 2050 for commercial fusion reactors using natural lithium and enriched (90%) lithium-6 breeding blankets, respectively (see the section Lithium Demands by a Fusion Reactor Economy). Each figure gives fusion power demands for two different annual electrical growth rates, 1.4 and 2.5%. For comparison, the cumulative growth demands of 2.5% annually through 2040 for both conventional and battery consumption are given. These cumulative demands can be readily compared with the domestic reserves and resources included on each graph.

Conventional demand projections are usually based upon historical information and trends.

FIGURE 2 - Projected cumulative lithium demand for conventional uses, batteries and commercial fusion reactors using natural lithium breeding blankets.

FIGURE 3 - Projected cumulative lithium demand for conventional uses, batteries and commercial fusion reactors using enriched lithium-6 breeding blankets.

Most lithium specialists believe conventional consumption will grow at an annual figure of 5% to the end of the century. After the year 2000 a growth not exceeding 2.5% appears commensurate with the needs of a mature, industrialized nation and also the projected electrical demand. Stabilization of population growth would be expected to reduce the consumption rate. Cumulative conventional demand, therefore, will require about 7% of the domestic resources by 2010 and 25% by 2040.

A significant impact on lithium resources appears to come from batteries predicted for utility and vehicular use. Cumulative consumption at the end of the century has been estimated at 3×10^8 kg. Market demands beyond that date have not been predicted by either battery or lithium specialists. However, in line with predicted electrical growth, battery demands have been projected in Figures 2 and 3 at a 2.5% annual growth rate after the turn of the century. There is not sufficient evidence to project higher growth rates because of the likelihood of competitive batteries (e.g., sodium/sulfur) and, in the case of utilities, alternate means of energy storage (e.g., hydrogen).

The cumulative consumption, reflecting Chilenskas' demand projection to the year 2000 and a 2.5% rate thereafter, is shown in Figures 2 and 3. The rate of increase in cumulative battery demand for raw lithium reflects the effect of lithium battery recycling implemented around the year 2000. The effect of recycling is more evident in the plotting of annual demands as shown in Figure 1. Make-up lithium (new or raw lithium), amounting to about 10% of the lithium recycled, would be required to replace recycling losses. Cumulative consumption for battery uses is projected at 20% of domestic resources by 2010 and 45% by 2040.

The cumulative demands of both conventional and battery uses amount to 30% of domestic resources by 2010 and 70% by 2040.

The consumption by the fusion power industry is expected to become significant after 2020. Figures 2 and 3 both show the cumulative needs of the fusion power industry to be relatively small when compared to other commercial demands. Only after 2045 does the cumulative demand of all three consumers (conventional, battery, and fusion) exceed the total U.S. resources estimated at 3.6×10^9 kg by the lithium sub-panel.

With the use of enriched solid lithium breeding blankets, about 40% more raw lithium must be processed (greater production capacity) to obtain the necessary lithium-6 isotope. However, the enriched breeder blankets are less taxing upon the lithium resource base since the lithium blanket inventory is relatively small, perhaps less than 1/10 of natural lithium blankets. Therefore, for enriched blankets most of the lithium production could be returned to the marketplace after the lithium-6 has been removed. This lower lithium inventory is evident when Figure 3 is compared with Figure 2.

Since battery life expectancy is estimated at 10 yr, lithium recycling with 90% recovery would be expected to begin around the year 2000. The quantity of lithium involved in battery recycling each year would provide feedstock for isotopic separation of lithium-6. If lithium from all recycled batteries were isotopically processed, including make-up lithium, adequate lithium-6 would become available to satisfy fusion power needs to 2050 at the maximum electrical growth rate of 2.5% annually.

There appears no need, as some energy scientists have suggested, to begin immediate stockpiling of lithium-6 for the fusion power industry. With a readily available feedstock in recycleable batteries, isotopic separations could begin some time in the 2000-2010 time frame. A system for identifying and controlling batteries containing isotopically processed lithium would, of course, have to be developed. Because batteries provide a safe, long-term source of feedstock the decision on type of breeding blanket need not be hasty. In fact, the fusion power program schedule could suffer serious delays without adversely affecting the quantity or availability of the feedstock.

If the commercialization of lithium batteries should fail, substantial changes in the lithium supply and demand picture could be expected. The cumulative demand for conventional uses and fusion power (natural lithium breeder blankets) would appear as shown in Figure 4. By the year 2050 only two-thirds of our domestic lithium resources of 3.6×10^9 kg would have been consumed by these two areas of use. For the alternative in which enriched breeding blankets were used, the cumulative demands would appear as given in Figure 5. If isotopic processing of all lithium used for conventional purposes began about the year 2000, sufficient lithium-6 could be made available to meet the projected fusion power demands to the

FIGURE 4 - Projected cumulative lithium demand for conventional uses and commercial fusion reactors using natural lithium breeding blankets (no batteries).

FIGURE 5 - Projected cumulative lithium demand for conventional uses and commercial fusion reactors using enriched lithium-6 breeding blankets (no batteries).

year 2035 at the maximum electrical growth rate of 2.5% and beyond 2050 at a growth rate of 1.4%. Total lithium consumption, conventional and fusion, by 2050 would amount to less than one-half of the U. S. resources as reported by the lithium sub-panel.

Although the future demand for lithium appears large in terms of today's usage, it falls well within the limits of U.S. domestic resources up to the year 2050. As with all new technologies, delays can

be anticipated in the projected dates for commercialization of lithium batteries and fusion power. The timing and the coordination necessary for increasing production capabilities and isotopic separation of lithium-6, if necessary, appear to be the more urgent problems. The excellent communication among lithium specialists and energy scientists, as is now being demonstrated, should provide assurance that these and other problems will be solved in a timely manner.

Lithium-6 Requirements and Availability

Background

Irradiation of lithium-6 in government production reactors or other reactors and neutron-generating machines appears to be the only feasible way of meeting the projected tritium needs through the end of the 20th century. Tritium cannot be made available from other sources (fuel reprocessing plants, heavy-water reactors, etc.) until hydrogen isotopic separation technology has been developed for use with low-level tritiated water waste. Even then, sufficient quantities would not be available to satisfy the fuel needs of fusion experiments. Hence, these other sources of tritium can only be considered as a supplement to fission and fusion reactor-produced tritium.

Potential Lithium-6 Demands

To meet the tritium fuel needs of the fusion development program to the year 2000, the theoretical minimum lithium-6 requirement is 312 kg. The lithium-6 burnup achievable in heavy-water government production reactors can be assumed to be between 10 and 80%. The burnup is a function of many variables such as the type of reactor, energy spectrum, neutron flux, target position in the reactor, and irradiation time. Since production capacities and parameters of irradiation cannot be disclosed, one must assume the minimum burnup figure in projections of lithium-6 needs. Hence, a maximum of 3000 kg could be required at the 10 at. % burnup level.

The choice of tritium breeding blanket for a fusion reactor experiment could also greatly affect the lithium-6 demands and the need for isotopic separation plants. The use of a breeding blanket with the Experimental Power Reactor (EPR-1) in 1986-1988 is uncertain. This experimental machine is expected to be capable of producing electrical power and, if a blanket were used, tritium would not be bred in sufficient quantities to maintain the fuel cycle without supplementary fuel [85]. Blanket development and evaluation will be necessary in the EPR-2 (1990-1992) and in the TDPR (also referred to as DEMO) about the year 2000. If a solid breeding blanket were used for any of these fusion machines, the lithium-6 requirements would be typical of those shown in Table 15.

Currently there are no commercial or government facilities for the isotopic separation of lithium-6. DOE, however, would be expected to have classified quantities of lithium-6 reserves as a result of the lithium isotopic enrichment program of the 1950's which was implemented for the separation of lithium-6 for thermonuclear weapons. Information on the extent of these reserves cannot be made available here; however, the status of these reserves held by DOE is discussed in a classified document which is available to qualified individuals. The need and time scale for isotopic separation facilities hinges upon DOE's decision to divert any of these reserves to meet fusion power program requirements.

Isotopic Separation Facilities and Technology

No lithium-6 isotopic separations have been made in the United States since 1963 when extensive enrichment facilities at Y-12 Plant, Oak Ridge, Tennessee were either dismantled or placed on standby. Separation of lithium isotopes employed an amalgam/aqueous hydroxide system called the Colex process. The first large-scale separations began in January 1955 using the 19-in. (48-cm)-diameter Colex cascade in facilities called Alpha-5. In May 1955 this plant was augmented by a neighboring plant, Alpha-4, which used a cascade of 30-in. (76-cm)-diameter columns.

Lithium isotope enrichment was accomplished by means of countercurrent flows of lithium-mercury amalgam and aqueous lithium hydroxide solution in packed columns. Lithium-6 moves preferentially into the amalgam and lithium-7 into the aqueous phase.

Lithium amalgam was produced from lithium hydroxide and mercury by electrolysis. This lithium amalgam was then pumped from the lower portions of the separation column into the upper portions of succeeding columns arranged in cascade. The amalgam then was allowed to flow downward by gravity countercurrent to an aqueous lithium hydroxide phase which was forced to flow upward in the columns by pumping.

At the product end of the Colex plant, a portion of the lithium-6 in the desired

Table 15

SOLID LITHIUM BREEDER BLANKET DEMANDS

Year	Fusion Capacity [MW(e)]	Fusion Reactor or Experiment	Potential Lithium-6 Required (kg)
1986- 1988	20-50	EPR-1	80-200 ^a 480-1200 ^b
1990- 1992	100-400	EPR-2	400-1600 ^a 2400-9600 ^b
2000	500-1000	TDPR	2000-4000 ^a 12,000-24,000 ^b
2010	1,750	Annual Commercial Requirement	7,000 ^a 42,000 ^b
2010	5,000	Cumulative Commercial Requirement	20,000 ^a 120,000 ^b
2020	11,500	Annual Commercial Requirement	46,000 ^a 276,000 ^b
2020	87,500	Cumulative Commercial Requirement	350,000 ^a 2,100,000 ^b

^aBased on a nominal lithium-6 requirement of 4 kg/MW(e)
(Reference 88).

^bBased on a nominal lithium-6 requirement of 24 kg/MW(e)
(Reference 89).

isotopic concentration was withdrawn as the hydroxide after the amalgam had been decomposed by catalysts in contact with water. Lithium-6 hydroxide not withdrawn as product was returned to the top for reflux while the mercury was returned to the amalgam cells for repeat of the amalgamation process.

At the tails (lithium-7) end of the Colex plant a portion of the lithium hydroxide depleted in lithium-6 was withdrawn for disposal (storage, stockpile, or resale) while the remainder was returned to the amalgam cells for reflux.

Enriched lithium-6 is generally stored as the hydroxide monohydrate. As the metal is required, the lithium is reduced electrolytically and packaged in heliarc-welded aluminum cans under an argon atmosphere. The three-step metal preparation involves neutralizing the hydroxide with hydrochloric acid, drying, and electrolyzing a molten eutectic of lithium chloride and potassium chloride.

Although any enrichment could be obtained, the top product of the plants, under the operating parameters at that time, was 95.5 at. % lithium-6.

The Alpha-5 facility was shut down in March 1959 and dismantled in 1965 and 1966. A portion of Alpha-5 was operated for a period of time from 1958 to 1959 and 1962 to 1963 to produce high-purity lithium-7. Presently only Alpha-4 facilities exist and they have not been operated since 1963. If lithium-6 were needed for either weapons or the fusion power program, DOE/Oak Ridge believes that existing facilities at Alpha-4 could not be economically renovated.

According to Oak Ridge Operations, no effort is being made to retain the capability to restart this facility [90]. Modifications necessary to meet current safety and environmental regulations, particularly those associated with the handling of large quantities of mercury, would be difficult and costly. The technology to design, build, and operate a lithium-6 production facility still exists, however.

A complete summary documenting the lithium enrichment technology and installed facilities at Y-12, Oak Ridge has never been prepared. Procedures on processing of material in the Y-12 production facilities also have not been compiled. However, a

series of detailed status and technical feasibility reports beginning with the development of the isotopic separation process in late 1952 is available. With declassification of some research preceding the pilot-scale development, details of lithium isotope separation factors for two-phase equilibrium systems have appeared in the open literature [91].

Commercial enrichment facilities, intended for lithium-7 production, may be in the offing [92]. DOE is now encouraging private industry to undertake lithium-7 enrichment to satisfy the future needs of the light-water reactor industry. High-purity lithium-7 (99.9% or better), as the hydroxide, is used chiefly for pH adjustment in the primary coolant of pressurized water reactors (PWR). A 1000-MW(e) PWR may need up to 17 kg of lithium-7 for the first year of operation and a minimum of 10 kg/yr thereafter. The actual usage, however, is apparently dependent upon the PWR operator, frequency of resin bed replacement, and whether the PWR is operated in a load-following manner.

Oak Ridge Y-12 Plant, which has been the only source of lithium-7 for utilities, has been allocating this commodity since 1976 because current supplies are expected to run out some time in the next 2-4 yr [92,93]. To augment these supplies until enrichment facilities are constructed, Eagle-Picher Industries has begun conversion of lithium fluoride to obtain the hydroxide for sale to utilities.

Eagle-Picher Industries expects to undertake the construction of a small lithium-7 isotopic separation facility at Quapaw, Oklahoma. The plant, estimated to cost \$3 million, will use the lithium amalgamation (Colex process) originally developed and used at Oak Ridge. The plant, of course, will be much simpler and will contain fewer cells than did the Oak Ridge facilities. It will be using highly enriched feed stock of up to 98.5% lithium-7 "tails" stockpiled by Oak Ridge from the late 1950's campaign of lithium-6 separation. According to EPI, the design of the plant will allow the flexibility of using either "tails" or natural lithium as starting materials.

The design of the plant, which is now finished, includes all of the latest improvements for environmental control of mercury. Construction, originally planned for completion in 1978, has been delayed [93]. There is uncertainty about when new lithium-7 production will be required since reserves appear to be lasting longer than projected. In addition, the 98.5% lithium-7 tails have been

considered for use in pH adjustment of the PWR coolant. The consequence of using isotopically impure lithium is a marked increase in tritium generation in the coolant. When these questions are resolved, there seems to be little doubt that construction of this separation plant will begin.

The lithium-7 output of the new plant is expected to be 1000 kg/yr at an isotopic purity of 99.99%. This production rate should meet the yearly demand up to 1985 assuming a PWR population of 130 reactors by that date. Expansion to a production level of 2000 kg/yr is economically feasible, thereby probably meeting reactor needs up through 1990.

It should be noted that this plant, with some modifications, could be devoted to lithium-6 enrichment. Oak Ridge Y-12 Plant has developed computer programs with which the lithium-6 processing capacity of this proposed plant can be determined [94]. Because of weapons association, lithium-6 separations done commercially would probably carry the same security restrictions currently imposed on lithium-6 processing technology and capacity.

Recent investigations outside of DOE on the separation of light and heavy hydrogen in the reaction of lithium amalgam with water have led to a preliminary design of a cascade that simultaneously enriches lithium-6 and deuterium [95].

In the event that lithium-6 isotopic enrichment were to be renewed, the time scale is sufficiently long to permit other isotopic separation concepts to be evaluated. Such schemes do not involve the hazards of handling huge quantities of mercury and the associated capital investment and operational controls to meet OSHA and EPA guidelines. If the Colex process were still considered superior after the evaluation of various alternate techniques, mercury reserves in the United States are adequate to satisfy an extensive lithium separation program through the 21st century. A synopsis of the mercury reserves is given in Appendix E.

A laboratory-scale enrichment process which has proven to be an ideal separation process for calcium isotopes may be equally applicable to lithium-6 and -7. Called the crown enrichment process because of the use of a new class of complexing agents (dicyclohexyl 18-crown-6), isotopic separation is accomplished in a counter-current liquid-liquid chemical exchange reaction. A short description and cost estimates of the crown process as applied to lithium-6 are given in Appendix D.

Availability of Helium-3 and Helium-4

Background

The D-³He fuel cycle, which uses the reaction $D + {}^3\text{He} \rightarrow {}^4\text{He} + p$, is being considered for fusion reactors. This fuel cycle should lend itself to high-efficiency, direct conversion since the Bremsstrahlung radiation loss is substantially less than the fusion energy production rate [96].

The subsidiary D-D reaction associated with the D-³He cycle produces not only helium-3 but also tritium which further reacts with deuterium to generate 14-MeV neutrons. According to studies by the University of Texas, the 14-MeV neutron flux could be limited to less than 10% of the flux in a D-T reactor by operating in a pulsed dual-cycle mode [96]. This concept involves the production of energy with the first phase or mode of the D-³He plasma in which the density ratio of helium-3 to deuterium is large. The second mode begins with the injection of large quantities of deuterium, which lowers the plasma temperature and increases the density ratio of deuterium to helium-3. D-D reactions are more numerous in the second mode, rapidly producing helium-3 and tritium, but this phase is of short duration. Energy is produced in mode 1 and helium-3 is bred in mode 2.

After completion of mode 2, the energy-containing plasma is adiabatically expanded and the energy is extracted by direct conversion [96]. The total neutrons produced are substantially lowered by a factor of 10 because of the D/He density ratios and the relative time scales of modes 1 and 2. This 10-fold reduction in 14-MeV neutron flux could be of significant help to fusion reactor designers because of the very critical first-wall problem in D-T fuel cycle reactors.

