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POSSIBILITIES OF TRITIUM REMOVAL FROM WASTE WATERS OF PRESSURIZED
WATER REACTORS AND FUEL REPROCESSING PLANTS

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TRITIUM RECOVERY AND SEPARATION FROM CTR PLASMA EXHAUSTS AND
SECONDARY CONTAINMENT ATMOSPHERES

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OPENING REMARKS OF SESSION CHAIRMAN:

We have only 3 papers, but I feel that the subject of tritium is going to grow during the next couple of decades. Tritium production has been increasing in association with the weapons program and the spawning of a nuclear power economy. In addition to the weapons program and miscellaneous R&D, we see that each of the segments of the nuclear industry, including the LWR programs and the liquid metal fast breeder reactor program is coming on line rapidly and is producing its own set of problems with respect to the handling, containment, and air cleaning, if you will, of tritium. Nevertheless, I don't think we have yet reached the great "crunch" with respect to the production of tritium. The Barnwell Plant, which will process a quantity of LWR fuel, is projected as a source of 400,000 curies per year. They will release 100 percent of the tritium which evolves. However, an initial look at a fusion power plant shows that it will burn deuterium and tritium on a 1:1 ratio as fuel. It will require something like 60 million curies a week just to fuel the machine. When I look at that in terms of potential, I think of 2 or 3 or 4 billion curies per year required to run one of these machines. So, the quantity of tritium we will be handling in the coming decades is going to grow and I think this is a timely topic. I think everyone here realizes the kind of problems that will be encountered during handling, containing, and working with kilogram quantities of tritium.

POSSIBILITIES OF TRITIUM REMOVAL FROM WASTE WATERS OF
PRESSURIZED WATER REACTORS AND FUEL REPROCESSING PLANTS*

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Abstract

Starting from parameters known for heavy water production processes, a parallel was made with separation of tritium from water. The quantity in common is the total cascade flow. The most efficient processes appear to be hydrogen sulfide - water exchange, hydrogen- and water distillation. Prospects of application of new processes are discussed briefly. Problems concerning detritiation of pressurized water reactors and large fuel reprocessing plants are analyzed. Detritiation of the former should not present problems. With the latter, economical detritiation can be achieved only after some plant flow patterns are changed.

I. Introduction

The radioactive isotope of hydrogen, tritium, is being formed by several different processes tied to the technology of nuclear power. These sources are generally the following:

1. Tritium is a product of ternary fission and accumulates with other fission products in the fuel elements;
2. It is formed by neutron reactions with boron and lithium, which are being added to reactor coolants for reactivity and pH control, as well as in poison rods and other reactor materials;
3. Neutron reactions with deuterium, particularly in the moderators of heavy-water reactors, are producing appreciable quantities of tritium;
4. The process of nuclear fusion, both as a weapon and as a future source of controlled energy, involves great amounts of tritium.

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The following discussion will be concerned with the first two sources, with particular emphasis on pressurized water reactors and fuel reprocessing plants, which are presently the largest producers of tritium released to the environment.

Despite the fact that tritium appears to be one of the most innocuous radioisotopes, and presently does not seem to be a radiological danger to the population, the rapidly expanding industry of nuclear power will be producing increasing amounts of it. In the year 1980 a release of 1.5 millions of curies of tritium by the U.S. nuclear power plants is foreseen (1). This amount will be ten times as great by the end of the century. A distinct trend toward the release of this activity into the atmosphere is being felt. A need for efficient methods for tritium removal from waste waters may therefore arise in the near future.

II. Processes of Tritium Separation

The problem of separating tritium from protium has been encountered some time ago particularly in measurements of natural and other low-level tritium activities, in order to produce tritium concentrates with measurable counting rates. The most frequently used method is water electrolysis (2, 3, 9), but thermal diffusion (4), water distillation (5) and gas chromatography (6, 10) have been used also. The amounts of water treated this way were of the order of liters, but nevertheless this procedure appears to be quite costly. Libby (7) states, for example, that preparation of a single sample for counting (using electrolysis) costs between \$100 and \$200.

When dealing with the problem of tritium extraction from large quantities of water, of the order of tens of tonnes (tonne = 1000 kg) per day, it is at first approximation safe to assume that any efficient heavy-water production process will be applicable to tritium-protium separation, since these two procedures are essentially the same. Some differences should be, however, taken into account.

Specific Aspects of Tritium Separation

1. The elementary (single-stage) separation factors, α , of H/T separation are by the rule larger when compared to H/D separation. If the former is known experimentally, the relationships due to Bigeleisen (8):

$$\log \alpha_T = 1.40 \log \alpha_D \quad (1a)$$

and

$$\frac{\log \alpha_T}{\log \alpha_D} = 1.38 + \frac{0.026}{\log \alpha_D} \quad (1b)$$

can be used for equilibrium and rate processes respectively. The consequence of this is a considerable decrease in energy requirements and volume of the separation equipment for an equal extent of separation.

2. The amounts of water to be treated are smaller than the capacities of large-scale heavy water production plants in use today. The consequences are higher processing costs of a unit quantity of water.

3. The concentration of tritium in all the flows of a separation cascade stays very low in the absolute sense. This rather formal difference enables a considerable simplification of calculations involving separation cascades.

4. In some cases, as it will be shown later, a thorough stripping of the tritiated water might be attempted. Such a separation cascade will have a very extended stripping section, unlike usual heavy water production cascades working with their optimum deuterium recovery (stripping) factors. An illustration of this statement is given in Fig.1 where shapes of three ideal cascades of

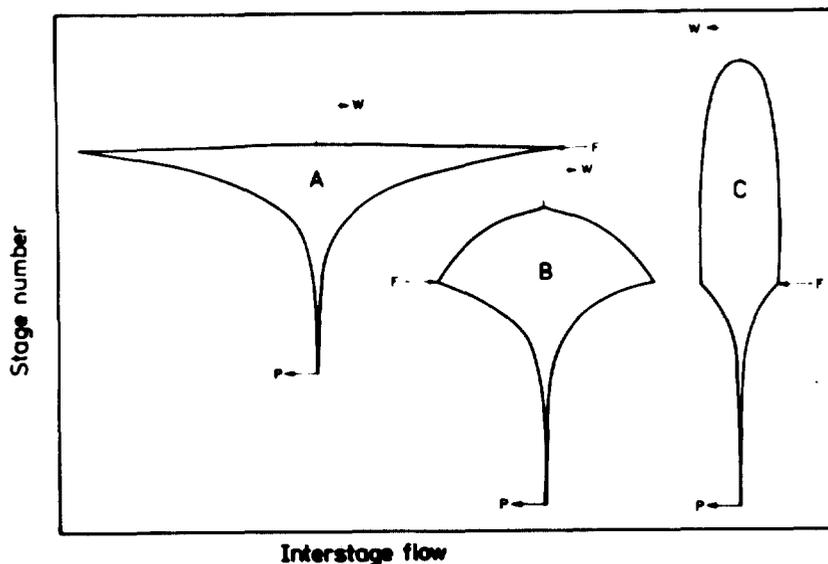


Figure 1. Three ideal cascades of equal total flows. Cascade A: recovery factor 0.18, cascade B: 0.9, cascade C: 0.999. F, P, and W are the feed, product and waste points respectively.

equal total flows are shown. The cascade A would correspond to the common heavy water production process of bithermal H_2S/H_2O exchange, cascade B to distillation of hydrogen, and cascade C to tritium separation when a stripping factor of 1000 is applied.

5. Many of the heavy water production processes are designed to operate as hydrogen gas producers, i.e. the hydrogen depleted in deuterium is being used for other purposes (e.g. ammonia synthesis), diminishing thus the price paid for isotope separation. It is questionable whether hydrogen, still containing some radioactivity, could be used similarly.

Two Separation Schemes

The approach to the problem of tritium separation from water can be made in two different ways. The first one is to process all the water leaving a reactor or fuel reprocessing plant, producing two streams: one of low tritium content, fit to be released to the environment, and a second of a considerably higher concentration (and smaller volume) which can be either stored as water or in another form. This scheme will be further referred to as the stripping scheme. The second way produces a similar tritium concentrate, but the water is being detritiated only partly and is returned to the reactor (or plant), maintaining a desired steady-state concentration within. This is the recycling scheme.

As it will be shown later, the choice of the separation process depends on the separation scheme chosen. The same applies to the price to be paid for detritiation.

A Connection Between Heavy Water Production and Tritium Separation

The differences of the shapes of tritium and deuterium cascades, as well as different elementary separation factors, prevent a straight comparison of these two isotope separation processes. However, a common parameter for both can be the total cascade flow, which is proportional to the energy consumption and very closely so to the processing costs.

From equations of the flow of an ideal cascade (11) applied to deuterium separation on one side, and to tritium on the other, relations were derived (12) defining a heavy-water equivalent, P_D , of a tritium cascade as

$$P_D = 8 \times 10^{-5} F_T n f(r), \quad (2)$$

where F_T is the necessary feed of the tritiated water, n is the logarithm of the over-all stripping factor of the tritium cascade*

* The separation factor of the enriching section of the cascade does not play a significant role if greater than 10^3 (12).

and $f(r) = r / \log \frac{1}{1-r}$, r being the optimum fraction of deuterium recovered from the feed by the deuterium cascade. In other words, the amount of water to be detritiated with a factor of 10^{11} is correlated to the amount of heavy water which would be produced in a cascade of equal flow.

When applied to the stripping scheme, Eq. 2 becomes (12):

$$P_D = 8 \times 10^{-5} \frac{A}{x_F} n f(r), \quad (3)$$

where A is the total tritium release in unit time (e.g. curies/yr) and x_F is the tritium concentration in the feed.

For the recycling scheme a similar relation holds:

$$P_D = 8 \times 10^{-5} \frac{A}{x_F - x_W} n f(r), \quad (4)$$

where x_W is the tritium concentration in the stream being returned to the tritium pool.

By comparing Eqs. 3 and 4 it can be seen that the difference between the two schemes is in the factor $1/x_F$ (stripping) and $1/(x_F - x_W)$ (recycling). The latter will therefore always be more efficient for the same values of n and r .

It should be noted that the heavy-water equivalents, P_D , do not depend on the quantity of water which is contained within the reactor or plant, when a continuous withdrawal is being undertaken. On the other hand, if a batch detritiation is being performed (where the stripping scheme is applicable only), the amount of flow (or separative work) for the same value of A , will increase with the quantity of water to be processed. Any unnecessary dilution of the once tritiated water will therefore lead to an increased decontamination effort.

Relative Prices of Various Separation Processes

In order to get a feeling of efficiencies of different separation procedures, when working according to the two schemes, heavy-water equivalents per curie of tritium released are calculated and given in Table I for six most common heavy water production processes. For both schemes x_F was set to a value of $2.5 \mu\text{Ci}/\text{ml}$ /the highest activity tolerable in PWR coolants (31)/. The stripping scheme, marked "Str.I", corresponds to a waste activity of $3 \times 10^{-3} \mu\text{Ci}/\text{ml}$ (the presently recognized maximum permissible T activity, MPC), while the stripping scheme "Str.II" decontaminates only to $0.3 \mu\text{Ci}/\text{ml}$, i.e. the waste would require a 100-fold dilution to attain the MPC.

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To get the cost of detritiation, C_T , minimum heavy water prices, C_{D_2O} , applicable to large-scale production, were used according to the relation

$$C_T = C_{D_2O} P_D / A$$

with an adjustment as follows. The heavy water processes which are "parasitic" (hydrogen producing) were treated with specific D_2O prices increased for the price of hydrogen they would have produced with their respective recovery factors, r . This applies to the column containing all the recycling data and the stripping process II, assuming the hydrogen gas to be too radioactive to be used as such. The stripping process I, decontaminating to the MPC, was calculated with the basic prices.

The derived prices are surely lower than attainable in the practice of detritiation. The quoted heavy water prices are mostly projections to plants producing hundreds of tonnes of D_2O per year. The capacity required for a single power reactor or a fuel reprocessing plant is far lower, and these figures have a comparative value only.

On the Choice of the Separation Process

From the preceding considerations it may be concluded that the separation principle should be a recycling one whenever feasible, if a continuous tritium extraction is to be undertaken. The relative costs listed in Table I suggest immediately the use of either bithermal hydrogen sulfide - water exchange, hydrogen- or water distillation.

Despite the lowest costs associated with the first named process, it suffers from the disadvantage of operating with one component which is very toxic and corrosive. Besides special precautionary measures in case of H_2S liberation, a thorough purification of the returning depleted water stream would be absolutely necessary.

The cryogenic nature of hydrogen distillation should not be a limiting factor for its application. The compactness of the equipment is its great advantage. The tritium transfer from water to hydrogen could be done by electrolysis at the feed point and combustion at the waste point. Alternatively, both these operations could be performed with single-stage hydrogen - steam exchangers.

Water distillation looks quite tempting inspite of its highest specific cost among the three considered processes. The first reason is the possibility of using cheap (or free) exhaust steam of the same plant whose water is being decontaminated. The process does not require conversion and no foreign substances are involved. The process is rather easily automated and no development for the purpose is needed. The disadvantage is its large volume.

Table I
Heavy water equivalents and minimum prices of tritium separation
(PWR with $x_F = 2.5 \mu\text{Ci/ml}$)

Separation Method	r_{opt}	(a) Prices, $\$/\text{kg}$			10^n (rec.)	P_D/A , $\text{kg/Ci}\cdot\text{yr}$			Minimum C_T , $\$/\text{Ci}\cdot\text{yr}$		
		Min. D_2O	H_2^b	Min. $+\text{H}_2$		Str. I	Str. II	Rec.	Str. I	Str. II	Rec.
Water electrolysis	0.62	405 ^c	235	640	3.74	0.137	0.044	0.037	55	28	24
Electrolysis and $\text{H}_2 - \text{H}_2\text{O}$ exchange	0.62	103 ^d	235	338	1.72 ^e	0.137	0.044	0.027	14	15	9
Bithermal exchange $\text{H}_2 - \text{NH}_3$	0.72	33 ^f	202	235	1.72 ^e	0.129	0.041	0.025	4	10	6
Water distillation ^g	0.05	103 ^h	-	103	1.07	0.264	0.084	0.042	28	9	4
Hydrogen distillation	0.9	53 ⁱ	162	215	1.72 ^e	0.084	0.026	0.016	4	6	3.5
Bithermal exchange $\text{H}_2\text{S} - \text{H}_2\text{O}^j$	0.18	38 ^k	-	38	1.32	0.335	0.105	0.059	13	4	2

a. Refs. 11 and 13.

b. Hydrogen at $\$/\text{kg}$ 0.20/kg.

c. Includes only electrical energy at 5 mills/kWhr.

d. Minimum 1954 cost, Ref.13.

e. Single-stage $\text{H}_2\text{O} - \text{H}_2$ equilibrium assumed.

f. Estimated for 100 t/yr plant in 1968, Ref.14.

g. For this process the constant term in Eq.2 is 20% higher. Based on Ref.15 data, explained in Ref.12.

h. Projected 1967 price. Ref. 16.

i. Minimum 1954 cost. Ref. 13.

j. Constant term of Eq.2 is 1.35×10^{-4} if calculations of tritium equilibrium constants in Ref. 17 are correct.

k. Minimum price for production of 200 t/yr in 1960. Ref. 18.

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Among the isotope separation processes not used in large-scale heavy water production some could become competitive or even more efficient compared to the above considered ones. The authors' point of view will be stated briefly in the following.

1. An improved design of the hydrogen-steam exchange process developed by Mercea et al. (19, 20) appears to have a good chance. The process involves catalytic exchange in a newly designed column, combined with water distillation and electrolysis. A recent calculation of Mercea (21) was comparing this process with water distillation when applied to decontamination of a PWR. It was shown that the costs associated with this exchange process are about 4 times lower. In addition, the size of the equipment is about 5 times smaller when compared to water distillation.

2. Water electrolysis by itself is far too expensive to be used despite its simplicity and compactness of the equipment. Application of the principle of reversible electrolysis, which was proposed some time ago for heavy water production (22) could, in principle, decrease the electrical power consumption for some 80%. To our knowledge it has never been applied. The original proposal involves hydrogen-permeable palladium membranes which are rather expensive. It has been shown recently (23) that workable bipolar electrodes can be made of much cheaper carbon, presenting thus a possible new tritium separation process.

3. Laser-beam photochemistry has in recent years made very promising advances (24, 25). Applied to isotope separation, the most significant result appears to be the one of Mayer et al. (26), who succeeded to achieve an almost complete separation of H and D in a gaseous mixture by irradiating with a powerful infrared laser. The aspect of selective molecular excitation offers great potentialities, especially when dealing with very dilute isotopic mixtures such as tritiated water.

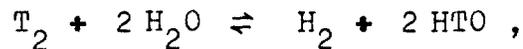
III. Application

The problems involved in detritiation of light-water reactors and fuel reprocessing plants differ in several aspects and shall be discussed separately.

Light-water Reactors

Coolants of both types of light-water reactors, the boiling water reactor (BWR) and the pressurized water reactor (PWR) are being contaminated with fission tritium which diffuses through the cladding of fuel elements. Even though the tritium entering the water can be anticipated to be mainly in the form of T_2 , it will rapidly exchange with water according to the reaction

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which is most probably radiation catalyzed (27). The rate of leakage is dependent on the type of cladding. Zircaloy is in this respect found far superior to stainless steel. The leakage through the former is found to vary between 0.1 and 1 per cent of the tritium formed, while the latter may allow 30 per cent or more to escape into the coolant (1, 28). Since a tritium activity of some 19 curies is being produced for one gigawatt-day of thermal power released, a quantity between 6 and 0.02 Ci/GWd will be introduced into the primary coolant.

In a PWR additional tritium is being formed by neutron reactions with boron and lithium dissolved in the coolant. The activity of tritium from this source in a 1000 MW(e) PWR was found to be about 1100 Ci/yr (1). This would mean a production of about 1 Ci/GWd of thermal power.

The tritium entering the coolant of a BWR is being diluted by a considerably greater quantity of water compared to a PWR. The PWR coolant is also being contaminated by the tritium from the dissolved boric acid. For these two reasons a PWR will build up considerably higher tritium activities which are found to reach 4 μ Ci/ml, while the highest activity in a BWR coolant found was only 0.03 μ Ci/ml (1). Only pressurized water reactors shall be therefore considered.

An approximate calculation will be made for a PWR of 1000 MW(e). The annual tritium build-up from boric acid is as quoted above, 1100 curies. Ten per cent leakage from the fuel would add 1630 Ci (a 300-day year and thermal efficiency 0.35 assumed) making a total of 2730 Ci/yr.

For an amount of 400 tonnes of water in the primary loop and in a hypothetical completely closed system (all effluents returned to the coolant), at the above tritium production rate, the specific activity after the first year of operation will be 7 μ Ci/ml.

If a leakage of only 10% is taken, the equilibrium activity built up after (long) time will equal 70 μ Ci/ml, with the situation that the leaking water will contain all the tritium produced in the same time.

It is assumed that the maximum tritium activity in the primary loop is 2.5 μ Ci/ml which is to be maintained by a recycling separation device. As an example plain water electrolysis will be applied since for this process the predominant expenses are electrical energy and the costs can be calculated simply. The single-stage separation factor for this process is taken as 14. The necessary feed is found from Eq.4 as 1.5×10^6 kg/yr. A five-stage electrolytic cascade is applied, whose relative flows and concentrations are shown in Fig.2. As it can be seen, the amount of water to be electrolyzed is 1.357 times the feed, i.e. 2.0×10^6 kg/yr. In practice, some

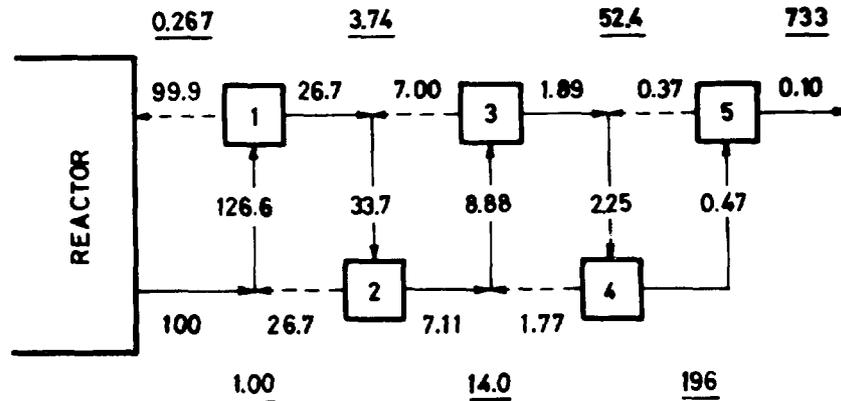


Figure 2. A five-stage electrolytic cascade for H/T separation. Figures in the cascade are relative flows, underlined figures are relative concentrations.

6.6 kWhr of electricity is needed in order to electrolyze one kg of water. The total power consumption will therefore equal 1.3×10^7 kWhr/yr, which amounts to 0.2% of the plant's electrical output. The heavy-water equivalent of this cascade is 100 kg D₂O/yr.

Judging from the Table I data, other processes could obviously perform with a considerably better economy.

Fuel Reprocessing Plants

The major part of fission tritium is released in the fuel processing plants. The amount varies according to the type of the fuel elements. Firstly, with stainless steel clad fuel a sizeable fraction of tritium might have escaped into reactor coolants. Secondly, the amount of tritium per unit weight of spent fuel has to depend on the degree of burn-up and, related to this quantity, to the degree of ²³⁵U enrichment in the original charge. Fuel initially containing some plutonium, or being pure Pu, should contain more tritium since plutonium fission produces about twice as much tritium compared to uranium. It is therefore not surprising that the amount of tritium contained in one tonne of spent fuel was found to vary between 18 and 710 curies (1).

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A simplified flowsheet of a typical fuel reprocessing plant utilizing the Purex process is shown in Fig.3, with approximate pathways of tritium.

As an example, actual flows and tritium activities of the Allied-Gulf reprocessing plant at Barnwell, S.C., will be taken (1). It is designed to process 1500 tonnes of spent fuel (3% ^{235}U) annually. The fuel, containing 415 Ci of tritium per tonne (expectation), enters the dissolution at a rate of a tonne every 3 hrs. Ten to twenty per cent of the tritium will appear in the dissolver off-gases. Most of this activity is to be released to the plant stack. The rest of tritium, in the form of HTO and TNO_3 , is contained in the solution which is generated at a rate of approximately 1000 liters per hour. After passing the first cycle extraction stage, freed from U, Pu and Np, and containing the fission products including practically all the tritium, it is being concentrated. About one tenth of tritium stays with the high activity waste (HAW) while the rest, after further decontamination, flows partly back to the dissolver and is partly being evaporated to the stack at a rate of 5100 liters/hr. (The excess water, compared to the input, arises from other stages of the plant, not shown in the flowsheet). The release of tritium at this point is expected to be about 560,000 Ci/yr. Combined with the off-gas emission, the total tritium release of the plant is to be 622,000 Ci/yr^{**}.

The following calculation will explore possibilities of controlling this tritium emission.

Case I. The waste stream of 5100 liters/hr, containing most of the tritium, is fed to a separation device which reduces its activity by a factor of ten. The process taken for example is hydrogen-steam exchange combined with electrolysis with parameters $n = 1$, $f(r) = 1.475$ and $x_F = 0.0244$ Ci/kg H_2O . From Eq.3 the heavy-water equivalent is found to be 2700 kg D_2O /yr. The flow and dimensions of such a separation device would obviously be far too costly to be considered further.

Case II. The high cost of the above case is due to the great amount of water which is mixing in from other streams. Suppose the dissolution and first cycle extraction are working as a closed system, the only "leakage" being the amount of water flowing to HAW. After several cycles the activity of the water will build up to an equilibrium value of 1.24 Ci/kg and HAW will carry practically all

* To be in operation by early 1976.

** Other examples in the U.S. are the Nuclear Fuel Services and the G.E. Midwest plants releasing 300,000 and 120,000 Ci of T respectively per year (1).

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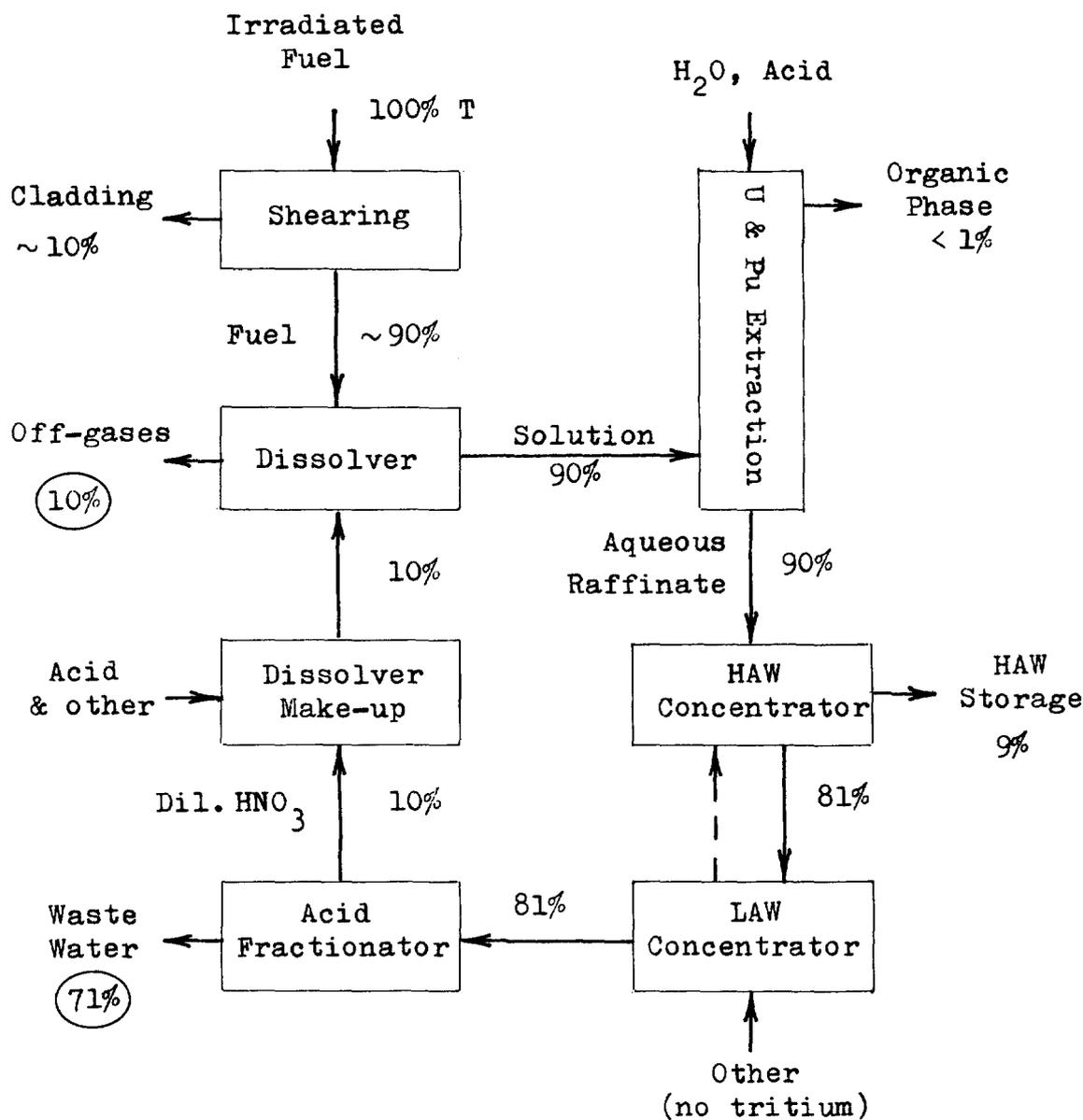


Figure 3. Pathways of tritium in a typical fuel reprocessing plant (simplified). HAW - high activity waste, LAW - low activity waste. Encircled figures show flows flows released to air or surface streams.

the newly produced tritium. Without doing any effort for isotope separation, the tritium is now contained in about 450 tonnes of water per year.

Case III. The HAW water from the previous case has eventually to find its way to the environment. Suppose this water is treated with a stripping separation device with $n = 3$, using the same process as in Case I. The equivalent is now far lower and equals 159 kg D_2O /yr.

Case IV. A separation device working on the recycling principle is connected to the isolated first cycle extraction stage. It extracts 83% of the tritium introduced, the rest going to HAW. The equilibrium activity will in this case be 0.207 Ci/kg. The equivalent is here 149 kg D_2O /yr.

Case V. For one half of tritium extracted with a recycling device, the equilibrium activity will be 0.62 Ci/kg, the other half going to HAW. The P_D value is here 30 kg D_2O /yr only. (Treating the remaining HAW water would still equal to Case III).

A summary of all the considered situations is given in Table II. The last column contains a price per curie tritium extracted into the concentrate. It was derived by taking a value of \$500 for a kg of D_2O -equivalent, which we consider reasonable for separation equipment of such low capacities.