The potential capital costs of fusion machines involving the D-³He and D-T reactions may differ. The direct-conversion energy cycle of the D-³He reactor would probably require a larger-volume vacuum chamber, which in turn increases the size of the costly magnetic field coils. The University

of Texas study indicates that a significant cost saving in reactor moderation, breeding blanket, and reactor shielding can be achieved with the D-³He reactor. First, design requirements of the blanket (and associated tritium extraction and purification facilities) are reported to be greatly simplified because there is no need for tritium breeding in the blanket. Second, the blanket cooling and shielding requirements are greatly reduced because the 14-MeV neutron energy is less than 10% of the total energy produced. The study of the D-³He reactor concept identifies new problems such as cyclotron radiation loss and plasma confinement at very high ion temperatures.

The feasibility of developing fusion power based on the D-³He cycle must be concerned with the availability of helium-3. Helium-3, unlike deuterium, does not exist in significant quantities in nature. Quantities in the earth's atmosphere are extremely low although relatively larger quantities may exist in natural abundance helium found in natural gas fields.

The most significant sources of helium-3, therefore, would be from indirect and direct production in nuclear fission and fusion reactors. These would include:

- (1) Decay of tritium produced in a production reactor (highly enriched uranium-235 fueled, heavy-water moderated and cooled),
- (2) Decay of tritium bred in a D-T fusion reactor with a high breeding ratio.
- (3) Production within the fusion plasma (mode 2 of D-³He fueled fusion reactor).

The quantity of helium-3 available from tritium is easily calculated from the half-life of tritium and the tritium production rate. In the D-³He fuel-cycle reactor, advantage must be taken of the subsidiary D-D reaction for breeding the helium-3 while keeping the tritium production and 14-MeV neutrons to a minimum.

To support fusion experiments initially, dependence must be placed on existing helium-3 inventories or recovery from natural gas wells.

Current Inventory of Helium-3 in the U. S.

DOE possesses a classified inventory of helium-3 which is the byproduct (decay of tritium) of the tritium production carried on at the Savannah River Plant for thermonuclear weapons applications.

Helium-3 is supplied to Mound Facility where it is purified and sold chiefly for research and development activities throughout the world. Mound Facility is the only sales site in the United States.

The current selling price of helium-3 is \$170.00 per liter (STP) in 1 to 299-liter quantities. For large-quantity purchases (e.g., 7000 liters) the cost is about \$60/liter or \$450/g, decreasing with quantity purchased.

Tritium Production as a Source of Helium-3

The easiest manner to obtain helium-3 in quantity is from the decay of production tritium. Obviously this is a very expensive source due to the huge inventories of tritium which must be maintained and the high neutron costs associated with tritium production. Technology is well developed for both the production and the storage of tritium. Since the decay rate for tritium is about 5.5% per year, a tritium inventory of 18 kg would be required for each kilogram of helium-3 required per year.

The storage and monitoring costs would be minimal when compared with the initial production cost of the tritium inventory. Secondary containment, of course, would be mandatory for all storage facilities and gas-handling equipment. Helium-3 separation facilities would also be required. Separation and purification can be done simply and inexpensively through the use of palladium diffusers or beds of uranium and molecular sieves. These combined costs would also be relatively small compared to initial inventory costs.

As indicated elsewhere in this report, the cost of tritium in large quantities can be assigned a value of \$7500/g which is the currently quoted cost by Oak

Ridge National Laboratory, Isotope Sales for large quantities (>25,000 Ci) [97]. Therefore, for a production need of 1 kg of helium-3 per year, initial tritium inventory could cost a maximum of \$135,000,000. Excluding nominal storage and separation costs, the cost to produce 1 kg of helium-3, therefore, might run as much as \$8,000,000/kg. Obviously large quantity tritium production could reduce unit costs, although neutron costs, the controlling cost factor in tritium production, probably cannot be reduced significantly. In contrast, the cost of helium-3 obtained as a by-product from existing tritium or from natural gas would be expected to be appreciably less.

Atmosphere as a Source of Helium-3

Although helium is the second most abundant element found in the universe, the natural abundance of helium in the earth's atmosphere is only slightly greater than 5 ppm. The atmosphere appears to be an inexhaustible source due to constant replenishment as helium, generated by radioactive materials within the earth, continuously diffuses into the atmosphere. The atmospheric concentration of helium-4 equilibrates at 5 ppm due to a continuing helium loss to the stratosphere and outer space.

Helium-3 concentration in atmospheric helium is only one atom in 10^6 [98]. The steady-state concentration of helium-3 results from a balance of losses to outer space and generation from decay of tritium. Tritium (except for man-made contributions) is also at equilibrium between generation and radioactive decay. Natural tritium production is estimated to occur at a nominal rate of 0.5-1.0 tritium atom/cm²/sec, giving rise to a steady-state world-wide tritium inventory of 70-140 MCi [99]. The major tritium generation process is thought to be irradiation of nitrogen by cosmic rays. More than two-thirds of the tritium is probably produced in the stratosphere from which it is slowly released to the troposphere.

Commercial extraction of helium from the atmosphere appears to be unlikely until existing supplies are exhausted which is projected to be some time in the first half of the 21st century [100]. Beginning some time in the first quarter of the next century, helium-dependent energy-related technologies (fusion coolants,

energy storage, and energy transmission) may require sizeable quantities of helium-4. If it is found necessary to extract helium-4 from the atmosphere to meet these needs, helium-3 will appear in the extracted helium-4 in the isotopic ratio of 1:10⁶.

Koelling and Balazik, in a Bureau of Mines report, indicate that the energy required for helium extraction from air would be at least 1000 times greater than from natural gas [101]. Others estimate the cost of extraction to be 150-300 times greater than current commercial costs for extraction from natural gas. As an example, energy requirements for extraction of 1 billion cubic feet (Bcf) of helium are estimated to be 16% of current annual coal production or 70% of the annual Alaskan pipeline oil output [100]. As a by-product, the helium-3 amounting to about 0.8 kg would be subject to additional but very nominal isotopic separation costs.

Natural Gas Fields as a Source of Helium-3

For the next 25-30 yr, the cheapest and most readily available natural source of helium is the gas fields of the western United States. This source could become significant only if specific policies of conservation were implemented within the next few years. Natural-abundance helium (helium-3 and helium-4) occurs in natural gas in amounts from trace quantities (less than 0.005%) up to about 8% [101]. According to data from the Bureau of Mines, the helium-3 concentration in helium-4 will average 200 + 15 ppb, although the range is generally 175 to 225 ppb [102].

The availability of helium-3, therefore, has a direct relationship with known and potential helium-4 resources and their probable rate of recovery from natural gas. Under current practice, however, most helium in natural gas is expected to be dissipated as the gas is used for fuel. For example, of the 240-280 billion cubic feet (Bcf) of proved recoverable helium reserves, it is projected that by 1990 15 Bcf will have been used, 200 Bcf wasted, and only 65 Bcf (which includes currently stored helium of 38 Bcf) will remain [100].

Two documents published in 1975 address the topics of projected helium-4 resources, energy-related applications, and recommendations for helium management [100,101]. One is a Bureau of Mines bulletin concerned with resources and the other is a broad

detailed study submitted to the President and Congress by ERDA (now DOE). Another Bureau of Mines report documents natural gas resource projections made by the Potential Gas Committee in 1973 and derives helium resource projections from these natural gas estimates [103].

The latter 1973 reference has identified known recoverable helium reserves and estimated total helium contained in potential natural gas resources in the United States by applying the average helium content of various reported areas to the natural gas resources estimated by the Potential Gas Committee (PGC). PGC is sponsored by the Potential Gas Agency, an organization with members representing industry, government and producers whose primary purpose is to develop projections of known and potential natural gas supplies [104].

For discussions here, helium resources (by definition, Reference 103) include identified (proved and probable) gas fields and undiscovered sources from which economic extraction is currently or potentially feasible. Reserves are defined as helium in identified gas reserves having either more than 0.3% helium by volume (helium-rich) or less than 0.3% (helium-lean).

Total helium resources were shown by the Bureau of Mines in 1973 to be 694 Bcf and were divided into the following categories:

Helium in storage by the Bureau of Mines:	35 Bcf
Helium in measured helium- rich (>0.3%) gas reserves:	120 Bcf
Helium in measured helium- lean (<0.3%) gas reserves:	63 Bcf
Helium in indicated or un- discovered gas resources (hypothetical and spec- ulative):	476 Bcf

A more recent 1975 Bureau of Mines report indicated a slightly improved picture for helium-rich reserves [101]. As of January 1, 1975, the total domestic helium reserves in natural gas with a minimum helium content of 0.3% were estimated at 154 Bcf with 38 Bcf additional held in conservation storage by the Bureau of Mines. An additional 54 Bcf of helium were estimated to exist in proved gas reserves with a helium content of less than 0.3%.

The bulk of helium-rich reserves are found in five fields in the states of Wyoming, Kansas, Oklahoma, and Texas. Two-thirds of these reserves were in gas fields being produced in 1975 and 1976 with only a third of this natural gas being processed for helium removal. Reserves of helium are estimated to be decreasing at the rate of about 6%/yr [101]. Although the Bureau of Mines instituted a continuing program for analyzing gas samples from new wells and fields, no significant helium discoveries are being made.

The ERDA (ERDA-13) study on the other hand presents a very conservative picture of helium reserves [100]. A wide range of total helium resource estimates, varying from 340 to 1420 Bcf, was listed, referencing five different information sources. Future gas supplies were expected to come from deeper wells which in turn are expected to give lower helium concentrations. The average concentration of helium in remaining reserves was estimated at 0.075%. Conclusions of the ERDA-13 report, however, indicate that undiscovered recoverable helium resources should be in the range of 600 to 700 Bcf. The remaining potentially recoverable "proved reserves of helium" are given as 280 Bcf. This compares favorably with Bureau of Mines' 240 Bcf of proved reserves.

Because of the wide geographical distribution of gas wells and pipeline systems and projected low helium concentrations, it is thought that, with existing extraction plants, only one-half of the remaining helium reserves could actually be recovered. This most recent study concludes, therefore, that actually recoverable reserves consist of only the 65 Bcf identified as "proved nondepleting reserves", (38 Bcf of which is already in conservation storage) plus a collection of "probable nondepleting reserves", ranging from 7 to 63 Bcf, yielding a maximum recoverable reserve of 110-120 Bcf. These estimates and their effect on the helium-3 recovery potential are shown in Table 16.

With the exception of this 110-120 Bcf of nondepleting reserves (helium under storage and helium in nonfuel gas reserves) this ERDA report concluded that all other sources of helium will have been depleted by the year 2000. It is not believed that sufficient helium-lean natural gas will remain to warrant new plant construction or the continued operation of existing plants. If one assumed that natural gas supplies were discovered at a rate necessary to meet

demands up through 2020, the helium recovery potential could range from 10 to 12 Bcf/yr [103]. To achieve total or even partial recovery, extraction plants would have to be built around a central or master gas transmission system in order to process all gas removed from the ground.

The current potential production capacity of helium-4 in the United States is more than 4 Bcf/yr from two Bureau of Mines plants and 10 industrial operators [100]. Production of high-purity helium totaled 0.775 Bcf in 1975, with exports accounting for nearly a quarter of the sales. Similar production figures are projected for 1977 and 1978. Most of the extraction plants are now operating below capacity, some are on standby status, while others remove liquified petroleum gas (LPG) and discharge the helium to the atmosphere. Demand of conventional uses is expected to grow slowly, reaching 1.4 Bcf/yr by the year 2000, according to ERDA projections.

In the early part of the 21st century the helium industry may be impacted by large demands from three energy-related technologies. The technologies are superconducting magnetic energy storage, superconducting power transmission, and fusion reactors; their needs and impact are discussed in detail in ERDA-13 [100]. Helium will be used as a heat transfer medium as well as a refrigerant for superconducting magnets for magnetic confinement fusion reactors. The annual demand for these energy-related prospects could increase to 1-3 Bcf by the year 2030. Other energy-related uses could raise the figure to 5 Bcf/yr. The cumulative demands from all sources by the year 2030 may range from 100 to 180 Bcf, the wide range primarily due to differing requirements of fusion reactor designs and assumptions of growth.

Current market demands are being satisfied by processing helium-rich gas reserves, which because of over-capacity have helped sustain low prices in the marketplace. Prices for high purity helium in 1975 were: private industry, \$26 per thousand cubic feet; and Bureau of Mines, \$35 [101]. Costs are expected to be unchanged up through 1978. Costs to recover helium from domestic natural gas sources containing as low as 0.09% helium (using present low-temperature liquefaction technology) are in the range of \$50 to \$80 per thousand cubic feet (37.5 liters of liquid). This is a two-to-threefold increase in cost over recovery from helium-rich gas reserves.

Table 16

POTENTIAL HELIUM-4 AND HELIUM-3 AVAILABLE

Action for Recovery of Helium-4 from Natural Gas	Reference to Helium-4 Estimate	Helium-4 Production (Bcf/yr)	Cumulative Helium-4 (Bcf)	Potential Helium-3 Recoverable ^a		
				Yearly (kg)	Cumulative 1980 to Year 2000 (kg)	Total (kg)
Processing average yearly demand of helium-4 to year 2000 (assuming natural gas availability)	100	1.1	22	0.84	17	17
Processing at maximum capacity of all existing extraction plants from 1980 to 2000	100	4	80	3	60	60
Processing of 38 Bcf currently stored by Bureau of Mines	101	--	--	--	--	29
Processing all reserves projected to be available by ERDA-13 for helium recovery	100	--	65-110	--	--	49-86
Processing all known reserves of 245 Bcf estimated by Bureau of Mines	101	--	245	--	--	186
Processing all resources (known recover- able resources plus hypothetical and speculative resources) as projected by Bureau of Mines	103	--	694	--	--	527

^a Assumes helium-3 concentration in helium-4 to be 0.2 ppm.

Natural-abundance helium may become available from abroad as the large-volume gas liquefaction projects planned in North Africa, the Near East, Caribbean areas, etc., are developed. The liquefaction of natural gas of very low helium concentrations, required for economic shipment of gas abroad, yields a helium-rich, small-volume waste stream which only needs liquefaction for purification and use.

An Appraisal of Helium-4 and Helium-3 Availability

The current demand for helium-3 is small. Future demand, projected to depend on the growth of research and development activities, is uncertain because the use of helium-3 for fusion reactors is not included in any primary long-range planning. Because of the dependence of helium-3 on helium-4 availability, the factors affecting recovery of natural-abundance helium must be examined to determine the potential quantities of helium-3 that could be supplied if fusion power demand arose during the next two decades.

Large disparities appear in projections of helium resources as shown earlier and as given in Table 16. This is not surprising because there is wide divergence in natural gas resource estimates as well as the manner in which basic resource data are handled. For helium, however, the situation is more complex. Concentrations of helium in natural gas vary widely with location, making projections subject to large error limits. The recovery potential depends on many limiting factors: most helium-rich gas supplies are located in depleting reserves (gas currently being consumed for fuel); existing extraction plant capacity and technology are based on recovery from helium-rich (>0.3%) gas resources; and the wide dispersion of wells and pipelines limits recovery to a fraction of the total gas available for processing.

Under 1960 legislation, the Department of Interior was authorized to buy and store helium from private producers under a program which was to be self-liquidating. A majority of the existing industrial extraction plants were built as a result of this incentive. Up to 1973, when this conservation effort was terminated, 38 Bcf of helium had been recovered and stored by the Bureau of Mines in underground reservoirs.

Analysis of the data in Table 16 would seem to indicate that 240-280 Bcf of helium-4 remain in proved recoverable gas reserves. At this point in time, however, the only helium assured of being available for helium-3 separation is the 38 Bcf of reserves in storage by the Bureau of Mines. Also potentially available for helium-3 extraction is a projected 22 Bcf which might be produced over the next 20-25 yr for beneficial industrial use. It is projected in ERDA-13 that this amount may be only 15 Bcf because much of the existing helium-rich gas resources will have been consumed (for fuel) by 1990, leaving insufficient gas reserves available for processing by existing helium extraction plants [100]. Although existing helium extraction capacity is about 4 Bcf annually, maximum projected cumulative yield, assuming storage of excess helium production, would be only an additional 19 Bcf by 1990.

If existing in-place extraction plant capacity could be used to capacity up through the year 2000, 80 Bcf could potentially be recovered, with about 60 Bcf going to storage (see Table 16). This appears unlikely since a renewed search for helium-rich gas deposits has not been fruitful and prospects of finding them in the United States are now very dim. After 1990 demand is expected to exceed supplies, and by the year 2000 helium recovery from natural gas may cease altogether.

According to ERDA-13, realistic cumulative recoverable helium reserves up to the year 2000 may be between 65 and 110 Bcf, with 38 Bcf of these quantities already in storage [100]. With optimum action in legislation, federal funding, and incentives for private industry, up to 245 Bcf could be recovered. This appears to be the most optimistic, if not speculative figure, for recoverable reserves. Assuming total helium-3 recovery, up to 186 kg might be made available.

The construction of master gas distribution centers and accompanying processing plants for helium recovery and storage before further local consumption or interstate transmission appears to be the only way of recovering reserves estimated at 240-280 Bcf. Although complicated to implement and certainly not without economic impact, the unit cost would be but a fraction of that for helium extraction from air.