Comments on Application

It is seen that the decontamination of pressurized water reactors presents a problem differing in some respects from the treatment of a large fuel reprocessing plant. With a reactor the allowed tritium activity is quite low, while in the plant streams the general radioactivity overshadows the one of tritium, and much higher activities could be allowed.

The heavy water equivalents derived are of the same order of magnitude for separation devices working on a 1000 MW(e) reactor and a 1500 tonnes U/yr plant. Since a plant of this size treats spent fuel of some 50 reactors, and involves approximately 200 times larger amounts of tritium, the specific cost of extracting one curie has to differ considerably. The plant tritium separation could meet the price of \$0.10 which was advanced as economically justified for separation (29), but the reactors obviously cannot, unless different criteria are applied. The low price for the plants does not include, however, the cost of the necessary rerouting of the plant streams, which is unknown.

Table II
Possible ways of tritium removal from a fuel reprocessing plant
(capacity 1500 tonnes U/yr, tritium input 5.6×10^5 Ci/yr)

Treatment	Separation scheme	Plant stream activity Ci/kg H_2O	Concentration tonnes/yr	Concentration activity Ci/kg H_2O	Curies T in concentrate (%)	Total activity released $Ci \times 10^{-3}/yr$	P_D kg D_2O/yr	Price per Ci removed \$/Ci
None	none	0.14	none	-	-	560	-	-
I.	Decontaminates 9/10 of waste	0.14	206	2.44	90	56	2700	2.68
II.	Isolates 1st cycle extraction	1.24	450	1.24	100	0	-	-
III.	Treats concentrate from II	1.24	0.44	1244	99.9	0.6	159	0.14
IV.	Continuous removal of 5/6 T from isolated 1st cycle	0.207	2.25	207	83	0	149	0.16
V.	Continuous removal of 1/2 T from isolated 1st cycle	0.62	1.0	311	50	0	30	0.05

III. Conclusions

1. The isotope separation processes found to be most efficient for tritium separation from water are the bithermal hydrogen sulfide - water exchange and distillation of hydrogen. Distillation of water would cost more but is the simplest in operation. Essentially the same conclusion was made by Lin (30) by considering the situation in a somewhat different way.

2. Promising processes which might be applied for tritium separation are an improved design of hydrogen - steam exchange, reversible water electrolysis and, possibly, selective molecular excitation.

3. The problem of tritium decontamination of light-water reactor coolants can be solved most economically by the use of a recycling isotope separation device which would maintain the tritium concentration in the coolant at a desired level. The cost of separation will be proportional to the total amount of tritium released in unit time, and inversely proportional to the tolerable tritium level. Application of an electrolytic separation cascade to a pressurized water reactor, maintaining an activity of 2.5 $\mu\text{Ci/ml}$ in the primary loop, would be consuming 0.2% of the plant's electrical output. Other procedures could work more economically.

4. The major fraction of fission tritium appears in the waste waters of fuel reprocessing plants, with the tendency to become evaporated to the atmosphere at the end of process. In order to reduce the tritium emission from a 1500 tonnes U/yr plant to one tenth, by treating the existing waste streams, an expenditure of the order of $\$ 10^6$ annually would be necessary. By rearranging the plant streams to isolate the first cycle extraction loop, the expenses could be lowered by a factor of 10 or more, with practically no tritium emission.

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DISCUSSION

YARBRO: First I have a comment on the recycling approach. I agree that it is very effective with tritium. I would like to point out that to prevent any loss of water in a fuel re-processing plant, to maintain a factor of, say, a hundred, you will have to release less than one part per million of water per day while drying 100,000 cubic feet of air. With respect to your cost figures, would you tell me how much it costs to remove, by a factor of a hundred, tritium from a gallon of water?

RIBNIKAR: This will depend on the process used. For a large-scale stripping operation the minimum prices will be in cents/gal for a separation factor S:

	S=10 ²	S=10 ³
Plain water electrolysis (0.5c/kWhr)	58	85
Electrolysis & H ₂ /H ₂ O exchange	30	45
Water distillation	18	26
Hydrogen distillation	12	18

YARBRO: In order to retain tritium by recycling water, you have to prevent loss of water from your system. There is ventilation air that represents a rather significant loss mechanism because it can be saturated with water.

RIBNIKAR: Obviously, you can not prevent all of it. Ten percent is going to get away, anyway. You can not prevent it by present technical means. But I think you have misinterpreted what we are doing. We do not handle moisture from air. The water we are treating or handling is just liquid where it's coming out. We don't have to dry anything for that purpose.

LASER: In table 1, you have stated that water distillation, hydrogen exchange, is the cheapest method, and that water distillation is the most expensive of these methods. You have calculated this data from big plants: from the cost for tritium separation in big plants. In small plants, the order may be otherwise because of very different cost structures: because capital costs and operating costs are very different in these methods.

RIBNIKAR: I agree fully with that statement. I stressed that these figures apply to very large plants and, particularly, the water distillation plants are not very well defined. The price of the steam which heats the boilers, in our case, being just next to a power plant, is low. We would have plenty of free exhaust steam with which to do the job. The price would go down even when the cost of distillation, which is very high, would be predominant.

KIRKPATRICK: Do any of the processes that you have considered operate at the same pressures as any other reactor now in operation,

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KIRKPATRICK (cont.): or do they all operate at lower pressures?

RIBNIKAR: All are much below the pressure of the reactor.

KIRKPATRICK: In evaluating the prices of PWR detritiation, have you taken into account the work of recompression of the detritiated water into the reactor?

RIBNIKAR: No. The proposed point of attachment of the detritiating device is on the CVCS letdown loop where the pressure is already relieved.

13th AEC AIR CLEANING CONFERENCE

TRITIUM EFFLUENT CONTROL LABORATORY

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Abstract

A new "Tritium Effluent Control Laboratory" is described. The function of the laboratory is to provide experimental and pilot type facilities for research and development of tritium effluent control systems for recovering tritium from waste gas streams. The goal of the facility is to develop and demonstrate technology and equipment to maintain emissions to the atmosphere below 10% of Radioactivity Concentration Guide (RCG) levels.

Two helium atmosphere glovebox lines are provided. An air box which interconnects the two helium boxlines is used for equipment transfers and decontamination. In addition, a cryogenic helium purification system services both helium gloveboxes to maintain tritium levels at less than 1 ppm.

A catalytic oxidation and oxide adsorption air detritiation system (ADS) traps tritium released to the air box during equipment transfer operations. The air is recirculated for tritium removal before the air box is opened for equipment removal. This system is also used as an effluent treatment system to remove and contain tritium from other miscellaneous laboratory gas streams.

The laboratory support systems include an "Emergency Containment System" (ECS) which is actuated automatically upon accidental release of tritium to the laboratory or equipment room areas, preventing release of tritium from the laboratory air to the exhaust stack and outside environment. Upon actuation, personnel will be evacuated and the area will be sealed. The contaminated room air will then be recirculated through the ECS which consists of a catalytic oxidation reactor and an oxide adsorption column. The released tritium will be contained on the adsorption column in the oxide form. During this emergency condition, laboratory systems may be controlled from a location outside the contaminated area.

Glovebox experiments directed toward the development goal of a closed tritium cycle are described.

*Mound Laboratory is operated by Monsanto Research Corporation for the U. S. Atomic Energy Commission under Contract No. AT-33-1-GEN-53.

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I. Introduction

Mound Laboratory has as one of its assignments the recovery of tritium from various forms of tritiated waste generated by AEC contractors. These recovery operations at Mound primarily involve glovebox and fumehood type facilities with a wide variety of input materials for recovery.

The facilities are operated with the conventional inward air flow concept for radiation handling with the ventilation effluent released to the atmosphere through stacks.

The facility was originally designed and operated based on a concept of high volume air flows and dilution of effluents to maintain safe working conditions for the operators and to ensure that effluent concentration levels were less than the Radiation Concentration Guide (RCG) values at the plant boundary. Beginning in 1970, as a consequence of the new AEC "as low as practicable" criterion and the concomitant suggestion of moving the point of concentration control from the plant boundary to within the effluent stacks, an intensive tritium emission control effort was put into effect at Mound Laboratory. This effort has as its goal an ultimate objective of approaching zero emission and an engineering goal quantified in terms of maintaining stack emission levels at or below 10% of the present RCG values ($40 \mu\text{Ci}/\text{m}^3$ for HT and $0.2 \mu\text{Ci}/\text{m}^3$ for HTO).⁽¹⁾ To accomplish these goals facility design and operating philosophies were revised to those of containment and recycle as opposed to the past practice of high dilution and release. Over the past four years, implementation of this philosophy through modification and addition of facilities and changes in operating procedure has resulted in a 20-fold reduction in the gaseous tritium effluents released from the laboratory. These accomplishments and the 10-year reduction goals of this program are graphically shown in Figure 1. The details of the operation and facility changes applied to achieve these emission reductions have been previously described and were nearly all accomplished with state-of-the-art tritium handling technology.^(2,3) However, reduction of tritium effluent levels to 10% of RCG values at the point of emission and nearly complete recycle pose problems that are beyond ready solution with state-of-the-art tritium control technology.

To meet this advanced technology need, a Tritium Effluent Control Technology Project was initiated in January 1972. The experimental direction of this project was predicated on the results of an initial source and facility evaluation which revealed that as much as 80% of the total annual release to the atmosphere could be attributed to "background" diffusion from the gloveboxes and other containments to the room ventilation systems which are directly stacked. To treat the voluminous quantities of high humidity room air was deemed to be both

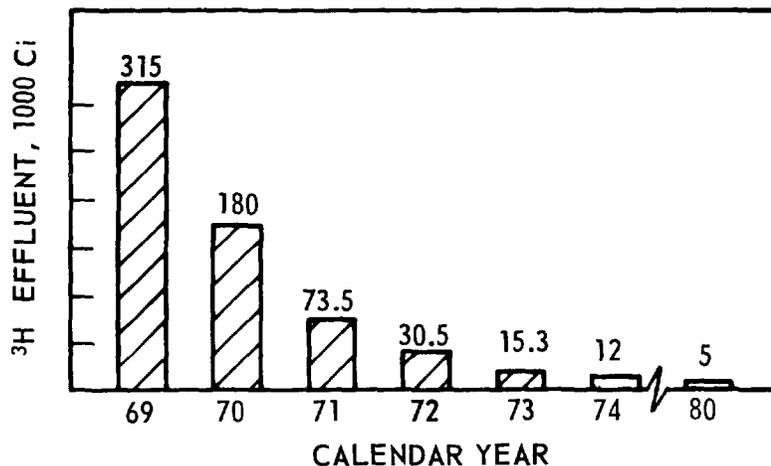


FIGURE 1 - Mound Laboratory effluent reduction accomplishments and goals.

economically and technically impractical, so emphasis was placed on confining the tritium at the source through the use of glovebox atmosphere detritiation and recovery systems and applying room air treatment only for emergency conditions in the event of accidental release.

Basic technology for the components was developed for a glovebox atmosphere detritiation and recovery system based on cryogenic adsorption and distillation and on an emergency containment system (ECS) based on catalytic oxidation and oxide adsorption concepts. Pilot type systems based on the above components and concepts were designed and incorporated into a test laboratory which will be described here.

II. Laboratory Concept and General Description

The design and operational concept for the experimental laboratory program is to integrate both pilot scale systems and basic component development experiments into a closed tritium cycle as shown in Figure 2. Both gaseous and liquid waste streams are treated and upgraded for recycle so that the quantity of tritiated liquid waste requiring disposal by burial is essentially zero and the gaseous effluents from the laboratory can be maintained below a 10% RCG level at the stack. How well this tritium balance cycle is closed, while at the same time performing meaningful research and development, will indicate the effectiveness of the program. The laboratory is located in a building away from other tritium processing facilities. This isolation provides the opportunity to make material balances for evaluating the effectiveness of the tritium inventory management without interference from other tritium operations.

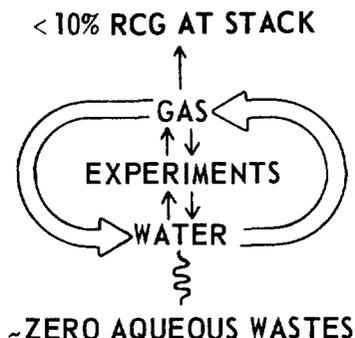


FIGURE 2 - Tritium effluent control laboratory concept.

The floor plan of the laboratory showing the three principal operating areas and associated change rooms is shown in Figure 3. Two helium atmosphere glovebox lines are provided. The left line is a single, 9-ft glovebox. The right line consists of three 4-ft gloveboxes. An air box which interconnects the two helium atmosphere boxlines is used for equipment and material transfers and decontamination. During normal operation, a pressure differential of 0.1 torr (0.05 in. water) is maintained between the contiguous rooms and corridors and the laboratory and equipment rooms. The control and change room ventilation systems are maintained at the pressure of the rest of the building. All controls, monitors, recorders, and alarm systems essential to the operation of the laboratory support system are situated in the instrument and control room. During emergency operation conditions, to be discussed in detail later, the laboratory and equipment room ventilation systems are separated from the building supply and exhaust system and circulated through the ECS. The laboratory is provided with a 120 gal/min, 65°F chilled water loop and a 5 gal/hr liquid nitrogen supply in addition to the standard laboratory services. Sumps are provided for collecting all low-level or uncontaminated waste water from the laboratory so that it can be sampled and routed either to a water recovery, burial disposal packaging, or to a normal discharge area depending upon determined contamination level.

The details of the laboratory will be discussed in terms of the various primary and secondary support systems which are shown in their interrelated perspective in Figure 4. Primary systems are defined as essential for safe operation of the laboratory and secondary systems as necessary for accomplishing the development goals of the laboratory and the project.