Recommendations for the management of existing helium reserves as given in ERDA-13 which affect the availability of helium-3 for isotopic separation include:

- 1) Continue current practices of recovering for beneficial use about 1 Bcf/yr up to the year 1990, after which government storage reserves of 38 Bcf could be released to supplement recovery activities up through the first half of the 21st century. During the period up to 2030, 20 Bcf could be obtained from current production and 95 Bcf from proved and probable nondepleting reserves yielding 110-120 Bcf. These quantities are not expected to adversely affect the growth of energy-related technologies.
- 2) A second recommendation, unlike the first, is expected to extend the supply of helium. The use of government storage inventories would be deferred, allowing demand to induce the use of imports and the construction of new helium extraction plants. This projected supplement, of only 10-20 Bcf, would provide some delay before use of government inventories would be required.
- 3) Private storage of excess helium production would allow 19 Bcf of helium to be added by 1990 to an existing storage inventory of 38 Bcf. Beyond 1990 the second alternative could then be implemented. This combination scheme is expected to permit meeting the demands of the most optimistic energy growth projection up through 2025.

The consensus is that it is inevitable that helium extraction from the atmosphere will be necessary beginning about 2030, depending upon the management route selected and the demand.

To induce more helium conservation, the Department of Interior has now lowered helium storage and handling charges. It is the conclusion of many that the federal government must assume the leadership for implementing and paying for the production and storage of helium for the next 50 yr [105]. Apparently helium is and has been the subject of numerous studies by many agencies. Little concrete action has been taken to date as

a result of these studies. Newly formed task forces will be outlining new helium management recommendations.

Current Technology for Helium Recovery from Natural Gas

Helium is normally extracted from natural gas by low-temperature (-151°C) liquefaction of the hydrocarbon components and separation of the gas (about 70% helium and 30% nitrogen) from the hydrocarbon liquid. Further reduction in the temperature of the helium gas mixture for nitrogen removal (-196°C) leaves helium gas which is purified to 99.995% by passing it over activated charcoal. The gas is then transferred to shipping containers unless liquid helium is desired for shipment. For the latter, the helium is liquified at -269°C and transferred to insulated shipping containers. Up to 1972, commercial liquid helium capacity from three major plants was 2000 liters/hr. In 1976 the liquefaction capacity was just under 5000 liters/hr. Consolidation of distribution centers and higher transportation costs could bring about the construction of additional liquefaction facilities.

A new prototype helium extraction plant being built in Canada may lead the way to lower helium recovery costs. The plant, a joint government and private industry endeavor, is designed to process natural gas with a helium content of 0.05 to 0.20% and will use diffusion separation techniques [101].

Enrichment Technology for Recovery of Helium-3 from Helium-4

Helium-3 availability is based on two assumptions: helium will be recovered and isotopic separation technology will become available. Assuming a nominal concentration of 0.2 ppm in helium-4, at least 29 kg of helium-3 could be recovered from the 38 Bcf of helium-4 reserves now in storage by the Bureau of Mines. Cumulative helium-3 could run as high as 86 kg if various helium conservation schemes were implemented in the next 20 yr (see Table 16). The most optimistic but unlikely figure would be 186 kg, assuming recovery of all known proved helium reserves in natural gas resources including non-depleting gas resources.

New low-temperature isotopic separation technology may allow helium-3 to be enriched on a large scale from natural-abundance helium obtained from gas

fields or the air. A preliminary analysis shows the economic feasibility of enriching helium-3 from natural-abundance helium which has already been liquified for transportation. Details of the technology along with estimated costs for small-scale recovery appear in Appendix F.

The feasibility of economical helium-3 recovery from natural-abundance helium lies primarily, therefore, with the expense of liquifying huge amounts of helium. The unit costs for isotopically separated helium-3 are given in Table F1 of Appendix F. The minimum unit

enrichment cost of about \$156/liter of helium-3 may be possible using a two-step process involving superleak separation and distillation for enrichment to 99%. These are estimated costs based on pilot-scale facilities processing up to 1000 liters of helium-3 per year with liquefaction costs for natural-abundance helium being borne by helium-4 sales. With transportation and energy costs projected to rise continuously each year, there is every indication that liquefaction of helium may become a standard procedure for providing more economical distribution.

Acknowledgements

The authors are grateful to the following for information or assistance given in the preparation of this report:

J. C. Bixel, Monsanto Research Corporation, Mound Facility
D. R. Carter, Eagle-Picher Industries
B. E. Jepson, Monsanto Research Corporation, Mound Facility
C. J. Kershner, Monsanto Research Corporation, Mound Facility
H. T. Kite, Union Carbide Corporation, Y-12 Plant
J. H. Leonard, Consultant
L. H. Myer, E. I. DuPont de Nemours & Co., SRL
J. A. L. Robertson, Chalk River Nuclear Laboratories, AECL
R. A. Schwind, Monsanto Research Corporation, Mound Facility
A. Shapiro, University of Cincinnati

We are also indebted to R. P. Ratay, Monsanto Research Corporation, for technical editing.

References

1. Fusion Power by Magnetic Confinement Program Plan, ERDA-76/110/1 (July 1976), 59 pp.
2. W. M. Stacey, Jr. et al., Prototype Experimental Power Reactor Preliminary Considerations, ANL/CTR-TM-64, Argonne National Laboratory, Argonne, Ill. (April 1976), 28 pp.
3. J. R. Powell, J. A. Fillo, B. G. Twining and J. J. Dorning, Proceedings of the Magnetic Fusion Energy Blanket and Shield Workshop, A Technical Assessment, ERDA-76/117/2 (August 1976), 898 pp.
4. G. L. Kulcinski et al., "TETR - A Tokamak Engineering Test Reactor to Qualify Materials and Blankets for Early DT Fusion Power Reactors," in Proc. Second Topical Meeting Tech. Controlled Nuclear Fusion, CONF-760935 (1976), pp. 73-94.
5. B. Badger et al., UWMAK-I, A Wisconsin Toroidal Fusion Reactor Design, UWFD-68, University of Wisconsin, Madison, Wisc. (Mar. 15, 1974), pp. VIII-A-1 to VIII-R-1.
6. J. R. Powell (ed.), Preliminary Reference Design of a Fusion Reactor Blanket Exhibiting Very Low Residual Radioactivity, BNL-19565, Brookhaven National Laboratory, Upton, N. Y. (Dec. 1, 1974), 114 pp.
7. B. Badger et al., UWMAK-II, A Conceptual Tokamak Power Reactor Design, UWFD-112, University of Wisconsin, Madison, Wisc. (October 1975), pp. IV-A-1 to IV-G-27.
8. B. Badger et al., UWMAK-III, A Noncircular Tokamak Power Reactor Design, UWFD-150, University of Wisconsin, Madison, Wisc. (July 1976), pp. VII-A-1 to VII-H-5.
9. R. G. Mills (ed.), A Fusion Power Plant, MATT-1050, Princeton Plasma Physics Laboratory, Princeton, N. J. (August 1974), 580 pp.
10. D. Steiner et al., ORNL Fusion Power Demonstration Study: Interim Report, ORNL/TM-5813, Oak Ridge National Laboratory, Oak Ridge, Tenn. (March 1977), 111 pp.; and private communication, T. E. Shannon (Oak Ridge National Laboratory), Sept. 26, 1977.
11. D. Kearney, "General Atomic Noncircular Tokamak Demonstration Power Reactor: Blanket/Shield, Tritium and Power Conversion Systems," in Proc. Magnetic Fusion Energy Blanket and Shield Workshop, ERDA-76/117/2 (August 1976), pp. 363-428; and private communication, K. Schultz (General Atomic Corp.), December 1977.
12. R. A. Krakowski, F. L. Ribe, T. A. Coultas and A. J. Hatch, An Engineering Design Study of a Reference Theta-Pinch Reactor (RTPR), LA-5336/ANL-8019, Los Alamos Scientific Laboratory, Los Alamos, N. M., and Argonne National Laboratory, Argonne, Ill. (March 1974), 137 pp.
13. R. A. Krakowski and R. L. Miller, Reactor Plant Design Study for Alternative Concepts: A Preliminary Report in the Linear Theta-Pinch Reactor (LTPR) Concept, LA-UR-78-180, Los Alamos Scientific Laboratory, in press.
14. R. L. Hagenson, R. A. Krakowski and K. I. Thomassen, "A Toroidal Fusion Reactor Based on the Reversed-Field Pinch (RFP)," in IAEA Conference and Workshop on Fusion Reactor Design, Madison, Wisc., Oct. 10-21, 1977, (to be published).
15. R. A. Krakowski, R. W. Moses, R. L. Miller and R. A. Gerwin, "Fusion Power from Fast Imploding Liners," in IAEA Conference and Workshop on Fusion Reactor Design, Madison, Wisc., Oct. 10-21, 1977, (to be published).

16. J. D. Lee et al., "Mirror Reactor Blankets," in Proc. Magnetic Fusion Energy Blanket and Shield Workshop, ERDA-76/117/2 (August 1976), pp. 477-572.
17. G. A. Carlson, Parametric Design Study of Tandem Mirror Fusion Reactors, UCRL-79092, Lawrence Livermore Laboratory, Livermore, Calif. (May 22, 1977), 34 pp.; and W. S. Neef, Jr., Mechanical Design Aspects of a Tandem Mirror Fusion Reactor, UCRL-79434, Lawrence Livermore Laboratory, Livermore, Calif. (Apr. 25, 1977), 26 pp.
18. W. C. Condit et al., "The Field Reversed Mirror as a Power Reactor," in Proc. Second Topical Meeting Tech. Controlled Nuclear Fusion, CONF-760935 (Sept. 21-23, 1976), pp. 107-118; and private communication, G. A. Carlson, Lawrence Livermore Laboratory, March 1978.
19. R. W. Conn et al., Solase, A Conceptual Laser Fusion Reactor Design, UWFD-220, Vol. II, University of Wisconsin, Madison, Wisc. (Dec. 6, 1977), pp. XVI-A-1 to XVI-F-3.
20. M. A. Abdou and C. W. Maynard, "Neutronics and Photonics Study of Fusion Reactor Blankets," in Proc. First Topical Meeting Technology Controlled Nuclear Fusion, CONF-740402, Vol. 2 (April 1974), pp. 87-100.
21. V. A. Maroni, "Tritium Processing and Containment Technology for Fusion Reactors: Perspective and Status," in Proc. Second Topical Meeting Technology Controlled Nuclear Fusion, CONF-760935-P3 (September 1976), pp. 799-818.
22. V. A. Maroni, An Analysis of Tritium Distribution and Leakage Characteristics for Two Fusion Reactor Reference Systems, CEN/CTR/TM-9, Argonne National Laboratory, Argonne, Ill. (Mar. 13, 1974), 41 pp.
23. M. A. Abdou, L. J. Wittenberg and C. W. Maynard, "A Fusion Design Study of Non-mobile Blankets with Low Lithium and Tritium Inventories," Nuclear Technology, 26, 400-419 (1975).
24. W. F. Vogelsang, "Breeding Ratio, Inventory and Doubling Time in a D-T Fusion Reactor," Nuclear Technology, 15, 470-474 (1972).
25. D. G. Jacobs, Sources of Tritium and Its Behavior upon Release to the Environment, TID-24635, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1968), 90 pp.
26. B. M. Abraham, "Tritium Production by Neutron Irradiation of Aluminum-Lithium Alloys," U.S. Patent 3,100,184 (Aug. 6, 1963).
27. Extraction of Tritium from Lithium Aluminate, W. Yunker (ed.), HEDL-TME-76-81, Hanford Engineering Development Laboratory, Richland, Wash. (September 1976), 85 pp.
28. A. B. Johnson, Jr., T. J. Kabele and W. E. Gurwell, Tritium Production from Ceramic Targets: A Summary of the Hanford Coproduct Program, BNWL-2097, Battelle Pacific Northwest Laboratories, Richland, Wash. (August 1976), 127 pp.
29. A. A. Kishbaugh, Extraction of Tritium from Lithium Aluminate Targets, DP-1058, E. I. du Pont de Nemours and Co., Aiken, S. C. (August 1966), 32 pp.
30. J. H. Owen and D. Randall, "Equilibrium and Kinetic Studies of Systems of Hydrogen Isotope, Lithium Hydrides, Aluminum and LiAlO_2 ," in Radiation Effects and Tritium Technology for Fusion Reactors, CONF-750989, Vol. III (March 1976), pp. 433-457.
31. W. H. Kohler and J. Voss, "Tritium Demand for Fusion Reactor Development," in Proceedings of the First Topical Meeting on the Technology of Controlled Nuclear Fusion, April 16-18, 1974, San Diego, California, CONF-740402-P1, Vol. 1 (1974), pp. 467-475.
32. Ph. Pautrot and M. Damiani, "Operating Experience with the Tritium and Hydrogen Extraction Plant at the Laue-Langevin Institute," in Separation of Hydrogen Isotopes, H. K. Rae (ed.), ACS Symposium Series, Washington, D. C., 1978, pp. 163-170.

33. E. J. Hennelly, "Fuel and Blanket Management and Supply in Commercial Fusion," in Proceedings of the First Topical Meeting on the Technology of Controlled Nuclear Fusion, April 16-18, 1974, San Diego, California, CONF-740402-P1, Vol. 1 (1974), pp. 476-484.
34. Nuclear Reactors Built, Being Built or Planned in the United States as of December 31, 1977, TID-8200-R37, USDOE (March 1978), 46 pp.
35. Research Materials, Oak Ridge National Laboratory, Oak Ridge, Tenn. (April 1973), p. 103.
36. A. A. Gates, P. G. McCarthy and J. W. Edl, Safety Analysis Report - Packages LP-50 Tritium Package, DPSPU 74-124-5, E. I. du Pont de Nemours and Co., Aiken, S. C. (April 1975).
37. T. B. Rhinehammer and P. H. Lamberger, Tritium Control Technology, WASH-1269, U. S. Government Printing Office, Washington, D. C. (December 1973), 530 pp.
38. H. Kouts and J. Long, "Tritium Production in Nuclear Reactors," in Tritium, A. A. Moghissi and M. W. Carter (ed.), Messenger Graphics, Phoenix, Ariz., 1973, p. 41.
39. J. A. L. Robertson, Chalk River Nuclear Laboratories, Chalk River, Ontario, personal communication (May 1976).
40. "World List of Nuclear Power Plants," Nuclear News Buyers Guide, 21, 49-62 (1978).
41. A. J. Mooradian, Energy for Five Thousand Years, AECL-4845, Chalk River Nuclear Laboratories, Chalk River, Ontario (July 1974), 5 pp.
42. A. J. Mooradian and O. J. C. Runnalls, CANDU - Economic Alternative to the Fast Breeders, AECL-4916, Chalk River Nuclear Laboratories, Chalk River, Ontario (September 1974), 17 pp.
43. L. R. Haywood, The CANDU Power Plant, AECL-5321, Chalk River Nuclear Laboratories, Chalk River, Ontario (January 1976), 43 pp.
44. J. L. Gray and I. N. MacKay, The Present Status and Future Development of Heavy-Water Reactors in Canada, AECL-4356, Chalk River Nuclear Laboratories, Chalk River, Ontario (January 1973), 7 pp.
45. J. L. Gray, Why CANDU? Its Achievements and Prospects, AECL-4709, Chalk River Nuclear Laboratories, Chalk River, Ontario (January 1974), 16 pp.
46. P. J. Dyne, Managing Nuclear Wastes, AECL-5136, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba (May 1975), 17 pp.
47. M. L. Rogers, P. H. Lamberger, R. E. Ellis and T. K. Mills, "Catalytic Detritiation of Water," in Separation of Hydrogen Isotopes, H. K. Rae (ed.), ACS Symposium Series, Washington, D. C., 1978, pp. 171-176.
48. J. P. Butler, J. H. Rolston and W. H. Stevens, "Novel Catalysts for Isotopic Exchange between Hydrogen and Liquid Water," in Separation of Hydrogen Isotopes, H. K. Rae (ed.), ACS Symposium Series, Washington, D. C., 1978, pp. 93-109.
49. M. Hammerli, W. H. Stevens and J. P. Butler, "Combined Electrolysis Catalytic Exchange (CECE) Process for Hydrogen Isotope Separation," in Separation of Hydrogen Isotopes, H. K. Rae (ed.), ACS Symposium Series, Washington, D. C., 1978, pp. 110-125.
50. H. Kouts and J. Long, "Tritium Production in Nuclear Reactors," in Tritium, A. A. Moghissi and M. W. Carter (ed.), Messenger Graphics, Phoenix, Ariz., 1973, pp. 38-45.
51. J. M. Smith and R. S. Gilbert, "Tritium Experience in Boiling Water Reactors," in Tritium, A. A. Moghissi and M. W. Carter (ed.), Messenger Graphics, Phoenix, Ariz., 1973, pp. 57-68.

52. J. Locante and D. D. Malinowski, "Tritium in Pressurized Water Reactors," in Tritium, A. A. Moghissi and M. W. Carter (ed.), Messenger Graphics, Phoenix, Ariz., 1973, pp. 45-57.
53. J. M. Gruhlke, "Pressurized Water Reactor Effluent Discharge Trends in the United States," presented at the 22nd Annual American Nuclear Society Meeting, Toronto, Canada, June 13-18, 1976.
54. Alternatives for Managing Wastes from Reactors and Post-Fission Operations in the LWR Fuel Cycle, ERDA-76-43, Vol. 1 & 2, Battelle Pacific Northwest Laboratories, Richland, Wash. (May 1976).
55. Nuclear Power Growth 1974-2000, WASH-1139(74), USERDA, Washington, D. C. (February 1974), 74 pp.
56. J. O. Blomeke, C. W. Kee and R. Salmon, Projected Shipment of Special Nuclear Material and Wastes by the Nuclear Power Industry, ORNL-TM-4631, Oak Ridge National Laboratory, Oak Ridge, Tenn. (August 1974), 65 pp.
57. J. O. Blomeke, C. W. Kee and J. P. Nichols, Projections of Radioactive Wastes to be Generated by the U. S. Nuclear Power Industry, ORNL-TM-3965, Oak Ridge National Laboratory, Oak Ridge, Tenn. (February 1974), 112 pp.
58. J. O. Blomeke, C. W. Kee and R. Salmon, "Shipments in the Nuclear Fuel Cycle Projected to the Year 2000," Nuclear News, 18:8, 62-65 (June 1975).
59. B. J. Kullen, L. E. Trevorow and M. J. Steindler, Tritium and Noble Gas Fission Products in the Nuclear Fuel Cycle, II. Fuel Processing Plants, ANL-8135, Argonne National Laboratory, Argonne, Ill. (March 1975), 70 pp.
60. L. N. Grossman and J. O. Hegland, Tritium Distribution in High Power Zircaloy Fuel Elements, GEAP-12205, General Electric Company, Pleasanton, Calif. (June 1971), 42 pp.
61. J. H. Goode and C. M. Cox, The Distribution of Fission Product Tritium in a Zircaloy-Clad UO₂ Blanket Rod from PWR-1, ORNL-TM-2994, Oak Ridge National Laboratory, Oak Ridge, Tenn. (February 1970), p. 17.
62. D. E. Rey, L. N. Grossman and F. H. Megerth, Zircaloy-Clad UO₂ Fuel Rod Evaluation Program, Quarterly Progress Report No. 11, GEAP-10217, General Electric Company, San Jose, Calif. (August 1970), p. 40.
63. B. C. Finney, R. E. Blanco, R. C. Dahlman, F. G. Kitts and J. P. Witherspoon, Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle for Use in Establishing "as low as practicable" Guides - Nuclear Fuel Reprocessing, ORNL-TM-4901, Oak Ridge National Laboratory, Oak Ridge, Tenn. (May 1975), 174 pp.
64. J. H. Goode and V. C. A. Vaughen, Experiments on the Behavior of Tritium During Head-end Processing of Irradiated Reactor Fuels, ORNL-TM-2793, Oak Ridge National Laboratory, Oak Ridge, Tenn. (February 1970), p. 13.
65. J. H. Goode (ed.), Voloxidation - Removal of Volatile Fission Products from Spent LMFBR Fuels, ORNL-TM-3723, Oak Ridge National Laboratory, Oak Ridge, Tenn. (January 1973), 137 pp.
66. The Safety of Nuclear Reactors (Light Water-Cooled) and Related Facilities, WASH-1250, U. S. Atomic Energy Commission, Washington, D. C. (July 1973), p. 7-33.
67. Lithium Resources and Requirements by the Year 2000, J. D. Vine (ed.), U. S. Geological Survey Professional Paper 1005 (December 1976), 162 pp.
68. A. L. Hammond, "Lithium: Will Short Supply Constrain Energy Technologies," Science, 191:4231, 1037-1038 (1976).
69. R. K. Evans, "Lithium Reserves and Resources," presented at the Symposium on Lithium Needs and Resources, Corning, N. Y., October 12-14, 1977.

70. J. N. Hartley, B. F. Gore and J. R. Young, "Potential Lithium Requirements for Fusion Power Plants," presented at the Symposium on Lithium Needs and Resources, Corning, N. Y., October 12-14, 1977.
71. I. A. Kunasz, "Quo Vadis, Litio," presented at the Symposium on Lithium Needs and Resources, Corning, N. Y., October 12-14, 1977.
72. H. B. Wood, "United States Lithium Supply and Demand and the Problems Involved in Compiling Statistics," in Lithium Resources and Requirements by the Year 2000, J. D. Vine (ed.), U. S. Geological Survey Professional Paper 1005 (December 1976), pp. 22-25.
73. J. J. Norton, "Lithium Resource Estimates - What Do They Mean?" in Lithium Resources and Requirements by the Year 2000, J. D. Vine (ed.), U. S. Geological Survey Professional Paper 1005 (December 1976), pp. 38-45.
74. J. J. Norton, "Lithium, Cesium and Rubidium - The Rare Alkali Metals," in United States Mineral Resources, U. S. Geological Survey Professional Paper 820 (1973), pp. 365-378.
75. J. D. Vine, "The Lithium-Resource Enigma," in Lithium Resources and Requirements by the Year 2000, J. D. Vine (ed.), U. S. Geological Survey Professional Paper 1005 (December 1976), pp. 35-37.
76. I. A. Kunasz, "Lithium Resources - Prospects for the Future," in Lithium Resources and Requirements by the Year 2000, J. D. Vine (ed.), U. S. Geological Survey Professional Paper 1005 (December 1976), pp. 26-30.
77. M. Steinberg and V. Dang, "Preliminary Design and Analysis of a Process for the Extraction of Lithium from Seawater," in Lithium Resources and Requirements by the Year 2000, J. D. Vine (ed.), U. S. Geological Survey Professional Paper 1005 (December 1976), pp. 79-88.
78. J. D. Vine, "Are Lithium Resources Adequate for Energy Self-Sufficiency?" Trans. Amer. Nucl. Soc., 22, 55-56 (November 1975).
79. J. D. Vine, "Lithium in Sediments and Brines - How, Why, and Where to Search," Jour. Research U. S. Geol. Survey, 3:4, 479-485 (July-August 1975).
80. C. E. Berthold and D. H. Baker, "Lithium Recovery from Geothermal Fluids," in Lithium Resources and Requirements by the Year 2000, J. D. Vine (ed.), U. S. Geological Survey Professional Paper 1005 (December 1976), pp. 61-66.
81. J. A. Whelan and C. A. Petersen, "Lithium Resources of Utah," in Lithium Resources and Requirements by the Year 2000, J. D. Vine (ed.), U. S. Geological Survey Professional Paper 1005 (December 1976), pp. 75-78.
82. Lithium - Commodity Data Summaries, U. S. Bureau of Mines, January 1976, pp. 94-95.
83. A. A. Chilenskas, "Commercialization Planning for the Lithium/Metal Sulfide Battery," presented at the Symposium on Lithium Needs and Resources, Corning, N. Y., October 12-14, 1977.
84. A. A. Chilenskas, G. J. Bernstein and R. O. Ivins, "Lithium Requirements for High-Energy Lithium-Aluminum/Iron-Sulfide Batteries for Load-Leveling and Electric-Vehicle Applications," in Lithium Resources and Requirements by the Year 2000, J. D. Vine (ed.), U. S. Geological Survey Professional Paper 1005 (December 1976), pp. 5-8.
85. S. L. Bogart, "Fusion Power and the Potential Lithium Requirement," in Lithium Resources and Requirements by the Year 2000, J. D. Vine (ed.), U. S. Geological Survey Professional Paper 1005 (December 1976), pp. 12-21.
86. B. F. Gore and P. L. Hendrickson, Fuel Procurement for First Generation Fusion Power Plants, BNWL-2012, Battelle Pacific Northwest Laboratories, Richland, Wash. (September 1976), 22 pp.

PAGES 65 to 66
WERE INTENTIONALLY
LEFT BLANK

Appendixes

APPENDIX A

MODIFICATION OF COMMERCIAL LIGHT-WATER REACTORS FOR TRITIUM PRODUCTION

External sources for supplying tritium fuel will be required continuously for experimental fusion reactors which do not breed tritium. One suggestion for supplying such tritium is to produce it in present commercial light-water power reactors by neutron capture in lithium-6 while simultaneously producing power. The technical feasibility and some cost estimates for the production of tritium from this source are examined in this study along with the breeder materials required for this application.

The costs of fabrication of the lithium-bearing breeder pins for insertion into the reactor and the processing plant for extraction of the tritium from the breeder materials will not be considered in this study. These costs should be approximately the same for whatever irradiation facility is selected to produce tritium. Only the impact of tritium production peculiar to commercial nuclear power plants is considered.

This assessment of potential tritium production from light-water reactors (LWR) was made for two conditions:

- o Minor modification of current-type pressurized-water reactors (PWR) to increase tritium production.
- o Major modification of new PWR's especially for tritium production.

The tritium production in a typical PWR (Table A1) was selected as the basis for estimates made for each of the two conditions. Because boiling-water reactors (BWR's) exhibit similar nuclear characteristics as PWR's, the results should be applicable to both types of LWR's.

MINOR MODIFICATIONS OF CURRENT-TYPE PWR'S TO INCREASE TRITIUM PRODUCTION

To increase tritium production, lithium (enriched to greater than 90% lithium-6) could be introduced into the reactor cores of existing types of PWR's in several ways. Lithium might be introduced in soluble form into the reactor coolant, in place of the boron used as a chemical shim. The tritium formed subsequently by neutron capture would appear, however, as very dilute tritiated water and its recovery would be expensive as discussed in Appendix B.

A more desirable method of introducing lithium would be in solid form, isolated from the coolant so that the tritium produced could be readily recovered. Solid lithium (as a stable high-temperature ceramic) could be introduced as cylindrical pellets approximately 1 cm in diameter. Such pellets could be inserted into one or more in-core instrumentation wells to form rods of a total length approximately equal to the active reactor core length, typically about 250 cm. Calculations indicate that the tritium production in one such 1-cm rod would be approximately 13 g/yr. If eight instrument wells were used per reactor, nearly 100 g/yr could be available from this source.

Solid lithium compounds, which retain most of the tritium at the PWR's temperature of 304°C, might also be substituted for boron as neutron absorber material in the burnable poison rods which are required to provide a negative temperature reactivity coefficient when using fresh fuel. An estimate for this potential source can be obtained from Table A1, initial cycle data, where boron in poison rods produces about 800 Ci of tritium per year, by the $^{10}\text{B}(n,2\alpha)^3\text{H}$ reaction. Nearly 10^3 more neutrons

Table A1
TRITIUM PRODUCTION IN TYPICAL 1000-MW(e) PWR
(SEQUOYAH PLANT)^a

Sources of Tritium	Tritium Production (Ci/yr)	
	Initial Cycle	Equilibrium Cycle
Ternary Fission (in fuel rods)	12,800	12,800
$^{10}\text{B}(n,2\alpha)^3\text{H}$ (in poison rods)	800	N.A. ^b
$^{10}\text{B}(n,\alpha)^7\text{Li}(n,\alpha)^3\text{H}$ (in poison rods)	1,500	N.A. ^b
$^{10}\text{B}(n,2\alpha)^3\text{H}$ (in coolant from soluble poison)	1,130	780
$^7\text{Li}(n,\alpha)^3\text{H}$ (limit 2.2 ppm ^7Li)	8.8	8.8
$^6\text{Li}(n,\alpha)^3\text{H}$ (purity of ^7Li =99.9%)	8.8	8.8
Total Tritium Produced	16,248	13,598

^aReference A3.

^bNot applicable.

are captured, however, by the nuclear reaction $^{10}\text{B}(n,\alpha)^7\text{Li}$. If lithium were substituted for boron and the absorption value of the poison rods remained the same, then lithium-6 would absorb neutrons at the same rate as does the latter boron-10 reaction, which produces tritium at a rate of 10^3 times 800 Ci/yr. As a result of lithium replacement of boron in the burnable poison rods nearly 80 g/yr of tritium could be realized per reactor. The combined tritium production from those two sources could yield approximately 180 g/yr. At the present value of tritium (\$7500/g) this tritium would have a value of \$1.35M. If 100 reactors were involved in such a program, the combined tritium production has the potential to be a sizeable 18 kg/yr.

As indicated earlier, however, burnable poisons are only used with fresh fuel and are not required after the first fuel loading when normally one-third of the fuel is replaced. If, instead of replacement of one-third of the core, the entire core is replaced with fresh fuel and burnable poisons, the fuel costs would triple or the cost of tritium production would be twice the yearly fuel costs. The fuel normally remains in the reactor for 78 weeks during the initial cycle compared with 49 weeks during the equilibrium cycle. Therefore, the cost of the tritium would be only 1.26 times the usual fuel cost, which is presently approximately 3 mills/kW-hr. At a 65% duty factor for a 1000-MW(e) plant the additional fuel costs per year can be estimated as follows:

$$\text{Fuel Cost Increase} = (1.26) \times (3 \times 10^{-3} \text{ \$/kW-hr}) \times (10^6 \text{ kW}) \times \frac{24 \text{ hr}}{\text{day}} \times \frac{365 \text{ days}}{\text{yr}} \times 0.65 = \$21.5\text{M/yr}$$

As noted previously the value of the tritium is only \$1.35M; therefore, this strategy would not be a cost-effective means to produce tritium.

MAJOR MODIFICATION OF NEW PWR'S FOR TRITIUM PRODUCTION

If major redesign of current types of power reactors is considered, substantial amounts of tritium could be produced. Conceptually, nearly all neutrons captured in uranium-238 to produce plutonium in current power reactor cores could instead be captured in lithium-6 to produce tritium in suitably designed replacement cores. This strategy is similar to that proposed for the breeding of fissile fuel in the Light-Water Breeder Reactor (LWBR) Program [A1]. Some of the nuclear reactor characteristics discussed in the LWBR study can be used to estimate the quantity of tritium which might be produced in a PWR. Additionally, information from the tritium production in the Hanford N Reactor Coproduct Program can be utilized [A2].

A criterion for measuring the performance of a reactor to produce new fuel is the conversion ratio, which is defined as the instantaneous rate of production of fissile fuel divided by the rate of destruction of fissile fuel. We will make the assumption that the production of tritium from lithium-6 can be approximated by this conversion ratio. The initial conversion ratio for uranium-235 in a UO_2 fuel rod is shown to be a function of the fuel-to-water ratio (Figure A1). The PWR design yields an initial conversion ratio of approximately 0.9. Higher conversion, and consequently more tritium, could be obtained if the core were redesigned to handle a fuel-to-water ratio at the intermediate value between the points for the PWR and LWBR, where the uranium-235 conversion ratio is greater than one (Figure A1).

Although the initial conversion ratio for a PWR is 0.9, this ratio rapidly decreases as the fuel is burned and some fission products become high neutron absorbers. For a fuel element exposed to a burnup of 30,000 MW-days/MTU (metric ton of uranium), the conversion ratio is only approximately 0.4 for the commercial PWR using 3%-enriched uranium-235 oxide fuel and increases to slightly over 0.6 for 5%-enriched uranium-235 fuel (Figure A2). The maximum tritium production by the irradiation of lithium-6 in a PWR will be assumed to be 0.6 also. With a 65% duty cycle the tritium produced in a 1000-MW(e) [3582-MW(th)] reactor would be:

$$\text{Tritium Production} = 0.6 \times 0.65 \times \frac{1 \text{ MTU}}{30,000 \text{ MW-days}} \times \frac{365 \text{ days}}{\text{yr}} \times$$

$$3582 \text{ MW(th)} \times 10^3 \text{ kg/MTU} = 6.85 \text{ kg/yr} = 18.8 \text{ g/day}$$

The core design for tritium production would require large amounts of lithium in place of uranium-238 presently contained in the slightly enriched uranium used as fuel. Such a reactor could be conceptualized as having some "seed" fuel elements containing highly enriched uranium oxide (>90% uranium-235) mixed with a neutron-inert diluent such as ZrO_2 . These seed elements would be surrounded with "blanket" elements containing lithium. Such a core separation would be necessary because the high neutron absorption cross-section for lithium-6 (675 barns) could interfere with the chain reaction if the lithium remained in the center of the core. Heterogeneous "seed-blanket" reactor cores have been designed and operated for the LWBR. Fuel element fabrication costs, however, are much higher than those for conventional slightly enriched elements.

FIGURE A1 - Conversion ratio versus water content at beginning of core life for UO_2 fuels (Reference A1).

BREEDER MATERIALS

In the previous discussions, the lithium breeder material is assumed to be contained in pins similar to Zircaloy-clad fuel pins. Tritium extraction would occur following the removal of the breeder pins from the reactor. The lithium compound used as the tritium breeder material in a PWR must be chosen carefully. Most importantly, it must retain the tritium at the operating temperature of the reactor so that the tritium release to the cooling water is minimized, both during normal operation and during off-normal operations if the cladding fails. The temperature of the breeder compound will be above the coolant temperature [500°F (288°C)], because the nuclear reaction ${}^6\text{Li}(n,\alpha){}^3\text{H}$ is exothermic. Its actual temperature will depend upon the pin design. Several classes of metallic and ceramic compounds are suggested for this use and will be discussed [A2,A4].