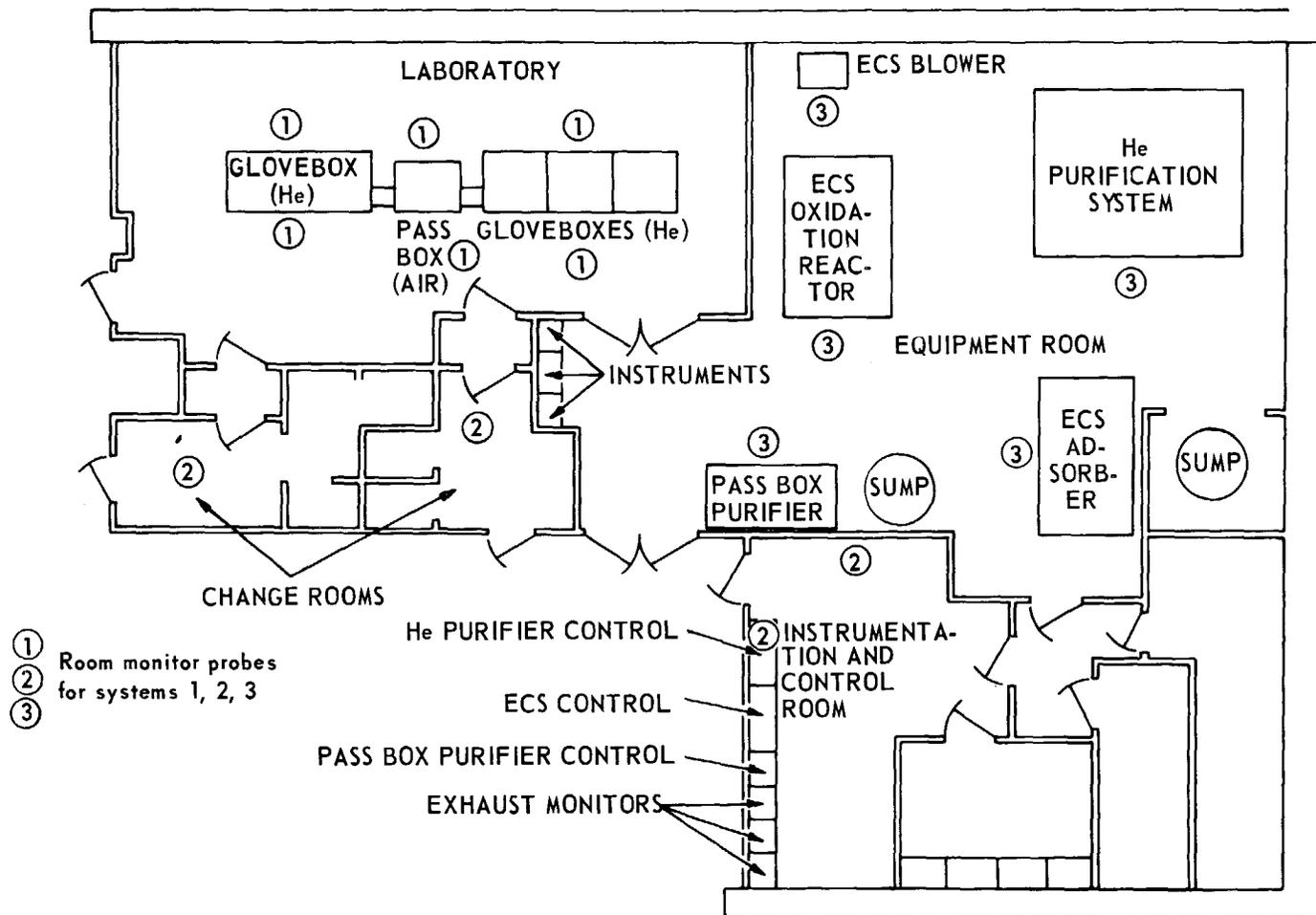


FIGURE 3 - Tritium effluent control laboratory (TECL).

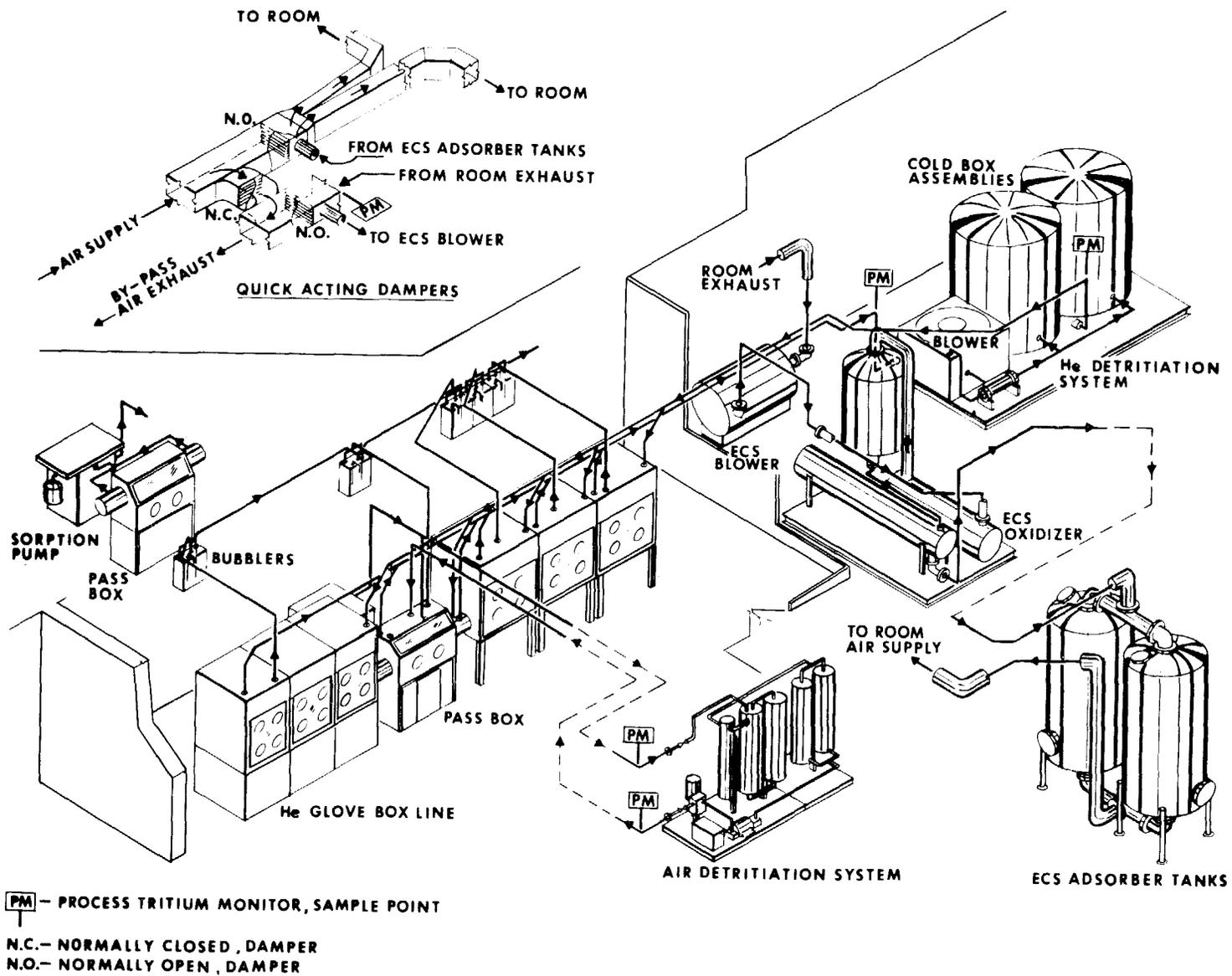


FIGURE 4 - Laboratory support systems and equipment.

III. Primary Support Systems

The primary support systems vital to the operation of the test laboratory are 1) the glovebox atmosphere detritiation system (GADS), 2) the air detritiation system (ADS), 3) the emergency containment system (ECS), and 4) the tritium monitoring system.

Glovebox Atmosphere Detritiation System

Concept The glovebox atmosphere purification and detritiation system is based on a helium flow loop where air contaminants and hydrogen including tritium are removed to levels below 1 ppm by adsorption on a fixed bed of molecular sieve pellets cooled by liquid nitrogen. Water vapor is removed in a precooling gas-to-gas heat exchanger and is collected in a liquid holding tank during the regeneration cycle warm-up. The adsorber beds are regenerated by heating to 250°F while purging with helium. The details of the regeneration gas treatment system will be discussed later.

Development Data Isotherm measurements for single component adsorption equilibrium at 77°K and low pressures were performed to provide adsorbent selection and adsorber design data for the GADS. Data were obtained for hydrogen, nitrogen, and oxygen on coconut charcoal as well as for hydrogen on Linde type 4A and 5A and Grace type 5A molecular sieves. A sample of these data is shown in Figure 5. As can be seen in Figure 5, Linde 5A molecular sieve has the best adsorption characteristics for hydrogen. Thus, because the adsorptivity of hydrogen in all cases is at least several orders of magnitude lower than the other air contaminants and the primary design consideration was given to hydrogen (tritium) removal, Linde 5A molecular sieve was selected for use in the GADS. Since the system is experimental in nature, provisions were made in the design of the adsorber beds for adsorbent replacement, should a superior adsorbent be found later.

The adsorbent choice was confirmed by dynamic studies with a flow loop scaled to simulate flow velocities and bed depths of the full scale unit. These experiments were performed using small adsorber beds with 79 g of adsorbent and 0.5 to 1 liter per minute helium flows with 2 to 7 ppm hydrogen containing trace tritium for analytical purposes. Hydrogen concentrations down stream of the adsorber were reduced by more than the design goal of 1000:1 and break-through times were greater than 24 hr (the design regeneration cycle).

Description and Specifications The GADS was fabricated by C. V. I. Corporation of Columbus, Ohio. The system has a nominal flow design of 100 ft³/min helium with dual column operation as shown in Figure 6. Each adsorber column containing 300 pounds of Linde 5A

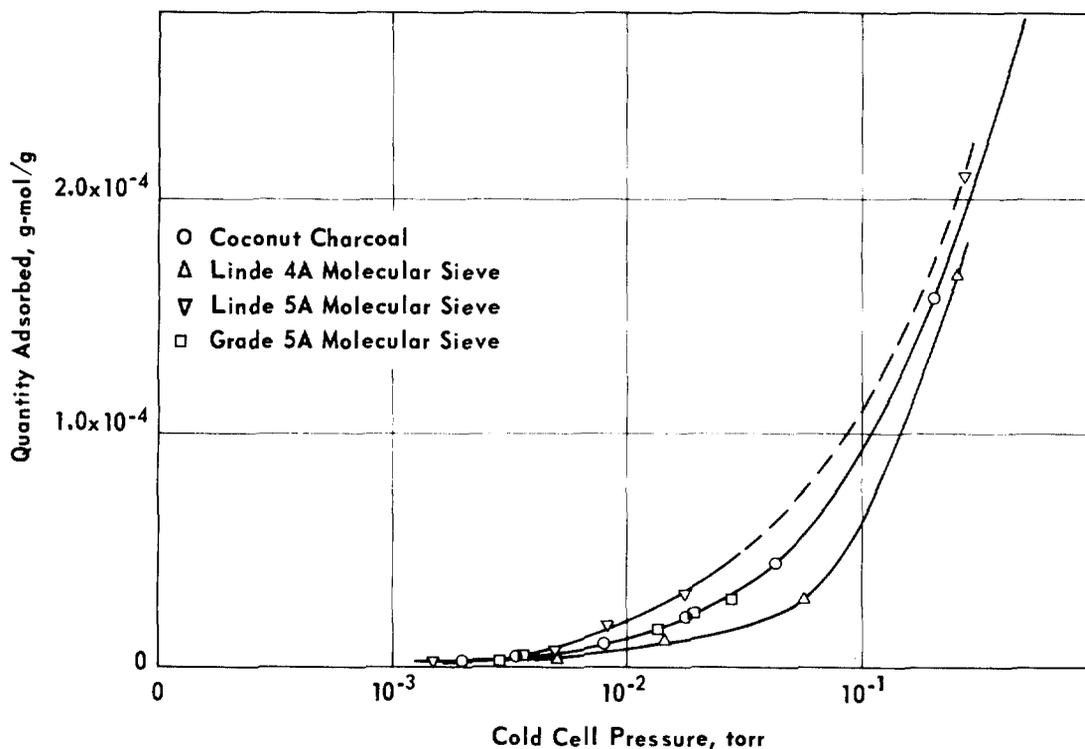


FIGURE 5 - Adsorption isotherms at 77.2°K for hydrogen on a coconut charcoal and two molecular sieves.

molecular sieve is on stream for 24 hr while the other is in regeneration mode. The columns operate near atmospheric pressure at 77°K when on stream and are regenerated by heating at 250°F with purge. The system has been designed to maintain outlet impurity levels of less than 1 ppm for oxygen, nitrogen, water, carbon dioxide, hydrocarbons, and hydrogen. In particular, total hydrogen isotopes are to not exceed 0.01 ppm at the outlet. In addition, the purifier was designed to remove and contain 1.0 g of hydrogen (tritium) on an emergency basis, said hydrogen (tritium) coming from a sudden release which would raise the concentration in the inlet helium atmosphere to 465 ppm.

Both adsorber beds during fabrication and one of the three heat exchanger units which were enclosed in each of the two cold boxes are shown in Figures 7 and 8, respectively. Gas flow is driven by an enclosed Miehle-Dexter blower which requires periodic maintenance shutdowns. Otherwise, the GADS is expected to operate continuously and automatically if desired.