Metallic lithium (180°C melting point) would exist as a liquid in the container tubes. The solubility of zirconium in liquid lithium has been reported to be small at these temperatures (7.6×10^{-4} at. % zirconium at 480°C). Violent reaction would occur and large amounts of tritium would be released, however, if the zirconium tube split and the liquid lithium contacted the hot water.

FIGURE A2 - Fissile fuel production efficiency versus relative initial uranium-235 inventory (fuel at 30,000 MW-day/MT in light-water reactors) (Reference A1).

The disadvantage of the low melting point for lithium could be overcome by the use of alloying elements such as aluminum, bismuth, lead, silicon, and tin which form intermetallic compounds which melt above 600°C. A drawback to the utilization of most of these intermetallic compounds is the appearance of a liquid phase at a much lower temperature as the lithium is consumed by nuclear transformation. Corrosive reactions between these eutectic liquids and the container tubing might occur and would need to be studied.

The compound LiAl (melting point 718°C) might be very useful because it exhibits a wide solubility range and the eutectic temperature with aluminum is approximately 600°C. Alternately, a solid solution of lithium in aluminum might also be used. The breeding and recovery of tritium from this latter solid solution have been demonstrated [A5]. The intimate contact compatibility of the aluminum solid solution with a zirconium cladding could lead to the formation of zirconium-aluminum compounds, which might weaken the cladding. Perhaps a ceramic coating could be used to form an interface between these two metallic phases. The LiAl breeder alloy might be jacketed with a high-temperature aluminum alloy, such as sintered aluminum powder (SAP), although its use in high-temperature pressurized water is doubtful.

Lithium oxide ceramics which have high melting points might be more useful for this application. The monoxide, Li_2O , has a high melting point and a high lithium atom density, but a high affinity for water; consequently, any water leaking into the tube would form a gelatinous mass of lithium hydroxide, which would make subsequent handling very difficult.

Lithium oxide forms compounds with alumina and silica which have high melting points, reasonably high lithium densities, and low affinities for water. Extensive information on the use of these compounds for tritium production has been reviewed by Johnson et al. [A2]. The compound lithium aluminate (LiAlO_2) has a melting point near 1700°C , and the eutectic liquid which would be formed as the lithium is transformed by neutron irradiation melts at about 1670°C . Lithium orthosilicate (Li_4SiO_4), melting point 1255°C , and metasilicate (Li_2SiO_3), melting point 1200°C , are stable compounds and may also be useful for this application.

Before the ceramic breeder could be utilized, it would be desirable to know the permeation rate of the tritium through the zirconium cladding of the breeder pins. The tritium permeation depends upon the partial pressure of tritium within the pins which is a function of the solubility of tritium in the breeder material. The solubility of hydrogen in a ceramic oxide has been found to be very small; however, before the tritium solubility in the breeder material can come to equilibrium, the tritium must diffuse through the breeder material and reach equilibrium with the gas phase. The diffusion of tritium in ceramics at the breeder temperature (approximately 400°C) is very slow [A4], between 10^{-12} cm^2/sec for Al_2O_3 to 10^{-20} cm^2/sec for BeO ; consequently, the slow diffusion greatly increases the tritium retention in a ceramic breeder. Because little information is known regarding the retention of tritium in LiAlO_2 , a calculation of the tritium pressure inside the breeder pins is not possible.

In a PWR fuel pin much of the tritium is held up by dissolution in the Zircaloy tubing and, as a result, less than 100 Ci/yr permeates into the cooling water. Because of the slower diffusion of tritium in LiAlO_2 compared with UO_2 , and a similar retention of tritium in the Zircaloy tubing, the permeation of tritium from an LiAlO_2 breeder pin may be no greater than that found for current fuel pins.

In order to prevent the loss of tritium in the reactor coolant, Johnson [A2] describes the use of an aluminum cladding for the LiAlO_2 inside of the Zircaloy-2 cladding. The tritium was successfully extracted from these breeder pins during post-irradiation anneals at 800 – 900°C .

The ratio of condensible product (HTO or T_2O) to noncondensable product (HT or T_2) appeared to vary with the temperature of the extraction and the type of apparatus (i.e., a stainless steel system versus an all-glass system). Further study of tritium release from the ceramic breeder both during irradiation and after irradiation would be desirable.

Also requiring further study is the amount of tritium which might be released if water flooded a defective breeder pin. It has been estimated that nearly 0.25% (30 Ci/yr) of the tritium formed by ternary fission is released by defective fuel rods in a 1000-MW(e) PWR. If this same failure rate occurred in the proposed breeder pins, the amount of tritium released to the coolant water would be excessive. Higher-integrity cladding or the use of the aluminum inner capsule would be required.

In summary, large amounts of tritium could be produced in a PWR designed especially for the production of tritium. Because this reactor utilizes highly enriched uranium-235 seed fuel pins, the cost for uranium enrichment would be greater than for present designs, but not excessively so. Present power reactor fuel utilizing 3–4% enriched uranium already includes most of the isotope separation cost. Credit for plutonium production could not be included for the redesigned core, but some credit would be applicable for tritium produced.

Such a redesigned power reactor of 1000 MW(e) would be very useful at a center for fusion reactor experiments. For instance, the Tokamak Engineering Test Reactor designed by the University of Wisconsin requires 360 MW(e) and a tritium supply of 3.4 kg/yr for sustained operation. The tritium-producing PWR could supply the tritium needs of the TETR and also supply the electrical power needs for the TETR and other plasma physics experiments which have high power requirements. The site would then be energy-independent of the local utilities.

Tritium accumulation in this modified PWR coolant water would be significantly higher than in present PWR's. Techniques are now being developed for the continuous and economical removal of tritium from water (see Appendix B). These techniques should be available in time for this modified PWR.

REFERENCES

- A1. Light Water Breeder Reactor Program, Final Environmental Statement, Summary and Background, ERDA-1541 (June 1976).
- A2. A. B. Johnson, Jr., T. J. Kabele and W. E. Gurwell, Tritium Production from Ceramic Targets: A Summary of the Hanford Coproduct Program, BNWL-2097, Battelle Pacific Northwest Laboratories, Richland, Wash. (August 1976), 127 pp.
- A3. Sequoyah Nuclear Plant, Units 1 and 2, Preliminary Safety Analysis Report, USAEC Report, Docket-50327-1 (Oct. 15, 1968).
- A4. M. A. Abdou, L. J. Wittenberg and C. W. Maynard, "A Fusion Design Study of Nonmobile Blankets with Low Lithium and Tritium Inventories", Nuclear Technology, 26, 400-419 (1975).
- A5. B. M. Abraham, "Tritium Production by Neutron Irradiation of Aluminum-Lithium Alloys, "U.S. Patent 3,100,104 (Aug. 6, 1963).

APPENDIX B

HYDROGEN ISOTOPIC SEPARATION PROCESSES

The availability of tritium from light-water reactors, fuel reprocessing plants, and heavy-water reactors will be dependent upon the development of isotopic separation (detritiation) processes. The isotopic removal of tritium from aqueous waste has received attention both in the United States and Europe primarily to meet future discharge regulations and reduce personnel exposures. A number of technical feasibility studies have been carried out on many detritiation schemes and, although a few have been under development, commercial application appears as far away as 5-10 yr [B1-B5]. Many alternative methods have been discussed in a review by Ribnikar and Pupezin [B1]. A short review of the more promising methods of detritiation having received some development success was included in the ERDA-76-43 document "Alternatives for Managing Wastes from Reactors and Post-Fission Operations in the LWR Fuel Cycle" [B6].

The economic feasibility of detritiating large volumes of low-level waste water (0.001 to 10 $\mu\text{Ci/ml}$) is highly dependent on the separation factor of the elementary isotopic separation process employed. The separation factor for most H/T isotopic systems is small, ranging between 1 and 2. Some exceptions are catalytic chemical exchange and water electrolysis with factors of 6 and 10, respectively. The more promising detritiation processes which are being studied in varying degrees are: 1) reversible electrolysis, 2) combined electrolysis-catalytic exchange, and 3) molecular photoexcitation.

Electrochemical decomposition of water can achieve high separation factors but the energy costs make this technique very unattractive. On the other hand, reversible electrolysis (now called bipolar electrolysis) appears promising because multistage separation can be accomplished with lower power consumption and without production of gaseous hydrogen between stages [B7,B8]. Separation factors of 8-20 have been achieved by the use of a palladium-silver bipolar membrane in the electrolysis cell. This technique, which has been under development at the Oak Ridge National Laboratory since 1974, is discussed in the following sections.

Both catalytic exchange and molecular photoexcitation have been examined by several DOE sites in the United States and these methods appear promising from the standpoint of versatility of application, energy consumption, and feasibility. The AECL (Atomic Energy of Canada Limited) has done considerable work with the catalytic exchange process as a possible alternate method for the extraction and enrichment of D_2O for their heavy-water reactor industry [B9,B10]. The molecular photoexcitation method has received attention from Battelle Pacific Northwest Laboratories, the Los Alamos Scientific Laboratory (LASL), and Mound Facility [B11,B12]. The LASL work has been directed at both deuterium and tritium. Mound Facility has been engaged in both combined electrolysis-catalytic exchange and molecular photoexcitation studies since 1974 [B13-B22]. The only current development work within the United States in these two areas of tritium isotope separation is believed to be at Mound Facility. Details of this work and cost estimates applicable to the aqueous waste are given in the following sections.

Since all three processes are still in varying degrees of development it is impossible to identify the most cost-effective process. Cost estimates, whenever discussed, are given for comparative purposes and involve only the primary isotopic separation process.

ISOTOPIC SEPARATION BY BIPOLAR ELECTROLYSIS

When a conductive barrier is inserted into the voltage gradient between the anode and the cathode of a conventional electrolysis cell so as to isolate the two electrodes, the barrier acts as both anode and cathode and hence becomes bipolar. Although the electrode reactions at the bipolar electrode are typical of a normal electrolysis cell, the differences are that gaseous hydrogen is not generated at the cathode surface, atomic hydrogen is sorbed and transported through the electrode by interstitial diffusion, and oxidation of the hydrogen takes place at the anode surface to form water.

A basic requirement of this process is that the bipolar electrode must be porous to hydrogen and also hydrophobic in order that separation of the electrolyte is maintained; that is, the protium-rich material in the terminal cathode compartment must be isolated from the deuterium or tritium-rich solution in the terminal anode compartment (see Figure B1). The use of a very thin metal membrane fulfills this requirement. Recent studies at Oak Ridge National Laboratory have shown the merits of palladium-25% silver as a bipolar electrode material which can readily sorb and diffuse hydrogen.

A simple bipolar separation cascade might appear as shown in Figure B1. In this scheme the flow of hydrogen is established through the cascade towards the terminal cathode. The mass transfer process apparently favors the transfer of the lighter isotopes. In the aqueous phase adjacent to the cathodic side of the bipolar electrodes, enrichment of the heavier isotope takes place. In practice, to achieve a maximum separation, the tritium-rich aqueous solution is probably swept from the cathode surface (bipolar electrode) and circulated countercurrent to the movement of the hydrogen through the cascade.

FIGURE B1 - Bipolar electrolysis cascade system for hydrogen isotope separation.

Bipolar electrolysis is reported to show a reduction in power consumption over that of conventional electrolysis by as much as 50-80%. This is due to the fact that the net standard potential across the bipolar electrode is zero. However, a small overvoltage is necessary across each bipolar electrode in order to achieve hydrogen transport at a measurable rate. The total power requirement of a bipolar electrolysis cascade may therefore be equal to some fraction of that required to achieve the same separation with conventional electrolysis cells. The composite separation factor for bipolar electrolysis is the product of the separation factors occurring at the terminal electrodes and at the bipolar electrodes.

Although bipolar electrolysis is expected to provide high separative capacity at low power consumption, difficulty may be encountered in scaling-up the process to obtain reasonable cell size and throughput for high-volume wastes. Throughput can be increased, however, by increasing the temperature which in turn decreases the separation efficiency. Some reduction in the latter can be accepted because of the large separation factor at the bipolar electrodes.

Information is not yet available for estimating processing costs.

ISOTOPIC SEPARATION BY COMBINED ELECTROLYSIS-CATALYTIC EXCHANGE (CECE) PROCESS

Many of the basic separation methods used for heavy-water production processes are technically feasible for detritiating water. Detritiation, however, requires larger stripping and recovery factors than does heavy-water production. To be capable of obtaining the needed high recovery, a feasible detritiation process will require a high isotopic separation factor.

The hydrogen-water chemical exchange process has the required high isotopic separation factor as shown in Table B1 and is uniquely suited to a water feed. In addition, the technical feasibility of hydrogen isotopic enrichment through the exchange between hydrogen and water is not questioned. The process has been employed to produce heavy water on a large scale [B23]. The HT/H₂O catalytic exchange process was selected, on the basis of high isotopic separation factor and technical feasibility, as a process for development and demonstration of waste water detritiation.

Work is in progress at Mound Facility to develop an improved version of the basic process and to demonstrate the separation of tritium for the particular concentrations and types of low-level aqueous wastes (LLAW) obtained from DOE contractors and fuel reprocessing plants. The process will also apply to the removal of tritium from heavy water used as the moderator and coolant in research reactors, U. S. production reactors, and power reactors (e.g., the Canadian CANDU reactors).

The improved approach to HT/H₂O catalytic exchange is based on the use of antiwetting, hydrophobic catalysts which permit the chemical exchange reactions between liquid water and gaseous hydrogen in direct contact, thus eliminating problems of catalyst deactivation and the complexity of reactor design normally associated with earlier hydrogen/water catalytic exchange techniques [B24-B26] involving gas-phase catalysis. Use of hydrophobic catalysts was first reported in relation to studies directed toward an improved heavy-water process [B27]. The catalyst consists of an alumina substrate, a platinum coating, and a coating of semi-permeable, water-repellent material such as silicone or Teflon.

The highest separation factors for HT/H₂O exchange are obtained at low temperatures because of the nature of the chemical equilibrium

with an isotopic separation factor of about 6 at 25°C (see Table B1). Processes which involve steam-hydrogen reactions in the vapor state require higher temperatures to prevent water condensation, resulting in lower isotopic

Table B1

EQUILIBRIUM CONSTANT FOR THE REACTION $\text{HT} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{HTO}$

Temperature (°C)	Equilibrium Constant
303	2.17
217	2.64
158	3.10
80	4.37
56	5.05
20	6.47

separation factors. The hydrophobic low-temperature mixed-phase system potentially has many advantages over the gas-phase system including higher isotopic separation factor, lower energy consumption, higher throughput rate, and simpler equipment.

There are two major alternative applications of the combined electrolysis-catalytic exchange process to detritiation of LLAW. The first alternative is to apply the process to the total waste stream and deplete the tritium to a degree that the resulting detritiated waste stream may be dispersed to the environment. This alternative has been referred to by Ribnikar and Pupezin [B1] as the stripping scheme. The second alternative application would produce a similar enriched tritium stream, but the water is detritiated to a lesser degree and returned to the reactor (or plant), thus maintaining a desired steady-state tritium concentration in accord with applicable regulations for in-plant exposure of operating personnel. Ribnikar and Pupezin have called this alternative the recycling scheme. Of course, a wide spectrum of options exists within either scheme when selecting a design basis for the detritiation system. For example, regulatory factors and in-plant parameters such as LLAW throughput quantity and tritium concentration levels could affect the size of the system and the necessary degree of separation and enrichment of the tritium.

The throughput required for removal of tritium from LLAW could vary over a wide range depending on the application. Likewise, the degree of separation and recovery required could vary considerably. For example, the internal flow of water in a PWR cooling water recycling detritiation application could be on the order of 10 to 50 liters/hr with an overall separation factor requirement of 100 to 1000. In comparison, application of the stripping scheme to the flow of LLAW from a fuel reprocessing plant could require a throughput of 500 to 2500 liters/hr with an overall separation requirement of 10^{11} to 10^{13} . Since the costs associated with detritiation of water increase with increased throughput and overall separation factor, the application of the stripping scheme to the fuel reprocessing plant would be the least favorable from a cost viewpoint, as both throughput and separation requirements are a maximum for the fuel reprocessing LLAW stripping application.

Of primary importance to the success of the demonstration of this process will be the effect of traces of organic solvents, HNO_3 , fission-product iodine, and metallic fission-product ions on the activity and life of the hydrophobic catalyst. Only data obtained in an actual demonstration test using LLAW from the PWR or fuel reprocessing plant will suffice to ultimately demonstrate the feasibility of the process.

The combined electrolysis-catalytic exchange (CECE) process, as the name implies, is made up of two sections: electrolysis and catalytic exchange. As with any detritiation system, various control, monitoring, and support systems are also required. Continuous electrolysis is necessary to provide

gaseous hydrogen. The use of solid-polymer-electrolyte (SPE) electrolysis cells eliminates the usual handling and separation problems associated with liquid electrolytes. The catalytic exchange section consists of simple catalyst-packed columns which are operated in series, the number and length controlling the composite separation factor.