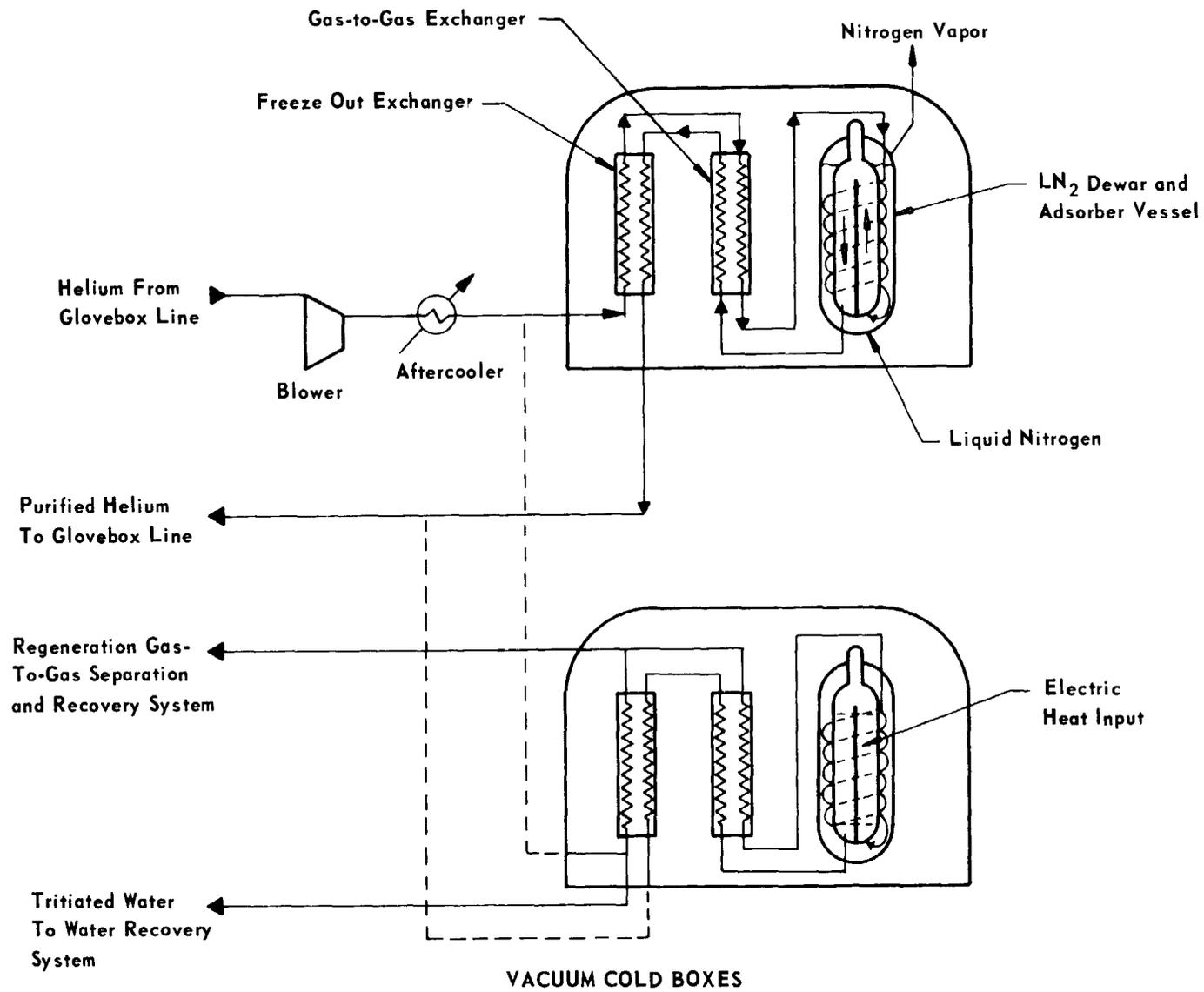


FIGURE 6 - Cryogenic helium purifier schematic (GADS).

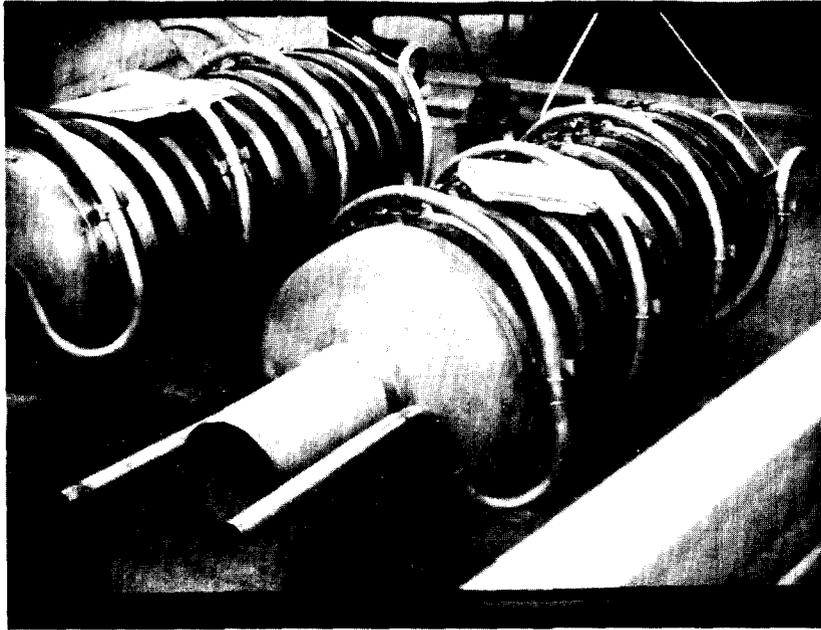


FIGURE 7 - Adsorption beds with precooling coils and regeneration heaters.

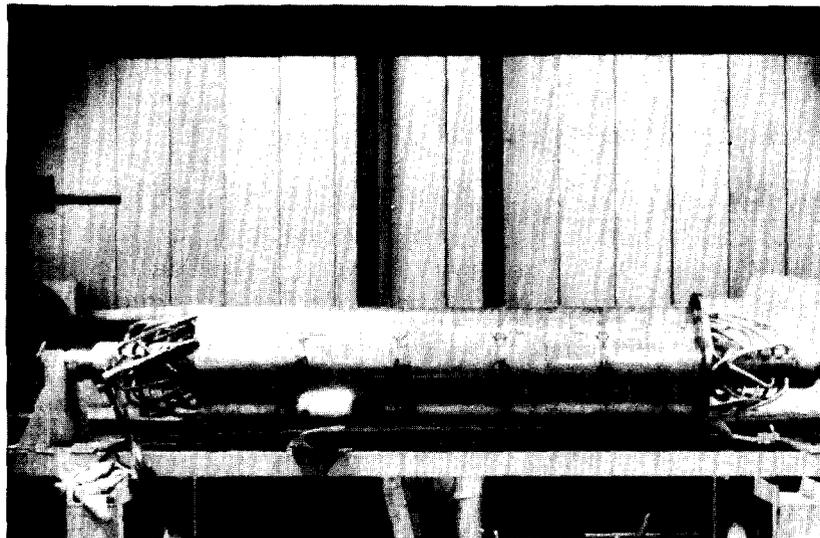


FIGURE 8 - Gas-to-gas heat exchanger for helium purifier.

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Air Detritiation System (ADS)

Concept An air glovebox is provided for ingress and egress operations for the main helium atmosphere glovebox line. This passbox serves as a buffer for decontamination and packaging operations between the contaminated glovebox line and the room atmosphere. The passbox with access through a large opening in the rear can be operated as a fume hood connected to the building air supply and exhaust system or as an air glovebox on a closed loop ADS. Although the passbox atmosphere detritiation is the primary function of the ADS, it serves as a treatment system for other contaminated air streams, such as the circulation loop for tented maintenance operations. The ADS is a small version of a 60 std ft³/min capacity effluent removal system (ERS) used on the main tritium operation facility at Mound Laboratory. ⁽²⁾

Experimental Data A new hydrogen catalytic oxidizer was developed for the ADS through a subcontracted project with Engelhard Minerals and Chemicals Corporation, Newark, N.J. To verify the applicability and to provide reactor design data, several tests were made at Mound Laboratory on an Engelhard No. Al6648 catalyst using a special catalytic reactor and dryer test loop.⁽⁴⁾ The catalyst was evaluated for air streams containing as high as 1.4 ppm tritium as HT, for reactor temperatures from 177-526°C, and for a flow velocity of 130 std ft/hr. The single pass conversion efficiencies ranged from 99.98 to 99.99997% over the temperature range 177 to 526°C. These efficiencies were maintained for oxygen-to-tritium mole ratios as low as 5:1 when the air stream was diluted with argon. Above approximately 300°C the catalyst was also capable of oxidizing tritiated hydrocarbons such as those arising from radiolytic decomposition of pump oils. The first order surface reaction rate constant for the oxidation of tritiated hydrocarbons on the catalyst was found to be:

$$k = 1.28 \times 10^7 e^{-21,000/RT} \text{ (liter/sec-liter catalyst)}$$

over the temperature range studied.

Description and Specifications The 15 std ft³/min ADS with the reactor, blowers, dual bed drier, and accessory equipment is shown schematically in Figure 9. The system was fabricated by Engelhard Minerals and Chemicals Corporation to Mound Laboratory specifications. Engelhard Catalyst No. Al6648 is used in the reactor, Linde type 13X molecular sieve is used in the dual bed dryers, and modified Rotron SL-4 blowers are used for driving the gas flow. The system was designed to provide the removal efficiencies given in Table I.

In addition to the impurity removal shown in Table I, the ADS is designed to contain 1.00 g of hydrogen (tritium) on an emergency basis, said hydrogen (tritium) coming from a sudden release which raises the hydrogen concentration in the inlet atmosphere to 2,000 ppm.

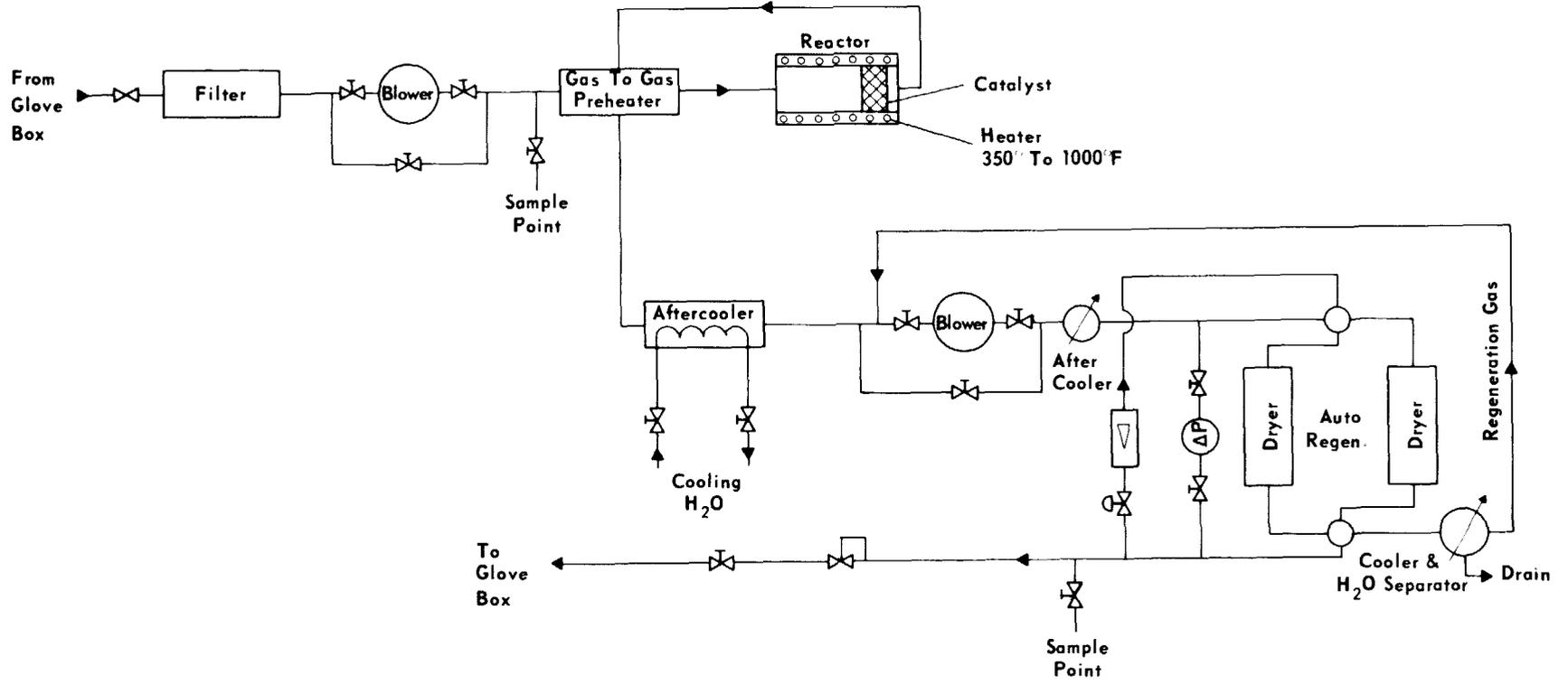


FIGURE 9 - Air detritiation system (ADS).

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Table I ADS removal design goals.

<u>Impurity</u>	<u>Inlet Conc.</u> (ppm, vol)	<u>Outlet Conc.</u> (ppm, vol)
H ₂ O	30,000	1.0
CH ₄	1.0	0.001
C ₃ H ₈	1.0	0.001
Hydrogen (tritium)	1.0	0.001

Emergency Containment System (ECS)

Concept The ECS is an automatically actuated room air detritiation system based on a catalytic oxidation reactor and presaturated oxide adsorption/exchange column concept. In the event of an accidental release of tritium to the laboratory or equipment rooms, the ECS is automatically activated and the quick acting pneumatic dampers shown in Figure 4 divert the room air supply and exhaust through the ECS until the room air concentrations are returned to safe operating levels. The released tritium is contained on the adsorption column in the oxide form. This adsorbent can be removed and disposed of, if required. During an emergency condition, the laboratory systems and the ECS can be controlled from the instrument and control room outside the contaminated area.

Development Data A development program identical to that described in the previous section was made for the catalytic oxidizer section of the ECS. In this study, activity and rate data were obtained for Engelhard Catalyst No. 50088 over a temperature range from 23 to 177°C. It was determined that a temperature of 177°C was required to meet the ECS design goal of 99.9% conversion of hydrogen (tritium) in air at inlet concentrations of 0.5 ppm. As a result of these experiments, the first order rate constant for the surface oxidation reaction of elemental hydrogen on the No. 50088 catalyst was found to be:

$$k = 2.27 \times 10^5 e^{-7,100/RT} \text{ (liter/sec-liter catalyst).}$$

Nuclear Consulting Services, Inc., of Columbus, Ohio, the fabricator of the ECS adsorber beds, made a series of adsorbent comparison experiments with silica gel, 13X molecular sieve, and a silica doped alumina (Alcoa H151) to select the adsorbent to be used. HTO adsorption on sample beds in dry and prehumidified conditions was studied. In the prehumidified (saturated with natural water vapor at approximately 24°C and 95% relative humidity) condition, the bed is operating in an exchange mode as described by Aune, et al.⁽⁵⁾ The experiments were made using 20, 30, 40, and 65 cm bed depths and the ECS design flow velocity of 100 ft/min. As a result of these investigations, the silica doped alumina was chosen for use in the ECS for its

13th AEC AIR CLEANING CONFERENCE

superior performance in the exchange mode and for its mechanical properties such as crush strength and hardness.

Description and Specifications The ECS is designed to provide the oxidation and adsorption capacities for a single pass decontamination factor of 1000:1 in a 1000 ft³/min air flow containing as high as 1 Ci/m³ tritium and 0.5 ppm natural hydrogen background. The 1000 std ft³/min capacity Engelhard oxidizer with electric preheater and water aftercooler is shown in Figure 10. The adsorber section of the ECS consists of two stainless steel vessels containing 3800 pounds of Alcoa alumina H151 adsorbent, saturated at 100% relative humidity. These vessels, shown in Figure 11, were sized to provide 10 hours of operation with an inlet activity of 1 Ci/m³ before a defined breakthrough of 100 μ Ci/m³ occurs. A Spencer turbine controls gas flow for the ECS.

Tritium Monitoring System

Concept Three different monitoring systems are used in the laboratory: 1) room monitors to ensure personnel protection and compliance with occupational exposure guidelines, 2) process monitors to provide information for process control and experimental data, and 3) high sensitivity stack monitors to provide the necessary information for limiting and reporting the quantity of tritium released to the atmosphere.

In all cases, except the high sensitivity stack monitors and collection sampling systems, ionization chambers with vibrating reed electrometers are used.

Because of a large difference between the RCG for tritium in the elemental and oxide forms, differentiating monitors are required on the stack. Thus, in addition to an ionization chamber monitor for total tritium measurements, a collection train sampling system with scintillation counting of the collected water, and a gas proportional counter with a HT/HTO separation train pretreatment are used on the stack.

The room monitoring systems use the "zone" concept which is achieved with an independent operating unit for each area, collecting samples from strategically positioned sampling probes. Solenoid valves on these sample lines allow remote activation of sample probes at any of the points shown on Figure 3.

Development Data The ionization chamber monitors used throughout the laboratory were developed by Overhoff & Associates, Cincinnati, Ohio, and are commercially available. Development data for the high sensitivity gas proportional stack monitor developed by Johnston Laboratories, Inc., Cockeysville, Maryland, on subcontract to Mound Laboratory, the freeze-out HT and HTO collection sample system, and

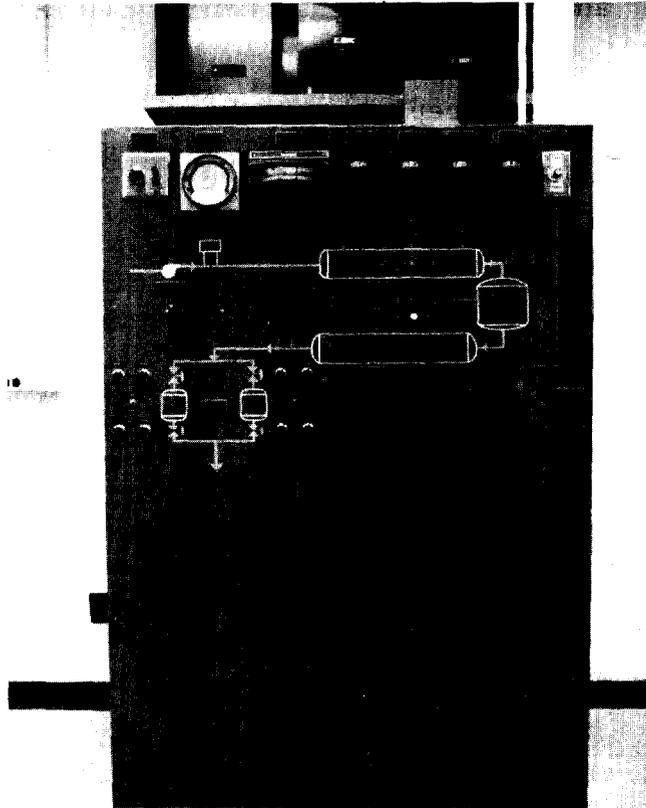
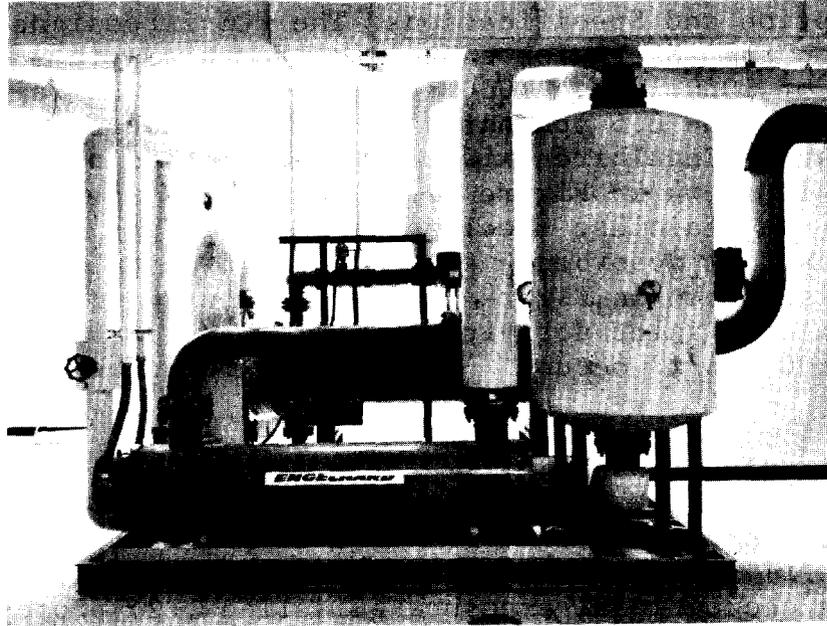


FIGURE 10 - ECS catalytic oxidizer.

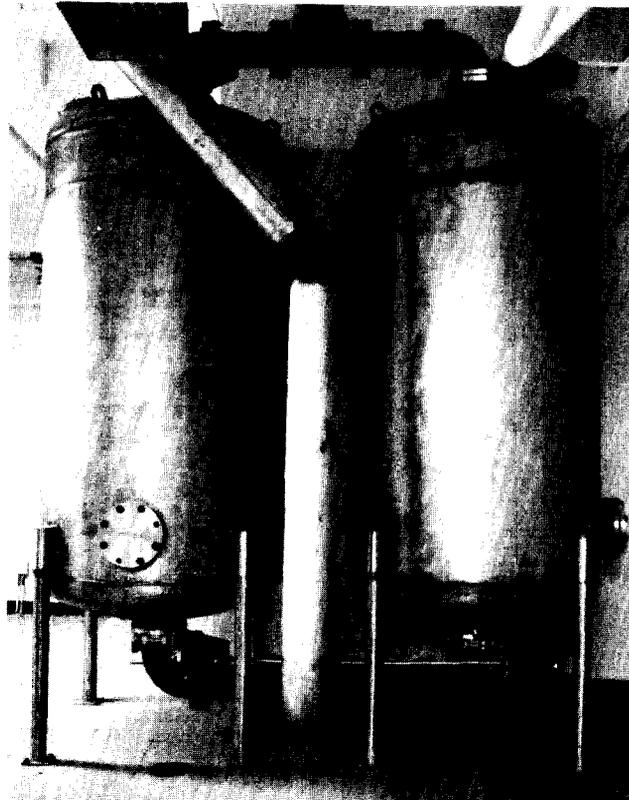


FIGURE 11 - ECS Adsorber beds.

the "zone" room monitoring system have been described in detail elsewhere. (6)

Description and Specifications The three monitors used on the room air sampling systems are Overhoff & Associates Betatec 100 20-liter ionization chambers with vibrating reed electrometers. These monitors have $1 \mu\text{Ci}/\text{m}^3$ sensitivity and a detection range from 1 to 20,000 $\mu\text{Ci}/\text{m}^3$ with digital and logarithmic recorder display. No gamma compensation features are required for the development laboratory, but a chamber compensation equal to 500 $\mu\text{Ci}/\text{m}^3$ was specified to allow for background compensation. A two-level alarm system is used which flashes a yellow light when the lower set-point is exceeded and flashes a red light along with an audible alarm when the higher point is exceeded. Bench experience with these monitors has demonstrated their ability to operate with a noise and short-term drift of less than $1 \mu\text{Ci}/\text{m}^3$.

Three process monitors are required: one for sampling the inlet and outlet of the GADS, one for sampling the inlet and outlet of the ADS, and one for actuating the ECS. The positions of all these sampling points are shown in Figure 4 with the designation "PM". All three of the monitors are modified Betatec 110/120 vibrating reed electrometer detectors with 2-liter ionization chambers. The units are similar to those used for the room monitors with the displays and

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alarms being identical, but with a detection range of $10 - 2 \times 10^7$ $\mu\text{Ci}/\text{m}^3$

The total tritium stack monitor is a Betatec 100 identical to the room monitors already described except that it has a gold-plated chamber to minimize chamber background contamination. Semicontinuous measurements at or below 10% RCG and differentiation between HT and HTO is accomplished with a high-sensitivity Johnston Laboratories, Inc., gas proportional counter system. This detector is based on an Oeschger counter with coaxial cylindrical design. (7) The counter is comprised of a sample section separated from a guard section by 72 ground-wires. The total volume of the 6-in. diameter by 25-in. long counter is 6 liters with a sensitive center volume of 2.27 liters. The particular arrangement of surrounding the sample counter with guard counters and accepting only anticoincident counts greatly reduces wall and memory effects and allows very low level counting. The HT and HTO discrimination is accomplished by a mode switching feature which either causes the samples to flow directly to the counting chamber or first through a dual-bed synthetic zeolite dryer. The signal is thus either total tritium or elemental only, and the quantity of oxide can be obtained from the difference, if the stream remains constant while HT and HTO are determined.

A parallel stack sampling system is planned which will permit the determination of HTO, HT, and tritiated organics with a series of bubblers or dessicant beds and noble metal catalyst beds operating at selective oxidation temperatures. Assay of the tritium in each fraction will be by liquid scintillation counting of HTO contained in the bubbler solutions or trapped on the dessicants.

Samples of the effluent air for all the stack monitors and sampler systems are obtained downstream of the exhaust fan to ensure a homogeneous sample.

IV. Secondary Support Systems

Secondary support systems needed to accomplish the development goal of a closed tritium cycle are: 1) a gas separation system to separate hydrogen and tritium from air components trapped on the GADS, 2) a cryogenic distillation system for the final separation of tritium from hydrogen and deuterium, and 3) a tritiated water recovery system. Of the three secondary support systems, only the cryogenic distillation has progressed to the pilot scale stage. Of the others, the gas separation system is in the design stage for the pilot scale unit, and the water recovery is in the fundamental process development stage.

Regeneration Gas Separation System

Concept In order for the tritium removed from the glovebox atmosphere by the GADS to be recovered and returned as feed material, it

must first be separated from the air constituents that were also adsorbed. To accomplish this, a temperature-zoned chromatographic separation technique is used as illustrated in Figure 12. Regeneration gas from the GADS is passed through three columns in series at -131°C , -160°C , and -196°C , respectively. The first column adsorbs air constituents while the hydrogen isotopes are eluted to the second and third columns. The second column, at -160°C , provides a transition zone containing mixed air constituents and hydrogen isotopes, while the third column, at -196°C , adsorbs only hydrogen isotopes. The adsorbent material is 5A molecular sieve, and the chromatographic columns are sized to be compatible with the GADS regeneration cycle. Helium purge gas is returned to the GADS. Table 2 illustrates the cyclic operation and regeneration of the chromatographic separation columns. For simplicity, air constituents are referred to simply as N_2 and hydrogen isotopes as H_2 .

Development Data Design data for the regeneration gas separation system were obtained on a chromatographic column of 30 cm length, 0.8 cm diameter, and containing 11.2 g of Linde 5A molecular sieve sized between 24 and 28 mesh. Nitrogen and hydrogen adsorption and regeneration parameter tests were conducted with a feed mixture containing

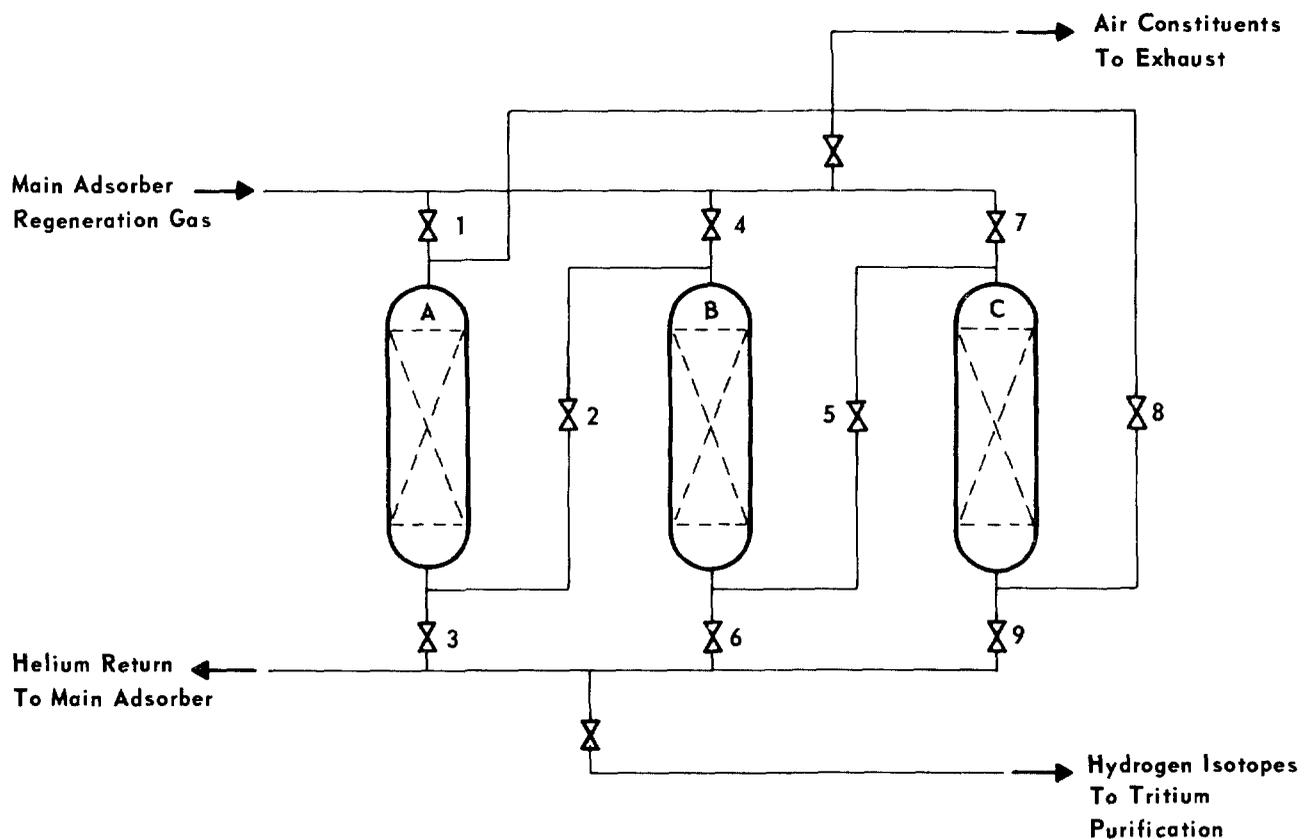


FIGURE 12 - Temperature zoned chromatographic separation.