A pilot-scale CECE system has been built at Mound Facility to establish both operating and scale-up parameters [B22]. From the simplified sketches of the CECE process (Figures B2 and B3), a brief description of the isotopic separation can be given. A flow of water enters the top of the first column in a cascade of columns filled with hydrophobic precious-metal catalyst. Feed water to be detritiated enters at a predetermined point in the column cascade, joining the controlled flow of water from the top. This water stream is enriched in tritium (as HTO) at the expense of a countercurrent flow of hydrogen (and HT) from the continuous electrolysis of the water collected at the end of the column cascade. Oxygen from the electrolysis is discharged; hydrogen (and HT) enters the base of the column to repeat the exchange process. Hydrogen gas, depleted in tritium, leaves the top of the column to be oxidized and can serve as a continuous source of water for the column. The remaining hydrogen (up to 50%) can be used as required for plant processes or as an alternate source of fuel, or it can be recombined with oxygen in a fuel cell for power savings of up to 20%.

FIGURE B2 - Electrolysis section of the combined electrolysis-catalytic exchange system for hydrogen isotope separation.

Product from the enrichment cascade can be removed either as highly tritiated water from the final electrolysis cell or as electrolyzed HT gas.

The major advantages of the CECE process are a large separation factor, the use of the solid polymer electrolyte, simplicity of design, and the ease of scale-up. The composite separation factor for CECE is the product of the separative factors for the columns and the electrolysis cell. The height of an equivalent theoretical plate for the column is 4.5 ft (1.4 m) for a separation factor of 7. Any desired detritiation factor can be easily achieved by adding column length. Throughput, increased by increasing the column diameter, will be limited by the SPE electrolysis capacity.

Preliminary data imply that, under continuous electrolysis, the water to be detritiated may be electrolyzed an average of 1.5 times to satisfy the needs of the catalytic exchange process. Although these parameters are yet to be determined, it appears that the total power consumption may be conservative relative to other detritiation techniques with the exception of molecular photoexcitation which is described in the following section.

FIGURE B3 - Catalytic section of the combined electrolysis-catalytic exchange system for hydrogen isotope separation.

ISOTOPIC SEPARATION BY MOLECULAR PHOTOEXCITATION

Selective photoexcitation has the potential for orders-of-magnitude higher separation factors and, in principle, requires much less separative work because the separation energy is applied to the minor constituent rather than to the entire feed mixture. In conventional multistaged separation processes, sufficient energy input is needed for processing the total feed quantity many times to maintain the total cascade flow required for the desired separation. Thus, selective photoexcitation is a very attractive process for an application where one is concerned with the isotopic separation of trace quantities from a voluminous quantity of water that will be discharged to the environment.

The basic process, which is carried out in the gas phase, consists of isotopically selective photodissociation of gaseous HTO in the presence of H_2 which scavenges the photoproducts. This photodissociation is achieved by a two-photon process employing an infrared (ir) laser and an ultraviolet (uv) flashlamp. The ir laser selectively excites the OT stretching vibration in HTO at $4.35 \mu m$, while the uv flashlamp is filtered to photodissociate only the vibrationally excited HTO molecules. The photoproducts T and OH both react rapidly with H_2 to produce HT and H_2O , respectively. By recycling the hydrogen stream the tritium may be significantly enriched relative to the water stream. An analysis of the kinetics indicates that, for low-level wastes, the effect of the tritium β -decay on regeneration of HTO places a more stringent limitation on the tritium level allowable in the hydrogen stream than does the reaction

Initial studies of photodissociation have been reported [B13-B21].

One such isotopic separation scheme using molecular photoexcitation with lasers is now under study and would be applicable to tritiated waste water from fuel reprocessing plants and light-water reactors. It consists of three basic steps:

- 1) Isotopically selective photodissociation of HTO in the vapor phase.
- 2) Scavenging of the photoproducts.
- 3) Separation of the scavenged photoproducts from the feed material.

Decontamination of aqueous wastes by molecular excitation depends on selective catalysis of reactions involving tritiated water (specifically HTO). The catalysis is achieved by selective excitation of HTO, which is possible because of the spectral alterations induced by isotopic substitution.

When one of the hydrogen atoms in water is replaced with a tritium atom, the most striking spectral changes occur in the transitions involving nuclear motion (that is, rotational and vibrational). Second-order effects arising from different zero-point vibrational energies and altered Franck-Condon factors are manifest in the electronic transitions. The low-lying (less than 10 eV) electronic states of water (Rydberg states) are dissociative, so the absorption spectrum is very broad. Moreover, the onset of absorption occurs at higher energies for HTO than for H_2O because of the smaller zero-point energy. Therefore, direct selective electronic excitation of HTO is not possible at energies less than 10 eV.

As shown in Table B2 the ground-state vibrational frequencies are significantly different in H_2O and HTO. In fact, the O-T stretch (ν_1) at 2295 cm^{-1} is well separated from the H_2O bands, so that very selective excitation of HTO can be readily achieved. However, the energy of the O-T stretch in HTO

Table B2
FUNDAMENTAL VIBRATIONAL FREQUENCIES FOR
H₂O, HTO, AND T₂O

Mode	Label	H ₂ O		HTO		T ₂ O	
		Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
Symmetric stretch ^a	v1	3652 ^c	3657	----	2295	----	2233
Bending	v2	1595	1595	1324	1343	996	998
Asymmetric stretch ^b	v3	3756	3756	3711	3703	2364	2365

^a Corresponds to O-T stretch in HTO.

^b Corresponds to O-H stretch in HTO.

^c Values are in cm⁻¹.

is 6.7 kcal/mole and the activation energy for reaction of water with other stable molecules is on the order of 50 to 100 kcal/mole. Thus, the vibrational excitation is a small fraction of the activation energy. The selective excitation may increase the reaction rate of HTO by several orders of magnitude relative to H₂O, but the overall rate will still be very slow.

In order for the selective excitation to be an effective catalyst, the excitation energy must be comparable to the activation energy. The activation energy may be decreased by using highly reactive species such as a radical, but handling such species would greatly complicate any decontamination scheme. Therefore, the alternative of increasing the excitation energy is more appealing.

One possibility would be to excite higher-energy overtone or combination bands. However, the transition intensity, in general, diminishes by one or more orders of magnitude for each additional quantum of vibrational energy that is excited. Moreover, at higher energies the bands of HTO and H₂O begin to overlap, so selectivity may also be diminished.

Another possibility is selective two-step photodissociation (STP) developed by Ambartzumian and Letokhov [B28]. In STP, two light sources are employed simultaneously. The first, usually an infrared (ir) laser, selectively excites some molecular vibration, while the second, usually an ultraviolet (uv) source, has enough energy to excite and subsequently dissociate only the vibrationally activated molecules. The result is selective photodissociation. The STP process is illustrated in Figures B4, B5, and B6.

FIGURE B4 - Selective two-step photodissociation for HTO/H₂O.

FIGURE B5 - H₂O absorption in the 155-185 nm region is due to the X'¹A₁ → A'¹B₁ transition.

FIGURE B6 -- The absorption due to the $X'A_1 \rightarrow A'B_1$ transition for vibrationally excited HTO.

Application of STP to HTO entails laser excitation of the O-T stretch at 2295 cm^{-1} ($4.36\text{ }\mu\text{m}$) followed by absorption of ultraviolet light with a wavelength greater than $1860\text{ \AA}$. For STP to be effective, the vibrationally excited HTO molecule must absorb the uv photon and dissociate before it loses or transfers the vibrational energy. To clarify this point, consider the rate equations:

where M is any species that acts as a collision partner and M^* is the excited state.

Electronic relaxation has been ignored since the quantum yield for photo-dissociation of water at $1849\text{ \AA}$ is known to be near unity [B29]. Also, we have assumed that the O-T bond will be broken selectively since it has been partially weakened by the vibrational excitation. Moreover, at the onset of absorption the O-T bond will be significantly stretched (compare Figure B6).

Application of the steady-state approximation to the concentration of HTO* and HTO** leads to the following expression for the rate of photodissociation:

$$-\frac{d(\text{HTO})}{dt} = \frac{k_{ir}}{1 + k_v(M)/k_{uv}}$$

The competition between vibrational relaxation and ultraviolet absorption is manifest.

Vibrational relaxation rates vary from 10 to 10^5 torr⁻¹-sec⁻¹. If we take (M) to be 10 torr, then an average value for $k_v(M)$ is 10^4 sec⁻¹. Using the absorption coefficient of 1 atm⁻¹-cm⁻¹ measured for H₂O at 1860Å [B30], the rate of ultraviolet absorption is related to the intensity I_{uv} (in W/cm²) by the expression:

$$k_{uv} = 4 \times 10^{-2} I_{uv} \text{ sec}^{-1}$$

Therefore, for $k_{uv} \approx k_v(M) = 10^4$ sec⁻¹, we require:

$$I_{uv} = 2.5 \times 10^5 \text{ W/cm}^2$$

This intensity is too great for a continuous-wave source, but may be obtained by a pulsed system. Moreover, since the ultraviolet excitation can extend over a range on the order of 1000 cm⁻¹, the required intensity should be obtainable with a broad band light source.

In 1974 Herbst, Fleming, and Byer reported the development of a high-power pulsed laser that is tunable from 1.4 to 4.45 μm [B31]. Output energies of 1 mJ for a 20-nsec pulse (corresponding to a power of 5×10^4 W) have already been obtained. Based on this development, a tunable infrared laser system has been built at Mound Facility for detritiation experiments. The system, shown in Figure B7, consists of a Nd:YAG oscillator with one stage of amplification to deliver a pulsed (50-mJ, 20-ns) beam of 1.06-μm wavelength light. The 1.06-μm beam is used to pump an optical parametric oscillator which is angle tunable from 1.4 to 4.5 μm. Beam splitters and blocking filters are used to insure that only the longer wavelength light reaches the photolysis cell.

The problem of scavenging the tritium atoms and hydroxyl radicals produced by the photolysis of HTO is very complex. If one selectively photolyzes an HTO/H₂ mixture, the tritium atoms will exchange with the light water, regenerating the HTO:

Therefore, some compound must be added to scavenge the tritium atoms before they exchange with water. Initial proof-of-principle experiments are being performed using H₂ as a scavenger. However, this process does not appear to be scalable due to the low efficiency of the ultraviolet portion of the excitation process.

A more promising approach would be to pump more infrared energy into the vibrationally excited HTO and dissociate with a longer-wavelength ultraviolet source. If this is done, the ultraviolet step becomes more selective and the economics of a scaled-up system become reasonable. Moreover, a non-hydrogen-containing scavenger can be used which allows product enrichment. As an example, CO may be used as the scavenger in the separation scheme as shown in Figure B8.

FIGURE B7 - Tunable ir laser system for HTO photodissociation experiments.

The scavenging of the photodissociation products by CO appears promising. The key reactions and rate constants are given in Table B3. To achieve the desired detritiation level of 20 nCi/liter it is clear that reactions (1) and (2) must dominate the HTO regeneration reactions (3), (4), and (5) by at least a factor of 10^7 ; i.e.:

$$\frac{k_1 [\text{CO}]}{k_5 [\text{H}_2\text{O}]} > 10^7 \quad (11)$$

and

$$\frac{k_2 [\text{M}] [\text{CO}]}{(k_3 + k_4) [\text{H}_2\text{O}]} > 10^7 \quad (12)$$

Substituting values for the rate constants from Table B3 into (11) gives

$$\frac{[\text{CO}]}{[\text{H}_2\text{O}]} > 2 \times 10^{-5}$$

and into (12) gives

$$\frac{[\text{CO}]}{[\text{H}_2\text{O}]} > 2 \times 10^{-3}$$

Hence,

$$\frac{[\text{CO}]}{[\text{H}_2\text{O}]} = 0.1 \text{ (i.e., } P_{\text{CO}} = 65 \text{ torr)}$$

is chosen to achieve the desired scavenging and detritiation level.

FIGURE B8 - Schematic of detritiation system for a nuclear fuel reprocessing plant waste.

KEY REACTIONS IN SCAVENGING OF HTO PHOTODISSOCIATION

Since the rate of reaction (6) is not known, the pathway by which the tritium is incorporated as formaldehyde is not clear [reaction (6) or (7)]. However, this is not important. On the other hand, as the concentration of formaldehyde increases, reactions (8)-(10) which regenerate HTO come into play. Reaction (9) is clearly the dominant mode of HTO regeneration from formaldehyde.

$$\frac{[\text{Formaldehyde}]}{[\text{CO}]} < 10^{-5}$$

The physical separation of the tritiated formaldehyde and the CO from the water stream is depicted in Figure B8. After the photo-reaction chamber in which the tritium is transferred from HTO to H₂CO or T₂CO, the process stream goes to a condenser (15°C) cooled by water. At 15°C the equilibrium vapor pressure for water is 13 torr so that 98% of the water is condensed. Because of its high solubility, the formaldehyde will stay with the liquid water.

The condensed water/formaldehyde solution is passed on to the evaporator. Upon evaporation paraformaldehyde, a high-molecular-weight, involatile polymer, is formed. The paraformaldehyde is expected to stay behind on the evaporator. Because of the very small concentration of formaldehyde present in the water, it may be necessary to add more formaldehyde to "salt" out the paraformaldehyde. Since addition of H_2CO would reduce the T/H ratio, addition of tritiated formaldehyde already extracted from the low-level aqueous waste may be desirable. On the other hand, care must be taken not to add so much tritium that the back exchange of the tritium into the water stream is promoted.

After the water has been removed, the temperature is increased to $200^{\circ}C$. The paraformaldehyde decomposes and vaporizes as formaldehyde. If no additional formaldehyde is needed to "salt" out the paraformaldehyde, then a product of gaseous formaldehyde with $T/H > 0.01$ will be produced at a rate of 10^2 - 10^3 cm^3/hr .

The power for the various stages of aqueous waste detritiation by photo-excitation is estimated at 1000 kW. Once the stream of tritiated formaldehyde has been extracted, any further processing of the tritium requires a negligible amount of energy, since the volume of the waste stream has been reduced.

Two possibilities for handling facilities are readily apparent. First, the formaldehyde may be decomposed into hydrogen gas and CO. The tritiated hydrogen gas may be sent to a catalytic exchange or cryogenic distillation apparatus for enrichment and ultimate use in fusion reactors. Second, after decomposition of formaldehyde the tritiated hydrogen gas may be oxidized to water, which may again be further enriched.

ECONOMIC EVALUATION OF DETRITIATION-ENRICHMENT METHODS CURRENTLY UNDER DEVELOPMENT

A preliminary economic evaluation of both the combined electrolysis-catalytic exchange and molecular photoexcitation isotopic separation methods has been made using as a base case the tritium stripping of low-level aqueous waste (LLAW) containing 0.2 Ci/liter. This base case assumes a tritium recovery of 750,000 Ci/yr, an aqueous waste feed rate of 500 liters/hr, operation for 330 days/yr, annual product stream of 75 liters at 10,000 Ci/liter, and a discharge stream of 20 nCi/liter. Since costs associated with detritiation of water increase with increased throughput and overall separation factor, the application of the stripping scheme represents the most costly application. This base case could be applicable to a fuel reprocessing plant in which process water is recycled within the plant (allowing the tritium concentration to reach 0.2 Ci/liter). The concentration of tritium in water discharged from an FRP (no water recycle) is generally stated to be below 0.1 Ci/liter. The cost estimates are given in Tables B4 and B5.

A summary of the data costs from Tables B4 and B5 is given in Table B6 along with cost estimates for tritium stripping of aqueous wastes of a wide range of tritium concentrations. All estimates in Table B6 assume the same general conditions with either an increase or decrease in the size of the tritium separation facilities for recovery of 75 g of tritium per year and a discharge stream of 20 nCi/liter. The electrical energy cost, as used in all three tables, was \$0.02/kWh.

Table B4

COST ESTIMATE FOR LLAW DETRITIATION BY COMBINED ELECTROLYSIS-CATALYTIC EXCHANGE

Detritiated Water - 3.75×10^6 liters/yr 750,000 Ci/yr @ 0.2 Ci/liter	Unit Investment: On Site \$4,676,000 Off Site 1,643,000
Recovered Tritium 749,999 Ci/yr 75 liters/yr @ 10,000 Ci/liter	Total 6,319,000

<u>Item</u>	<u>Quantity/yr</u>	<u>Cost/unit</u>	<u>Cost/yr</u>	<u>Cost/g</u>
Variable Costs:				
Cooling Water	60,000 kgal	\$0.02	\$ 1,000	
Electricity	4.2×10^7 kWh	0.02	840,000	
Catalyst	1000 lb	20.00	20,000	
Total Variable Costs			861,000	\$11,000

Fixed Costs:

Direct Labor	53,000	
Supervision	10,000	
Maintenance	190,000	
Supplies	19,000	
Payroll Burden	19,000	
Taxes and Insurance	140,000	
Depreciation 10% Straight Line	468,000	
Total Fixed Costs	\$899,000	\$12,000
Total Operating Cost	\$1,760,000	\$23,000

Table B5

COST ESTIMATE FOR LLAW DETRITIATION BY MOLECULAR PHOTOEXCITATION

Detritiated Water - 3.75×10^6 liters/yr 750,000 Ci/yr @ 0.2 Ci/liter	Unit Investment: On Site \$4,428,000 Off Site 1,476,000
Recovered Tritium 749,999 Ci/yr 75 liters/yr @ 10,000 Ci/liter	Total \$5,904,000

<u>Item</u>	<u>Quantity/yr</u>	<u>Cost/unit</u>	<u>Cost/yr</u>	<u>Cost/g</u>
Variable Costs:				
Cooling Water	8,000 kgal	\$0.02	\$ 1,000	
Electricity	7.1×10^6 kWh	0.02	142,000	
Total Variable Costs			\$143,000	\$2,000

Fixed Costs:

Direct Labor	\$ 53,000	
Supervision	10,000	
Maintenance	180,000	
Supplies	18,000	
Payroll Burden	19,000	
Taxes and Insurance	130,000	
Depreciation 10% Straight Line	443,000	
Total Fixed Costs	\$854,000	\$11,000
Total Operating Cost	\$ 997,000	\$13,000

Table B6

COMPARATIVE COST ESTIMATES^a FOR ISOTOPIC SEPARATION OF TRITIUM BY
COMBINED ELECTROLYSIS-CATALYTIC EXCHANGE AND MOLECULAR PHOTOEXCITATION

Typical Type of Feed	Aqueous Concentration	Cost of Isotopic Separation (\$/g)	
		Combined Electrolysis- Catalytic Exchange	Molecular Photoexcitation
Low-level waste (reactors, ^b DOE, etc.)	<0.02 Ci/liter	>160,000	>35,000
Fuel reprocessing waste (acid dissolu- tion plant)	0.1 Ci/liter	40,000	17,000
Base case ^a	0.2 Ci/liter	23,000	13,000
Heavy water (from HWR)	2 Ci/liter	4,500 ^c	7,300
Fuel reprocessing waste (voloxidation plant), DOE waste	200 Ci/liter	<2,000	-- ^d

^aBase of comparison is costs for tritium stripping to recover 750,000 Ci/yr (330 operational days/yr), yielding a product of 75 liters at 10,000 Ci/liter and a discharge stream below EPA drinking water standards of 20 nCi/liter. Energy costs of \$0.02/kWh.