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Table II Chromatographic separation cycles.

Adsorption Cycle No.	N ₂ Adsorption -131°C	N ₂ , H ₂ Mixed Adsorption -160°C	H ₂ Adsorption -196°C	Valves*	
				Open	Closed
1	A	B	C	1,2,5,9	3,4,6,7,8
2	B	C	A	4,5,8,3	1,2,6,7,9
3	C	A	B	7,8,2,6	1,3,4,5,9
1	A	B	C	1,2,5,9	3,4,6,7,8

Regeneration Cycle No.	N ₂ Desorption to Exhaust	N ₂ , H ₂ Mixed Adsorbate Hold @ -160°C	H ₂ Desorption to Tritium Purification
1	A	B	C
2	B	C	A
3	C	A	B
1	A	B	C

*Refer to Figure 12 for valve designations.

approximate concentrations of 5% nitrogen, 5% hydrogen, and 90% helium flowing through the bed at a rate of one liter per minute. Conclusions drawn from these experiments were that a 5A molecular sieve bed operating at -131°C is capable of separating hydrogen isotopes from air constituents, and the hydrogen holdup in the separated air constituents is less than 0.04 ppm.

System Description and Specifications The gas separation system consists of three stainless steel adsorber beds containing 6 lb of 5A molecular sieve each and connected as shown in Figure 12. Each bed is provided with a combination electric heating and liquid nitrogen cooling jacket so that temperatures from 77 to 573°K can be selectively applied to each of the beds. The design goal of the regeneration gas separation system is to recover 99.95% of the tritium and to provide a mixture of hydrogen isotopes containing no more than 0.1% air impurities that can be used as feed to a cryogenic distillation recovery system.

Cryogenic Distillation

Concept In the tritium effluent control development laboratory, a variety of tritiated effluents eventually will be reduced to a single gas stream containing the different isotopes of hydrogen. The purpose of the cryogenic distillation section of the laboratory is to

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separate the isotopes of hydrogen into two streams; one sufficiently depleted in tritium to be disposed of, and the other enriched to such an extent that the tritium can be reused in the experiments being performed in the laboratory.

Development Data and Experiments A computer program was prepared for the study of hydrogen isotope distillation, using as a basis a set of programs developed by Hanson et al.⁽⁸⁾ This program permits evaluation of the end concentrations in a distillation column as a function of the boilup, feed and product flows, and number of stages. The column pressure, the quality and composition of the feed stream, and the number of stages above and below the feed may also be varied.

A short distillation column was fabricated for the purpose of studying the behavior of protium-deuterium mixtures in a small-scale distillation system. These H-D studies provided the basis for later work with H-T mixtures. The column was 20 cm long and 0.6 cm in diameter. It was packed with Heli-Pak. Cooling was provided by a mechanical refrigerator with a capacity of 1.7 W at 21°K.

Measurements of HETP and flooding power indicated that an HETP of 1.4 cm or less is possible. Flooding was difficult to prevent, however, with H₂ concentrations in the boiler greater than 10%. The liquid flow into the boiler was evidently choked off by the rising vapor presumably as a result of the low liquid density. With more than 90% HD or D₂ in the boiler, this effect was eliminated, and the heat input to the boiler could be raised to the limit of refrigeration capacity without flooding the column.

Following tests with the 20 cm column, a longer, 56 cm long, column was fabricated. This column was packed with Eglin 3 mm packing. At a reflux ratio of 32, this column separated a mixture of H₂, HD, and D₂ into end products containing less than 0.21% D₂ (overhead) and 0.03% H₂ (bottom).

Description and Specifications The pilot system for tritium distillation consists of a packed distillation column, 56 cm long. The column has a diameter of 0.59 cm below the midpoint and 0.75 cm above the midpoint. The feed point is near the column midpoint, and provision has been made for one or more side stream removal points. A side stream, if used, is expected to be enriched in HT, while the overhead and bottom will contain mostly H₂ and T₂, respectively.

A heated catalyst will be provided for converting the side stream from mostly HT into a mixture containing 50% HT, 25% H₂, and 25% T₂. Mixing this converted material with the feed stream and returning it to the column will gradually convert the HT entirely into H₂ or T₂ so that the maximum separation may be achieved.

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The capacity of the refrigeration system is 1.7-2 W at the column condenser temperature. Operating with a reflux ratio of 30 permits the withdrawal of approximately 100 std cm³/min of overhead product. If one assumes equal quantities of protium and tritium in the feed, then a quantity in the order of 1.8×10^5 Ci of tritium could be separated in a 40-hr week; this is far in excess of what is anticipated, hence the column will be used only intermittently. Product concentrations are expected to be at least as good as those achieved with H-D mixtures, i.e., 0.1% H₂ in T₂ or vice versa. Feed and boilup rates will be externally controlled. The overhead removal rate will be determined by monitoring the column temperature, hence composition, at an intermediate level. Bottom flow will be controlled by the liquid level in the boiler as determined by a capacitive liquid level probe.

With the improved flow control systems, it is expected that improved separation will occur. An ionization counter will monitor tritium concentration in the overhead. The improved separation and increased analytical sensitivity to HT or T₂, compared to the mass spectrometer techniques used for HD on D₂, is expected to permit tritium concentrations in the overhead to be reduced below 0.01%.

Tritiated Water Recovery System

The three major types of contaminated liquid wastes that are encountered in a typical tritium research and development laboratory are: oil wastes from vacuum and transfer pumps, tritiated water condensates from detritiation and removal systems, and low-level tritiated water wastes from decontamination operations. Contaminated oil wastes are being avoided or minimized in the TECL facility through the use of an adsorption pump and helium purge system on the ingress and egress chambers and the use of specially designed two-stage rotary vane pumps where the use of a mechanical vacuum pump cannot be avoided.⁽⁹⁾ Since at this time no economically practical method is available for recovering the tritium from the low-level wastes which may range in tritium concentration from 0.2 to 100 μ Ci/ml, the small quantities produced in the TECL will be disposed of by standard burial techniques. Thus during the initial operation of the TECL, only the high-level liquid waste which can have tritium concentrations in the Ci/ml range is being considered for recovery. Research projects are in progress on water electrolysis and chemical decomposition as methods of converting the hydrogen in the high-level liquid wastes to feed for the cryogenic distillation recovery system. Extractive distillation, electrolysis-fuel cell cascades, hydrogen water catalytic exchange, and selective molecular excitation are being investigated as possible processes for liquid phase enrichment to be applied to the high-level and possibly the low-level tritiated water decontamination problem.

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V. Discussion and Conclusions

The laboratory is nearly completed at the present time, and sub-system tests are being performed before going "hot" with the entire facility. The facility is scheduled to go "hot" in January 1975, first with trace level experiments and then with design levels as full design performance is achieved. Initially alarm and evacuation levels will be set at those employed on the other tritium operating facilities at Mound Laboratory.⁽¹⁰⁾ However, as operating experience is achieved these will be adjusted to ensure that the control and release goals of the TECL are met.

The TECL is expected not only to provide actual field test data on the closed cycle concept and the various detriation and recovery processes required for its implementation, but also to serve as a test facility for new tritium control research and pilot scale development to meet the changing needs of the various tritium handling AEC contractors.

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10. Ibid., pp. 43-47.

DISCUSSION

DEMPSEY: I was curious about delay times that might be involved in your monitoring system and, also, I was wondering, what is the state of the art nowadays with respect to sensitivity of the monitors?

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KERSHNER: The monitors are a sort of work horse. The monitor that we are using in the lab is an overhauled Beta-tec 110, 120 unit or the Beta-tec 200, and, depending on the size of the ion chamber, they have a sensitivity of 1 microcurie for tritium. This is primarily a process monitor and it isn't really a problem. Problems arise in the stack, at least for off-site, uncontrolled areas, where sensitivity becomes important. That was part of the motivation for the program at Johnson Laboratory. A high sensitivity monitor is the design goal (a hundredth of a microcurie per cubic meter) because of background problems and build up, especially with tritium. We haven't been able to achieve this. Delay times and response times depend on the length of your sampling system and, of course, the volume of the chamber.

COHEN: I would like to explore this 10 percent of RCG goal that you mentioned. Was that goal imposed on you by some outside authority or is it a general interpretation of the Guides, and if so, is the figure arbitrary or is there quantitative reasoning behind it?

KERSHNER: No, it wasn't imposed upon us by an outside agency. It's what seemed to be an engineering possibility in terms of our analysis of our glove box atmosphere concentration level. We were considering our room atmospheres and what we would need to do in terms of concentrations. We are still playing with numbers because you can dilute further. We are really looking more at total releases. We are concerned with total quantity more than concentration because concentration is a rather nebulous figure considering air volumes and so forth.

COHEN: Are the population doses a consideration?

KERSHNER: It didn't come directly into consideration in our engineering goals.

CARR: The previous paper discussed the removal and concentration of tritium from waste liquid and gas streams. I would like to know what you propose doing with the concentrated tritium?

KERSHNER: We are looking at it in terms of recovering tritium in useful form. In our water condensate we have high level tritium. We always have some low activity waste streams that are about the same order of magnitude as you find in many places, 10 microcuries per milliliter or something like that, but most of our effort has been on the high activity waste to be recycled into a useful form of tritium .

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TRITIUM RECOVERY AND SEPARATION FROM CTR PLASMA EXHAUSTS AND SECONDARY CONTAINMENT ATMOSPHERES*

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Abstract

Recent experimental successes have generated increased interest in the development of thermonuclear reactors as power sources for the future. This paper examines tritium containment problems posed by an operating CTR and sets forth some processing schemes currently being evaluated at the Oak Ridge National Laboratory. An appreciation of the CTR tritium management problem can best be realized by recalling that tritium production rates for various fission reactors range from 2×10^4 to 9×10^5 Ci/yr per 1000 MW(e). Present estimates of tritium production in a CTR blanket exceed 10^9 Ci/yr for the same level of power generation, and tritium process systems may handle 10 to 20 times that amount.

Tritium's high permeability through most materials of construction at high temperatures makes secondary containment mandatory for most piping. Processing of these containment atmospheres will probably involve conversion of the tritium to a nonpermeating form (T_2O) followed by trapping on conventional beds of desiccant material. In a similar fashion, all purge streams and process fluid vent gases will be subjected to tritium recovery prior to atmospheric release.

Two tritium process systems will be required, one to recover tritium produced by breeding in the blanket and another to recover unburned tritium in the plasma exhaust. Plasma exhaust processing will be unconventional since the exhaust gas pressure will lie between 10^{-3} and 10^{-6} torr. Treatment of this gas stream will entail the removal of small quantities of protium and helium from a much larger deuterium-tritium mixture which will be recycled.

I. Introduction

Advances in the performance of several experimental devices for the confinement of thermonuclear plasmas have been described recently⁽¹⁾, spurring greater interest in the development of thermonuclear reactors as power sources for the future. Controlled thermonuclear reactors (CTRs) can rightfully be termed a "clean" source of power since they would produce and emit far less hazardous radioactivity than conventional fission reactors. Table I presents a comparison of the principal radioactive inventories of advanced fission reactors and of a reference fusion reactor. The relative biological-hazard potentials, calculated by Steiner⁽²⁾, represent the maximum possible impact upon the environment in the event of an accident. They do not take into account either circumstances which might prevent release of some fraction of

*Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

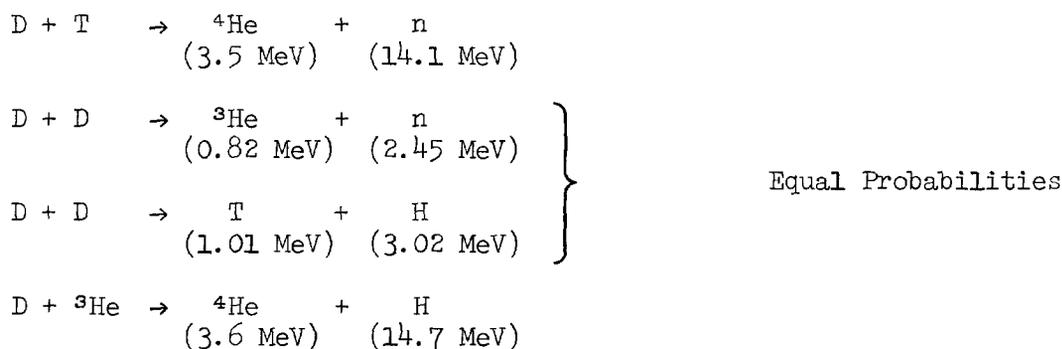
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the radioactive inventory or the relative mobilities of the various isotopes in the environment. One should note, however, that tritium is the only volatile radioactive material of concern in CTRs, while fission reactors and their associated reprocessing plants must contend with many such isotopes. An appreciation of the magnitude of CTR tritium management problems can be acquired from Table II, which gives annual tritium production rates for various fission reactor configurations⁽³⁾. For comparative purposes, the best available estimates of tritium production in a CTR blanket have also been included.

The plasma exhaust processing system for a 1000 MW(e) reactor will handle a projected 6×10^4 Ci/min (2×10^{10} Ci/yr) and will require a steady-state inventory of tritium exceeding 4×10^7 Ci. Thus, if tritium release rates to the environment are to be limited to a few curies per day, these power stations will require careful design with close attention given both to containment concepts and to atmosphere and plasma exhaust processing.

II. CTR Fuel Cycle

Most CTR designs have been based on one of the fuel cycles using deuterium as a reactant. The pertinent reactions are shown below:



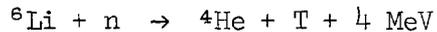
These reactions have special significance in that the required conditions of plasma temperature and density leading to ignition are the least demanding of the known thermonuclear fuel cycles. All of them will occur to some extent in either D-T or D-D fuel cycles. The D-T cycle, however, offers the most favorable cross sections and requires the most easily achieved conditions of plasma temperature, density, and residence time. A D-D fuel cycle offers the advantages of less tritium handling, large fuel supplies, and no breeding requirement, but the necessary plasma temperatures and confinement times will be far more difficult to achieve.

Table III lists operating parameters for a CTR proposal developed recently at ORNL⁽⁴⁾. Other designs being evaluated at ORNL and elsewhere⁽⁵⁻⁷⁾ have similar parameters. Observe that the tritium feed rate is large, whereas the percent reaction is quite small. The resulting plasma exhaust presents a unique processing problem wherein a small amount of ash, consisting of helium and protium, must be separated from a much larger recycle fuel stream before being discharged.