^bA recycling scheme of detritiation with a separation factor of 10^3 may be desirable for PWR's in order to achieve greater processing economy.

^cIn practice, the more economical recycle scheme of detritiation would be used for heavy-water detritiation.

^dCombined electrolysis-catalytic exchange and cryogenic distillation would be used for tritium concentrations greater than 2 Ci/liter because of the much lower fixed equipment costs and greater efficiency at higher tritium levels.

The data in these three tables show that: 1) the two detritiation processes are cost-effective over different tritium concentration ranges; 2) catalytic exchange is an energy-intensive process whereas photoexcitation is moderately capital-intensive; and 3) isotopic separation of tritium may be economically feasible (for effluents from fuel reprocessing plants and for moderator-coolant of heavy-water reactors). Since all detritiation processes discussed herein are in various stages of development, the costs as given here are relative and may change substantially up or down when costing data become available.

Common to all detritiation techniques is the necessity of providing feed material which has been purified to prevent degradation or poisoning of the detritiation process. In addition, all isotopic separation schemes are expected to require cryogenic distillation to provide the additional enrichment and purity necessary for the direct use of the tritium. The lesser costs of feed clean-up and final enrichment were not included in the estimates appearing in Tables B4, B5 and B6.

As indicated earlier, these estimates are for the more costly tritium stripping application. A recycling scheme of detritiation, however, would be more economical and practical. For the latter it must then be assumed that nearly all plant processing waters would be recycled (limited discharges) and the equilibrium tritium concentration of the plant water would be higher. A continuous side-stream from the plant would be detritiated by a factor of 10^2 - 10^5 before the stream was returned to the plant system. Because of the processing of higher concentrations and smaller feed volumes, the isotope separation system and energy consumption would be much smaller.

Molecular photoexcitation may have significant economic advantages at lower tritium concentrations. As shown in Table B5 the electrical power requirements are one-sixth of that for catalytic exchange, resulting in a 50% smaller total recovery cost relative to catalytic exchange for the base case. The sensitivity of catalytic exchange to feed volume and feed concentrations is evident in Table B6. This is chiefly a result of the power consumption by the electrolysis phase of the process.

Costs for processing wastes by molecular photoexcitation are affected less by changes in feed volume. The capital equipment investment and power requirements (energy for water evaporation) rise moderately with an increase in capacity. Photoexcitation becomes even more attractive if heat from excess steam capacity or waste energy sources can be used. However, detritiation costs, per gram of tritium recovered, are expected to rise significantly as the tritium level of the aqueous feed increases (>2 Ci/liter). Scaling down the capacity of the laser and laser support equipment is not expected to reduce fixed capital costs to the extent of that achieved with CECE processing.

Because of lower energy needs and the mode of isotopic separation, molecular photoexcitation may be more economical and efficient for large-volume waste treatment and for stripping to drinking water levels (e.g., PWR's). CECE may find its application to recycling schemes where water of higher tritium concentration is detritiated to a lesser degree and is returned to the point of origin, maintaining a constant tritium concentration within the plant system (e.g., HWR's).

For heavy-water reactors, a separation factor of 10^3 may be very satisfactory, providing economical recovery of the tritium and the return of heavy water to the reactor moderator. The tritium concentration of the heavy water would be maintained below 2 Ci/liter. Some degree of heavy-water enrichment (from H_2O) could be achieved during detritiation. The cost of tritium separation will be increased somewhat due to the lower isotopic separation factor for DT/D_2O which is about 2 at $25^\circ C$ as compared with 6 for HT/H_2O .

Although detritiation of the primary coolant of PWR's may be a desirable goal in the future, it appears unlikely that this can be achieved economically in terms of the value of recovered tritium. There are insufficient data to date to indicate the problems, processing limitations, and costs associated with detritiation of the coolant which would involve a nominal recovery of only 750 Ci/yr/1000-MW(e) reactor. Because of the low tritium concentrations (<2 μ Ci/ml), molecular photoexcitation, probably in a recycle processing mode, would be used to minimize energy and capital investment costs.

Isotope separation of tritium from aqueous waste or processing streams not only appears feasible but the technology should be adequately developed in 3-5 yr. Detritiation costs of PWR coolant may be 5-10 times current tritium prices. Costs of heavy-water detritiation may be below \$4500/g whereas recovered tritium from fuel reprocessing plants may range from less than \$2000 to \$17,000/g depending upon the headend process used and whether recycle of plant processing water is practiced.

REFERENCES

- B1. S. V. Ribnikar and J. D. Pupezin, "Possibilities of Tritium Removal from Waste Waters of Pressurized Water Reactors and Fuel Reprocessing Plants," in Proceedings of the Thirteenth AEC Air Cleaning Conference Held in San Francisco, Calif., August 12-15, 1974, CONF-740807, (March 1975), Vol. 2, pp. 929-945.
- B2. J. J. Kueck, Tritium Removal from Primary Coolant of a Power Reactor, Thesis submitted to the Department of Chemical and Nuclear Engineering, University of Cincinnati, Cincinnati, O., 1972.
- B3. K. H. Lin, Tritium Enrichment by Isotope Separation Technique, ORNL-TM-3976, Oak Ridge National Laboratory, Oak Ridge, Tenn. (December 1972), 31 pp.
- B4. L. L. Burger, The Separation and Control of Tritium, State-of-the-Art Study, PB-244928, Battelle Pacific Northwest Laboratories, Richland, Wash. (Apr. 14, 1972), 49 pp.
- B5. D. Jeger, D. Dirian and E. Roth, "Detritiation of Heavy Water from Nuclear Reactors," Energ. Nucl., 12:2, 135-142 (1970), AEC-tr-7464, 1973.
- B6. Alternatives for Managing Wastes from Reactors and Post-Fission Operations in the LWR Fuel Cycle, ERDA-76-43 Vol. 2, Battelle Pacific Northwest Laboratories, Richland, Wash. (May 1976), pp. 13.21-13.43.
- B7. F. T. Barr and W. P. Drews, "The Future for Cheap Heavy Water," Chem. Eng. Progress, 56, 49-60 (1960).
- B8. D. M. Drazic, L. Z. Vorkapic and M. Atanackovic, Yugoslav Patent Application No. 331/74.
- B9. J. P. Butler, J. H. Rolston and W. H. Stevens, "Novel Catalysts for Isotopic Exchange between Hydrogen and Liquid Water," in Separation of Hydrogen Isotopes, H. K. Rae (ed.), ACS Symposium Series, Washington, D. C., 1978, pp. 93-109.
- B10. M. Hammerli, W. H. Stevens and J. P. Butler, "Combined Electrolysis Catalytic Exchange (CECE) Process for Hydrogen Isotope Separation," in Separation of Hydrogen Isotopes, H. K. Rae (ed.), ACS Symposium Series, Washington, D. C., 1978, pp. 110-125.
- B11. T. J. Whitaker, J. R. Morrey, L. L. Burger and R. D. Scheele, Deuterium and Tritium Separation in Water by Selective Molecular Excitation, BNWL-B-432, Battelle Pacific Northwest Laboratories, Richland, Wash. (July 1975), 27 pp.
- B12. R. J. Jensen and J. L. Lyman, Laser Induced Recovery of Deuterium or Tritium from Water, LA-UR-74-429, Los Alamos Scientific Laboratory, Los Alamos, N. M. (1974), 9 pp.
- B13. C. J. Kershner and J. C. Bixel, Tritium Effluent Control Project Progress Report: April-June 1976, MLM-2382 (Dec. 10, 1976), 17 pp.
- B14. C. J. Kershner, Tritium Effluent Control Project Progress Report: July-September 1975, MLM-2288 (Mar. 19, 1976), 30 pp.
- B15. C. J. Kershner and J. C. Bixel, Tritium Effluent Control Project Progress Report: January-March 1975, MLM-2235 (Aug. 27, 1975), 28 pp.
- B16. C. J. Kershner and J. C. Bixel, Tritium Effluent Control Project Progress Report: April-June 1975, MLM-2270 (Nov. 17, 1975), 13 pp.

- B17. C. J. Kershner and J. C. Bixel, Tritium Effluent Control Project Progress Report: October-December 1975, MLM-2337 (July 30, 1976), 19 pp.
- B18. J. C. Bixel and C. J. Kershner, Tritium Effluent Control Project Progress Report: January-March 1976, MLM-2358 (Sept. 27, 1976), 19 pp.
- B19. Tritium Waste Control: April-September 1977, MLM-2484 (January 9, 1978), 42 pp.
- B20. H. F. Anderson and C. J. Kershner, Tritium Waste Control Project: October 1976-March 1977, MLM-2451 (Oct. 6, 1977), 27 pp.
- B21. H. F. Anderson and C. J. Kershner, Tritium Waste Control Project Progress Report: July-September 1976, MLM-2399 (Feb. 21, 1977), 8 pp.
- B22. M. L. Rogers, P. H. Lamberger, R. E. Ellis and T. K. Mills, "Catalytic Detritiation of Water," in Separation of Hydrogen Isotopes, H. K. Rae (ed.), ACS Symposium Series, Washington, D. C., 1978, pp. 171-176.
- B23. G. M. Murphy, H. C. Urey and I. Kirshenbaum, Production of Heavy Water, McGraw-Hill Book Co., New York, N.Y., 1955.
- B24. V. Mercea, N. Palibroda, T. Fodor and L. Stoicovici, "Depletion Column for the Collection of Protium Oxide, $^1\text{H}_2\text{O}$, by Isotopic Exchange between Hydrogen and Water," Isotopenpraxis, 4, 328 (1968).
- B25. P. Savic, S. V. Ribnikar and B. Pavlovic, "Efficiency of Some Catalysts in the Exchange Reaction Between Heavy Water and Hydrogen," Proc. Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva, 1955, Vol. 8, United Nations, New York, 1956, p. 414.
- B26. V. Mercea, Estimative Calculation of a Tritium Decontamination Unit for a Nuclear Power Plant, Institute for Atomic Physics of the Rumanian Academy of Sciences, Klug, Rumania, June 1974.
- B27. W. H. Stevens and F. P. Blackstein, "Heavy Water Production Using Hydrogen-Water Exchange", AECL Research and Development in Engineering, AECL-4606, Atomic Energy of Canada, Ltd., Winter 1973, pp. 16-18.
- B28. R. V. Ambartzumian and V. S. Letokhov, IEEE J. Quantum Electron., QE-7, 305 (1971); Appl. Opt., 11, 354 (1972); Chem. Phys. Lett., 13, 446 (1972).
- B29. C. A. Barth and H. E. Seurs, Z. Physik, 158, 85 (1960).
- B30. K. Watanabe and M. Zelikoff, J. Opt. Soc. Am., 43, 753 (1953).
- B31. R. L. Herbst, R. N. Fleming and R. L. Byer, Appl. Phys. Lett., 25, 520 (1974).

APPENDIX C

PROJECTED TRITIUM GENERATION RATES FOR PRESSURIZED WATER REACTORS

Tritium generation rates in Table C1 are based on projections of Case A from WASH-1139(74) [C1]. Case A is the lowest of four forecasts of nuclear capacity and assumes that delays (all sources) in bringing nuclear plants into operation will continue at the same level as in the early and mid-1970's.

Tritium generation rates in Table C2 are based on projections of the high case, Case C. Simply, Case C assumes much shorter delays in construction and regulatory processes, the continuation of the past relationship between energy consumption and GNP, and that electricity will remain cheap relative to oil and natural gas. Details of assumptions for nuclear power capacity projections are discussed in WASH-1139(74).

Table C1

TRITIUM GENERATION IN PWR COOLANT BASED ON CASE A
OF THE 1974 PROJECTION OF NUCLEAR POWER CAPACITY
FROM WASH-1139(74)

<u>Year</u>	<u>Installed PWR Capacity^a GW(e)</u>	<u>Number of PWR's^b</u>	<u>Tritium Generated in PWR Coolant^b (g/yr)</u>
1980	55.0	50	4.2
1985	150	136	11.3
1990	252	229	18.9
1995	352	320	26.4
2000	434	394	32.6

^aCapacity based on Case A, the lowest forecast, from Reference C1.

^bNumber of PWR's is based on the assumption that the average PWR will be of 1100 MW(e) capacity. Tritium generation rate is assumed to be 750 Ci/yr/1000 MW(e) in the coolant.

Table C2

TRITIUM GENERATION IN PWR COOLANT BASED ON CASE C
OF THE 1974 PROJECTION OF NUCLEAR POWER CAPACITY
FROM WASH-1139 (74)

<u>Year</u>	<u>Installed PWR Capacity^a [GW(e)]</u>	<u>Number of PWR's^b</u>	<u>Tritium Generated in PWR Coolant^b (g/yr)</u>
1980	76.8	70	5.7
1985	175.5	160	13.2
1990	344.9	314	25.8
1995	527.4	480	39.6
2000	683.9	622	51.3

^aCapacity based on Case C, the highest forecast, from Reference C1.

^bNumber of PWR's is based on the assumption that the average PWR will be of 1100 MW(e) capacity. Tritium generation is assumed to be 750 Ci/yr/1000 MW(e) in the coolant.

REFERENCES

- C1. Nuclear Power Growth 1974-2000, WASH-1139 (74), USAEC, Washington, D.C. (February 1974).

APPENDIX D

LITHIUM ISOTOPIC SEPARATION PROCESSES

CROWN CHEMICAL EXCHANGE PROCESS FOR LITHIUM ISOTOPIC SEPARATION

Isotopic separation of calcium based upon the chemical exchange reaction between calcium salts and macrocyclic polyethers, a new class of metal complexing agents, has been under study for some time [D1,D2]. This process is also applicable to the isotopic enrichment of lithium-7 or lithium-6. Lithium-7 tends to concentrate in the aqueous phase and lithium-6 in the organic phase of polyether. This isotope effect can be utilized by counter-current liquid-liquid extraction columns to achieve multistage enrichments.

The lithium isotope enrichment process description which follows is based primarily on the calcium isotope enrichment work and preliminary laboratory-scale experiments with lithium. These experiments have shown equilibrium separation factors (α) on the order of 1.01 with the first few polyethers chosen. In order for the process to be economically competitive, it is estimated that an α value greater than 1.03 will be needed.

Figure D1 shows a general schematic of the chemical exchange cascade for separation of lithium isotopes. The process consists of a series column train with an overhead reflux system and a bottoms reflux system. The facility could be used for either lithium-6 or lithium-7 enrichment. Lithium bromide is used as the feed material, polyether crown (dicyclohexyl 18-crown-6) as the complexing agent, and bromoform as the organic solvent. This process is particularly attractive because none of the constituent materials is flammable. Bromoform, a lachrymator, is easily monitored and is less volatile and hazardous than chloroform, for example.

The lithium isotope separation would take place in the series column train when an aqueous solution of lithium bromide contacts a countercurrent organic solution of lithium bromide complex in bromoform/crown solution. The aqueous LiBr solution tends to become enriched in the heavy lithium-7 isotope while the organic LiBr solution tends to become enriched in lithium-6.

The heavy-lithium-isotope enriched stream of aqueous LiBr from the overhead end of the column train passes to the overhead reflux system. Here the lithium-7-enriched LiBr is transferred from the aqueous phase to the organic phase as a lithium-7-enriched LiBr complex in bromoform/crown solution. This organic stream is then returned to the overhead end of the series column train countercurrent to the aqueous stream. The heavy-lithium isotope concentration gradually builds up in the overhead end of the system.

The bottoms reflux system removes the lithium-6-enriched LiBr from the organic stream and returns this LiBr to the LiBr reservoir in the aqueous phase. The organic solution (bromoform/crown) is returned to the bromoform reservoirs from which it reenters the system in the overhead reflux system. A side stream of bromoform/crown solution also flows from the bottoms reflux system to the intermediate reflux system (not shown). An ultraviolet monitor and recorder are necessary to monitor the concentration of crown in the bromoform/crown solution returning to the reservoir. The bromoform/crown solution is initially supplied to the system at the bromoform reservoirs. This material is otherwise referred to as crown, crown solution or bromoform/crown solution. An assumption of an "infinite reservoir" is made for the LiBr reservoir since the lithium-7 depletion is a very small percentage of the total in the reservoir. The LiBr in the reservoir is replaced with a fresh LiBr supply as needed.

COST ESTIMATE FOR LITHIUM-6 ENRICHMENT BY THE CROWN PROCESS

A rough estimate was made to evaluate the economics of a lithium-polyether system if it had an equilibrium separation factor of 1.03. As was previously mentioned, such a system has not been experimentally demonstrated. This estimate indicated that this chemical exchange system would be capable of producing 7500 kg/yr of 90% lithium-6 at unit cost on the order of \$600 per kilogram of lithium-6. This cost would appear to compare favorably with lithium enrichment costs which might be currently incurred by the Colex process, based upon the lithium-amalgam chemical exchange reaction. Current prices for 95-96% enriched lithium-6 are quoted at \$1.25/g (\$1250/kg) [D3]. Hence, one may assume that large-quantity purchases (and production) of 90% enriched lithium-6 produced by the Colex process may be between \$600 and \$1250/kg.

An in-depth study of engineering costs is necessary to ascertain which process could be economical in terms of 1978 dollars, current regulatory guidelines, and impact on the environment. Of course, additional research and development of the crown process and assessment of separation factors must precede any engineering studies.

FIGURE D1 - Schematic of chemical exchange cascade for production of lithium isotopes.

REFERENCES

- D1. B. E. Jepson and R. DeWitt, "Separation of Calcium Isotopes with Macrocyclic Polyether Calcium Complexes," J. Inorg. Nucl. Chem., 38:6, 1175-1177 (1976).
- D2. Mound Laboratory Activities for the Division of Physical Research: January-June 1973, MLM-2068 (Aug. 22, 1973), pp. 26-31.
- D3. Research Materials, Oak Ridge National Laboratory, Oak Ridge, Tenn. (April 1973), p. 35.

APPENDIX E

AVAILABILITY OF MERCURY

If additional enriched lithium-6 is needed near the end of this century, improved Colex-type processing facilities would probably be built in light of current lithium isotopic separation technology. Because of the high degree of automation in this separation process, the main operating costs involve electrical energy and mercury. Fortunately, the initially large quantities of mercury required can be recycled and reused. Hence, it is expected that increased demands on the mercury market could be met with minimum lead time. Procurement costs could increase manyfold without affecting the tritium production costs significantly since the price of tritium is heavily weighted by the cost of neutrons (from production reactors). For tritium produced in reactor breeding blankets, lithium isotopic separation costs would also be small when compared with tritium recovery and processing costs.

During the Colex process operating period of 1955-1962, the price of mercury in terms of 1973 dollars decreased from \$500 per flask (76 lb) to \$280, increased to a high of \$1000 by 1965, but moved into a continuous decline to \$140 by mid-1975 [E1]. The mining and production of mercury in the United States has declined so dramatically during the past 5 yr that imports now fill 85 to 90% of the U.S. demand. The Bureau of Mines predicts that imports will continue to provide a major share of U.S. requirements up through the year 2000 because of the competitive advantage of foreign production [E2]. When the high-grade foreign deposits become depleted, perhaps in 25 yr, it will become profitable to reopen American mines producing low-grade ore.

Because of pollution problems and anticipated controls, the demand as well as production and prices have diminished substantially in the past 10 yr [E2]. Annual usage nationwide in 1974 amounted to about 60,000 flasks. Projected 20-yr demand trends indicate annual consumption levels to be only slightly above that of 1974.

Production in the U.S. in 1974 totalled about 2500 flasks, but could be increased to 30,000 annually by expanded output of current producers and the reopening of less-profitable mines [E1]. The option of greater self-sufficiency was made possible in 1975 by the opening of a new mine in Nevada which is capable of meeting nearly one-half of the current primary demand or 25% of the projected annual demand over the period of 1975 to 2000. As part of the availability picture, mercury is stockpiled by the government under the Strategic and Critical Materials Stockpiling Act of 1946. Inventories at the end of 1974 totalled 200,062 flasks.

According to "Mineral Facts and Problems" prepared by the Bureau of Mines, "At \$1000/flask, world resources of over 17 million flasks are more than adequate to meet the forecast high-range rest-of-the-world cumulative demand of 6 million flasks and the U.S. high-range cumulative primary demand of 1.7 million flasks for 1973-2000" [E1].

For a commodity which experiences wide price fluctuations, projected costs by the year 2000 are not expected to exceed \$1000 per flask, twice that of the market value at the beginning of AEC's lithium-6 production effort in the 1950's.

It appears that projected uses or new technological breakthroughs will have little impact on mercury reserves during the next 25 yr. The U.S. Government considers mercury a strategic commodity, essential to the economy [E2]. Through the U.S. Geological Survey, Office of Minerals Exploration, financial assistance is provided in exploration for new mercury deposits.

REFERENCES

- E1. V. A. Cammarota, Jr., "Mercury," Mineral Facts and Problems, Bulletin 667, Bureau of Mines (1975), 14 pp.
- E2. E. H. Bailey, A. L. Clark and R. M. Smith, "Mercury", United States Mineral Resources, U.S. Geological Survey Professional Paper 820 (1974), pp. 401-414.

APPENDIX F

HELIUM-3 RECOVERY AND ENRICHMENT TECHNOLOGY

Recent advances in low-temperature separation methods may make it economically feasible to enrich helium-3 from natural-abundance helium which has already been liquefied for other reasons. However, several technical problems must be solved before a large-scale system could be considered feasible.

A large-scale enrichment method would consist of two separation processes operating at two different temperatures. First, helium-3 would be enriched to approximately 1% by passing natural-abundance liquid helium at 2 K through a superleak. Second, the 1% material would be enriched to approximately 99% helium-3 by either thermal diffusion or distillation. Since large quantities of natural-abundance helium are being liquefied in several plants in the United States, there are already relatively large quantities of approximately 4.4 K liquid helium available. The hurdle of high energy consumption for liquefaction may therefore be discounted.

The liquid helium must be cooled below the lambda point (2.17 K) before helium-4 becomes a superfluid and the superleak separation process becomes feasible. A flow sheet of the enrichment process is shown in Figure F1. Since the helium-4 stream remains nearly unchanged at 4.4 K, the only refrigeration required is that necessary to make up for the inefficiencies in the heat exchangers and the heat leak into the cold box containing the process equipment. It was estimated that less than 2 W of refrigeration would be required to keep the superleak container at 2 K for a flow rate of 100 million STP ft³/yr of helium feed.

The 2 K refrigeration could be obtained in one of two ways. One method is the use of a commercial 2-W, 2 K refrigerator at a cost of \$100,000. The other method is to pump on part of the 4.4 K liquid helium-4 with a vacuum pump and to return the exit gas from the vacuum pump to the inlet of the compressors used in the liquefaction plant. The capital and operating costs of the two methods are estimated to be roughly equal if the liquefaction plant has excess capacity. However, if the liquefaction plant is operating at full capacity, the addition of this system results in the lost production of an amount of liquid helium-4 equivalent to a boil-off rate of 2 W. Commercial 2 K refrigeration would therefore be used if the liquefaction plant does not have sufficient excess capacity. Figure F1 indicates the flow of helium in a system using an auxiliary 2 K refrigerator.

It is estimated that the capital equipment cost required to enrich the helium-3 to 1% is \$350,000. The production rate of helium-3 at an enrichment of 1% would be approximately 428 STP liters of helium-3 per year per 2.8×10^6 m³ (STP) of helium feed gas, assuming that 10% of the helium-3 passes through the superleak.

The further enrichment of the 1% helium-3 to 99% can be done by either thermal diffusion or distillation. However, distillation is the more economical method. It is possible that a distillation column could be placed in the same cold box as the superleak and that 99% helium-3 could be continuously withdrawn from the cold box as depicted in Figure F1. The additional capital equipment costs for the distillation column would be approximately \$20,000. As an alternate, the enrichment to 99% by thermal diffusion would require the shipment of the 1% helium feed to existing facilities such as those at Mound Facility and/or the construction of enrichment facilities adjacent to the liquefaction plant.

FIGURE F1 - Flow sheet for helium-3 separation from helium-4.

Estimated costs of enriching helium-3 to 99% from natural-abundance helium by the two-step method are summarized in Table F1. The costs of helium-3 are shown in parenthesis below the respective capital equipment costs.

It has already been demonstrated that enrichment of natural-abundance helium-3 is possible by means of superfluid flow [F1,F2], distillation [F3], and thermal diffusion [F4]. Initial experiments at Mound Laboratory have demonstrated the usefulness of the two low-temperature methods for enriching helium-3 at an abundance of 0.1% up to a concentration of greater than 99% and the usefulness of thermal diffusion to enrich about 1% helium-3 to greater than 99.9996%. Descriptions of this low-temperature work appear in References F5 through F8.

Table F1
CAPITAL EXPENDITURE^a AND UNIT COSTS
FOR LARGE-SCALE ENRICHMENT OF HELIUM-3

Capacity		Refrigerator for 2 K	
Helium-4 (m ³)	Helium-3 ^b (liters)	Distillation ^c from 1% to 99%	Thermal Diffusion ^d from 1% to 99%
2.83 x 10 ⁶	428	\$370,000 (\$156/liter)	\$350,000 (\$222/liter)

^aAll figures assume a 10-yr straight-line depreciation of capital investment.

^bHelium-3 content for calculations above assumes a concentration of approximately 0.15 ppm.

^cUnit cost assumes operating cost of 0.5 manyear at \$60,000/manyear.

^dUnit cost assumes operating cost of 1 manyear at \$60,000/manyear and the use of existing thermal diffusion capabilities.

In order to determine the feasibility of low-temperature recovery of helium-3, the properties of superleaks and continuous separation with a large-scale process must be investigated first. Specific questions must be answered:

1. Is it possible to recover more than 90% of the helium-3 in the natural-abundance helium feed to the superleak and simultaneously enrich the helium-3 to 1%?
2. Can 1% helium-3 be continuously withdrawn from the superleak container and used as feed to the distillation column without interruption of the superflow?
3. What are the critical parameters in the design of a large-scale superleak?

Initially, small-scale laboratory experiments would be necessary to ascertain if enrichment of natural-abundance helium-3 can be achieved with a useful recovery rate. A comparison of the quantity of recovered helium-3 with accurate determinations of the initial concentrations would allow a determination of enrichment factors and recovery rates for this process.

Based upon this laboratory experience, a continuously operating pilot plant would have to be designed, constructed, and operated to determine whether continuous separation of helium-3 from natural-abundance helium is practical on a large scale. It is anticipated that this would involve liquefaction

of feed gas, superfluid separation of the isotopes, and the recovery of the helium-3-rich product gas in cylinders and the liquid helium-4 by-product in storage dewars. Successful operation of such a plant would indicate the practicality of large-capacity plants.

REFERENCES

- F1. J. G. Daunt, R. E. Probst, H. L. Johnston, L. T. Aldrich and A. O. Nier, Phys. Rev., 72:6, 502-503 (1947).
- F2. C. T. Lane, H. A. Fairbank, L. T. Aldrich and A. O. Nier, Phys. Rev., 73:3, 256 (1948).
- F3. H. A. Fairbank, C. T. Lane, L. T. Aldrich and A. O. Nier, Phys. Rev., 71:12, 911-913 (1947).
- F4. A. Andrew and W. R. Smythe, Phys. Rev., 74:4, 496-497 (1948).
- F5. Stable Gaseous Isotope Separation and Purification: July-September 1967, MLM-1430 (Apr. 12, 1968), pp. 57-69.
- F6. Stable Gaseous Isotope Separation and Purification: July-September 1968, MLM-1529 (Feb. 13, 1969), pp. 37-45.
- F7. W. R. Wilkes, "Distillation of Helium Isotopes," Proceedings of ICEC-4, Eindhoven, 1972, IPC Science and Technology Press (1972), pp. 119-121.
- F8. W. R. Wilkes, ³He-⁴He Distillation Apparatus, MLM-2005 (Mar. 21, 1973), 15 pp.

Distribution

EXTERNAL

TID-4500, UC-20d and UC-20e (154)

J. L. Anderson, Los Alamos Scientific Laboratory
C. C. Baker, Argonne National Laboratory
J. E. Baublitz, DOE/OFE (100)
B. C. Blanke, DOE/DAO
G. A. Carlson, Lawrence Livermore Laboratory
R. W. Conn, University of Wisconsin
F. E. Coffman, DOE/OFE
R. K. Flitcraft, MRC
W. C. Gough, Electric Power Research Institute
H. N. Hill, DOE/DAO
A. B. Johnson, Jr., Battelle Pacific Northwest Laboratories
D. Kearney, General Atomics
H. T. Kite, Oak Ridge National Laboratory, Y-12
R. A. Krakowski, Los Alamos Scientific Laboratory
G. L. Kulcinski, University of Wisconsin
E. M. Larsen, University of Wisconsin
V. A. Maroni, Argonne National Laboratory
L. H. Myer, Savannah River Laboratory
J. A. L. Robertson, Atomic Energy of Canada, Ltd.
Z. Sabri, Iowa State University
T. E. Shannon, Oak Ridge National Laboratory
W. A. Swansiger, Sandia Laboratories, Albuquerque
J. S. Watson, Oak Ridge National Laboratory

INTERNAL

H. F. Anderson
V. L. Avona
J. C. Bixel
W. T. Cave
R. DeWitt
C. W. Huntington
B. E. Jepson
L. V. Jones
C. J. Kershner
P. H. Lamberger
J. R. McClain
T. B. Rhinehammer
M. L. Rogers
R. A. Schwind
R. E. Vallee
W. R. Wilkes
L. J. Wittenberg (50)
Publications
Library (15)
Records Management

87. J. D. Vine, "Nonpegmatite Lithium Resource Potential," in Lithium Resources and Requirements by the Year 2000, J. D. Vine (ed.), U. S. Geological Survey Professional Paper 1005 (December 1976), pp. 54-58.
88. Preliminary Reference Design of a Fusion Reactor Blanket Exhibiting Very Low Residual Radioactivity, J. R. Powell (ed.), BNL-19565, Brookhaven National Laboratory, Upton, N. Y. (December 1974), 114 pp.
89. M. A. Abdou, L. J. Wittenberg and C. W. Maynard, "A Fusion Design Study of Non-mobile Blankets with Low Lithium and Tritium Inventories," Nuclear Technology, 26, 400-419 (1975).
90. Private communication, H. D. Hickman, DOE, Oak Ridge Operations, Oak Ridge, Tenn. (May 1978).
91. A. A. Palko, J. S. Drury and G. M. Begun, "Lithium Isotope Separation Factors of Some Two-Phase Equilibrium Systems," J. Chem. Phys., 64:4, 1828-1837 (1976).
92. Private communication, R. W. Ritzmann, ERDA, Office of Industry Relations (May 1976).
93. Private communication, D. R. Carter, Eagle-Picher Industries, Joplin, Mo. (June 1978).
94. Private communication, H. T. Kite, Y-12 Plant, Oak Ridge, Tenn. (June 1976).
95. A. Valfells, "An Isotope Separation Process for the Concurrent Production of ⁶Li and Deuterium," Trans. Amer. Nucl. Soc., 21, 38-39 (June 1975).
96. W. E. Drummond, Fusion R & D on Advanced Fuels, Homopolar Generators, Circuit Breakers and Tokamak Diagnostics, EPRI 96-2, Electric Power Research Institute, Palo Alto, Calif., (September 1975), pp. 1-17.
97. Research Materials, Oak Ridge National Laboratory, Oak Ridge, Tenn. (April 1973), p. 103.
98. McGraw-Hill Encyclopedia of Science and Technology, Vol. 6, McGraw-Hill, Inc., New York, N. Y., 1977, pp. 444 and 449.
99. D. G. Jacobs, Sources of Tritium and Its Behavior upon Release to the Environment, TID-24635, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1968), 90 pp.
100. R. C. Seamans, The Energy-Related Applications of Helium and Recommendations Concerning the Management of the Federal Helium Programs - A Report to the President and the Congress of the United States, ERDA-13 (April 1975), 184 pp.
101. G. W. Koelling and R. F. Balazik, "Helium," in Mineral Facts and Problems, Bulletin 667, U. S. Bureau of Mines (1975), 11 pp.
102. Private communication, D. E. Emerson, U. S. Bureau of Mines, Amarillo, Tex., (June 1976).
103. B. J. Moore, Helium Resources of the United States, 1973, IC8708, U. S. Bureau of Mines (1973), 17 pp.
104. Potential Supply of Natural Gas in the United States, (as of December 31, 1972), Potential Gas Agency, Miner. Res. Inst., Colorado School of Mines Foundation, Inc. (November 1973), 47 pp.
105. E. V. Anderson, "Who Pays Is Key to Helium's Future," Chem. Eng. News, 11-13 (Dec. 6, 1976).