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Processing to remove helium from the plasma exhaust will perhaps utilize uranium traps or palladium membranes through which the isotopes of hydrogen diffuse readily. As indicated by Figure 1, the nondiffusing helium will be processed to remove residual tritium. Separation of the isotopes of hydrogen by cryogenic distillation, multistage diffusion through palladium membranes, or thermal diffusion has been demonstrated. Other separation techniques proposed include chromatographic or electromagnetic separations⁽⁸⁾.

Because tritium does not occur naturally in sufficient quantities to permit economic recovery, a D-T power reactor will be required to generate its own tritium fuel. The following reactions, utilizing D-T fusion-produced neutrons, will be exploited for this purpose:



The thermonuclear plasma must, therefore, be surrounded by a "blanket" containing lithium from which tritium is produced. Materials proposed for the blanket include lithium metal or molten salts, which act both as a breeding medium and as the primary heat transfer fluid. The use of stationary lithium compounds located near the plasma has also been suggested. Tritium produced in these solid materials diffuses into a heat transfer fluid from which it is continuously recovered.

There are several avenues of escape for tritium generated in the blanket; however, none is acceptable from an environmental or fuel-recovery point of view. All high-temperature ducts containing tritium, for example, will require secondary containment as a result of tritium's high permeability through most materials of construction. Heat exchangers producing steam for power-generating turbines have necessarily large surface areas and thus singularly provide the most extensive opportunity for tritium to escape. Secondary containment of these surfaces cannot be obtained, and isotopic exchange with water molecules makes recovery impractical. Development of permeation barriers can reduce the loss rate, but effective tritium recovery processes are also needed to maintain low concentrations (and pressures) in the blanket and coolant fluids. This could be the most difficult tritium handling problem in CTRs. Processing techniques for the recovery of tritium from proposed reactor coolants have been examined in previous papers^(9,10), and will not be discussed in detail here.

Figure 2 is a generalized flow diagram showing how tritium is recovered from the blanket-heat transfer system of an operational CTR. The required secondary containment of tritium-handling systems has been emphasized. Processing of these containment atmospheres will probably entail conversion of tritium to a nonpermeating form such as the oxide. In this form, the tritium could be trapped using conventional drying techniques which employ beds of desiccant material such as silica gel or molecular sieves. The decontamination factors obtained with these dryers may be further improved by isotopic dilution. In a similar fashion, all purge streams and process fluid vent gases must be subjected to tritium recovery prior to atmospheric release.

III. ORMAK-F/BX

Many of the difficulties and techniques likely to be involved in plasma exhaust recycle processing are illustrated in a recent conceptual design study. In anticipation of the needs of the U.S. CTR program in the late 1970s, such a study has been made for a tokamak experiment which would extrapolate present data to considerably larger systems and would include D-T burning. The project is called the Oak Ridge Tokamak Feasibility and Burning Experiments (ORMAK-F/BX). Roberts⁽¹¹⁾ has described the system parameters and the organization of that study. Early phases of the experiment will utilize H plasma to study the scientific feasibility of fusion in an injection-heated tokamak. Following these tests, shielding and containment modifications will be installed to permit investigation of D-T burning.

Preliminary designs of tritium handling and processing systems for the second phase of the project are nearing completion. Many design parameters have remained somewhat in a state of flux, affecting the size and physical arrangement of equipment; therefore, no detailed design drawings are presented here. However, the processing techniques and containment philosophy selected for tritium handling are described briefly.

Emphasis was placed on simplicity and reliability and on the use of existing technology whenever possible in the development of required tritium handling systems. In cases where it was necessary to use methods that had not been satisfactorily proven, high-risk techniques were avoided. Although efficient recovery is desirable from the standpoint of economics, there is little incentive for recoveries much greater than 95%; therefore, tritium containment was taken as the principal goal. Environmental considerations mitigate against routine release rates exceeding a few curies per day.

Tokamaks are not steady-state devices and as a result the plasma-filled torus, or liner, must be completely exhausted following each burning experiment. Several large cryosorption pumps, located around the periphery of the liner, will accomplish this. Figure 3 shows one of the cryosorption pumping units, enclosed in a containment module with its associated tritium recovery equipment and a containment atmosphere processing system. This modular approach to tritium handling (a complete process system for each vacuum pump) is a unique feature of this design and appears to offer several advantages. For example, the size and number of tritium-containing pipes are minimized, the consequence of a process failure is reduced, and additional flexibility in operations is available. Furthermore, the addition of subsequent processing equipment does not greatly increase the size of the vacuum pump enclosure and does not unreasonably increase the cost of the module. The pumps are the largest components of the process system, and they must be enclosed in any case.

Other tritium containment features of this design are illustrated in Figure 3. For example, tritium-containing pipes attached to the module are enclosed by larger pipes whose annular space is swept with nitrogen. Low-maintenance technology has been utilized wherever possible; and, with the exception of necessary valves and a small blower, there will be no moving parts. All containment atmospheres will be decontaminated prior to release by conversion of T_2 to T_2O followed by isotopic dilution (with steam) and drying.

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IV. Conclusions

If CTR prospects as a future power source continue to improve, the development of methods of tritium containment must be the subject of ongoing engineering research. Appropriate engineering responses to a few of the expected problems have been suggested here, and specific techniques considered for use with the ORMAK-F/BX program provide further points of discussion. Hopefully, the conjugate goals of effective tritium containment and recovery for use as a nuclear fuel can be achieved at reasonable cost.

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Table I. Radioactive inventories of advanced fission reactors and a reference CTR immediately after shutdown.

Inventoried Isotope	Activity [Ci/kW(t)]	MPC(air) ($\mu\text{Ci}/\text{cm}^3$)	Biological-hazard potential*
	<u>CTR</u>		
^3H	60	2×10^{-7}	0.30
^{95}Nb	155	3×10^{-9}	52
Total Nb Structure	714		240
<u>Advanced Fission Reactor (LMFBR)</u>			
^{131}I	31.6	1×10^{-10}	330
^{239}Pu	0.06	6×10^{-14}	1000
Total Pu Isotopes	18.2		8300

*The biological-hazard potential is defined as the activity divided by the maximum permissible airborne concentration (MPC). The units are cubic kilometers per kW(t), representing the volume of air required to dilute the given inventory to its MPC, assuming total release and uniform dispersal.

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Table II. Annual tritium production rates for various fission reactors and reference CTRs.

Reactor Configuration	Tritium Production [Ci/yr per 1000 MW(e) x 10 ⁻⁶]
HTGR	0.04
PWR	0.015
BWR	0.021
LMFBR (Reference)	0.03
MSBR (Reference)	0.92
CTR (Reference)	1.3 x 10 ³

Table III. Operating parameters for a typical ORNL CTR design.

Plasma temperature, keV	20
Ion density, ions/cm ³	10 ¹⁵
Tritium feed rate per 1000 MW(t), g/min	1.26
Percent reaction per pass	5

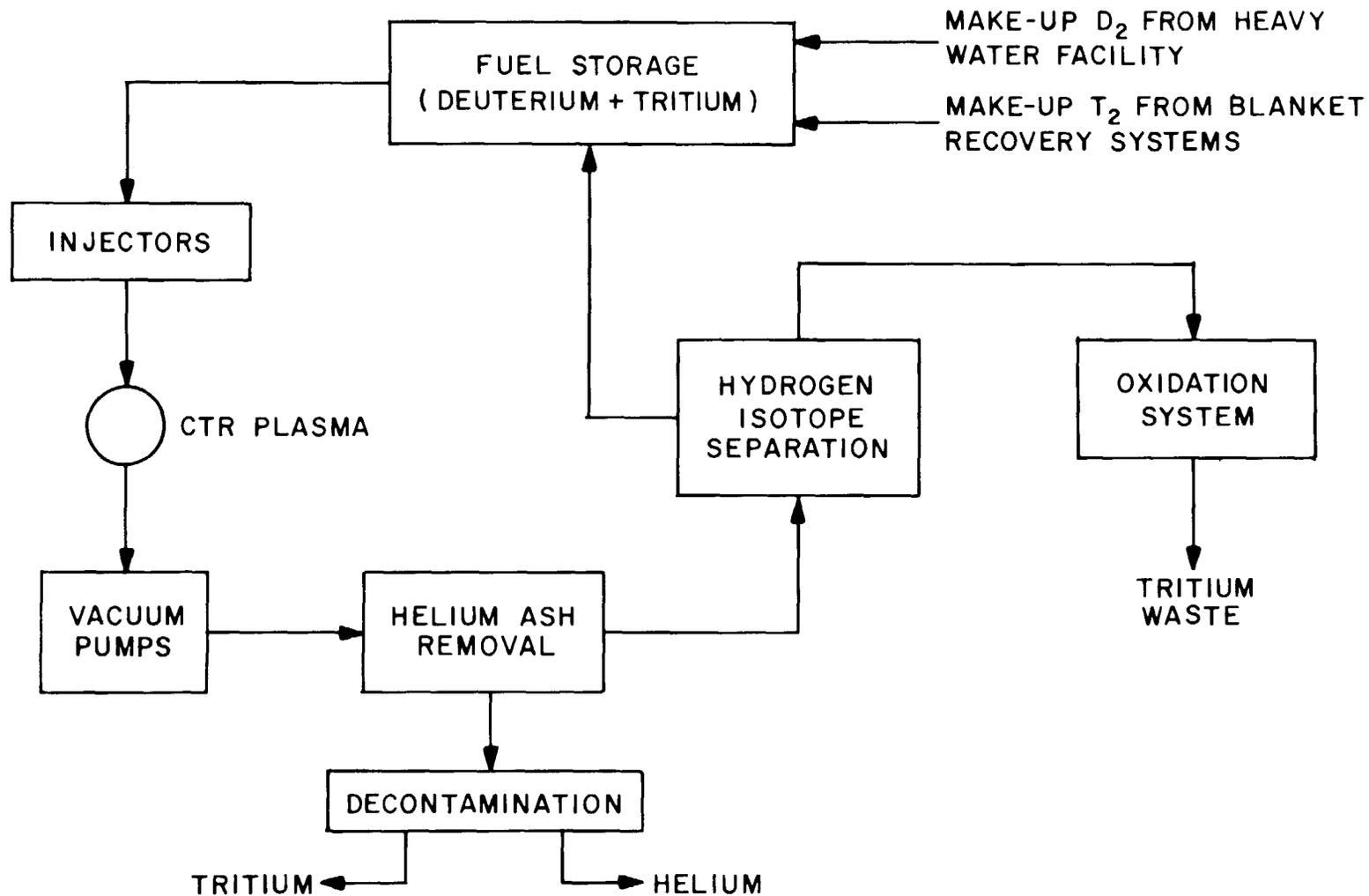


Figure 1. Generalized CTR plasma exhaust processing system.

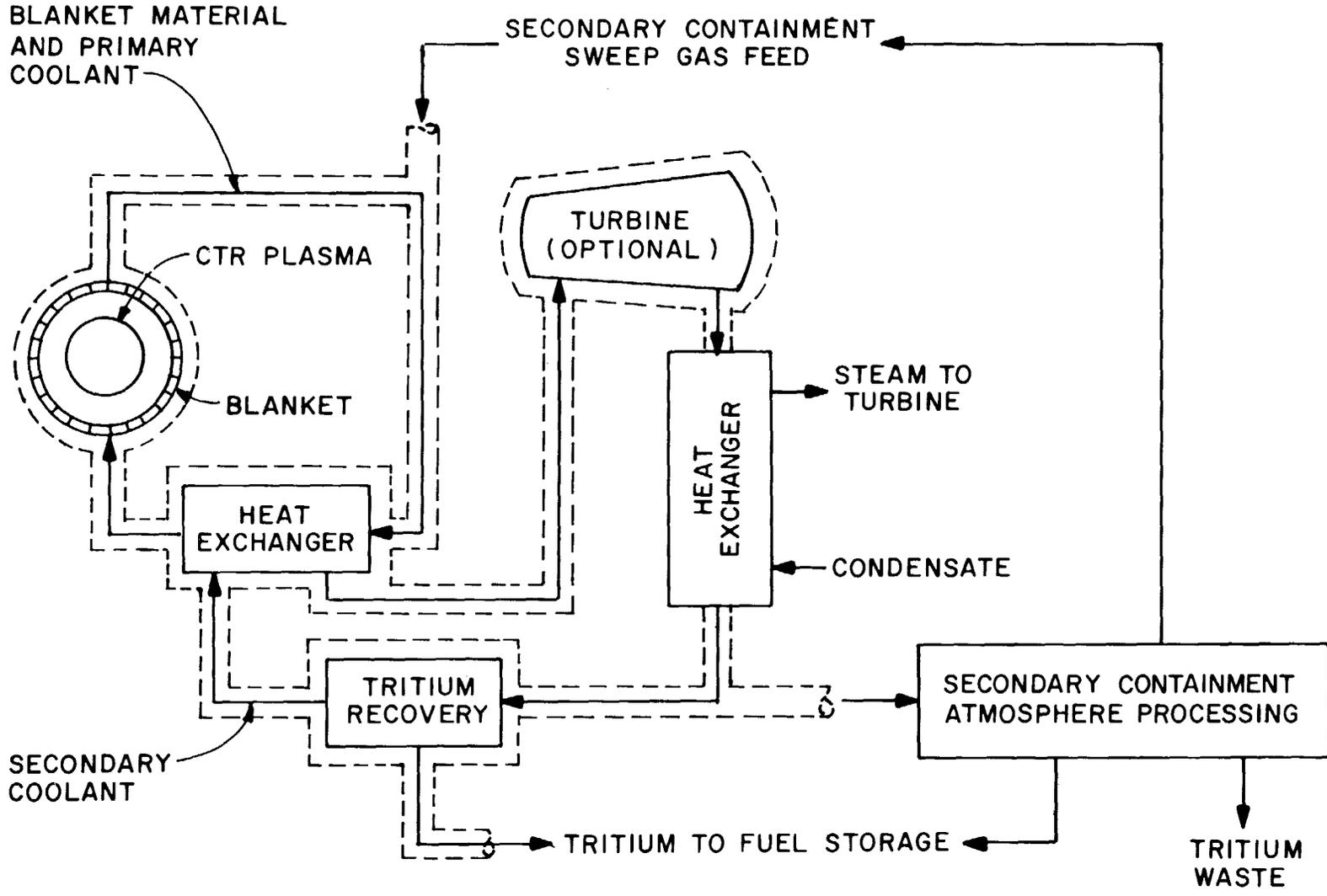


Figure 2. Blanket processing system for tritium recovery from an ORNL reference CTR design.

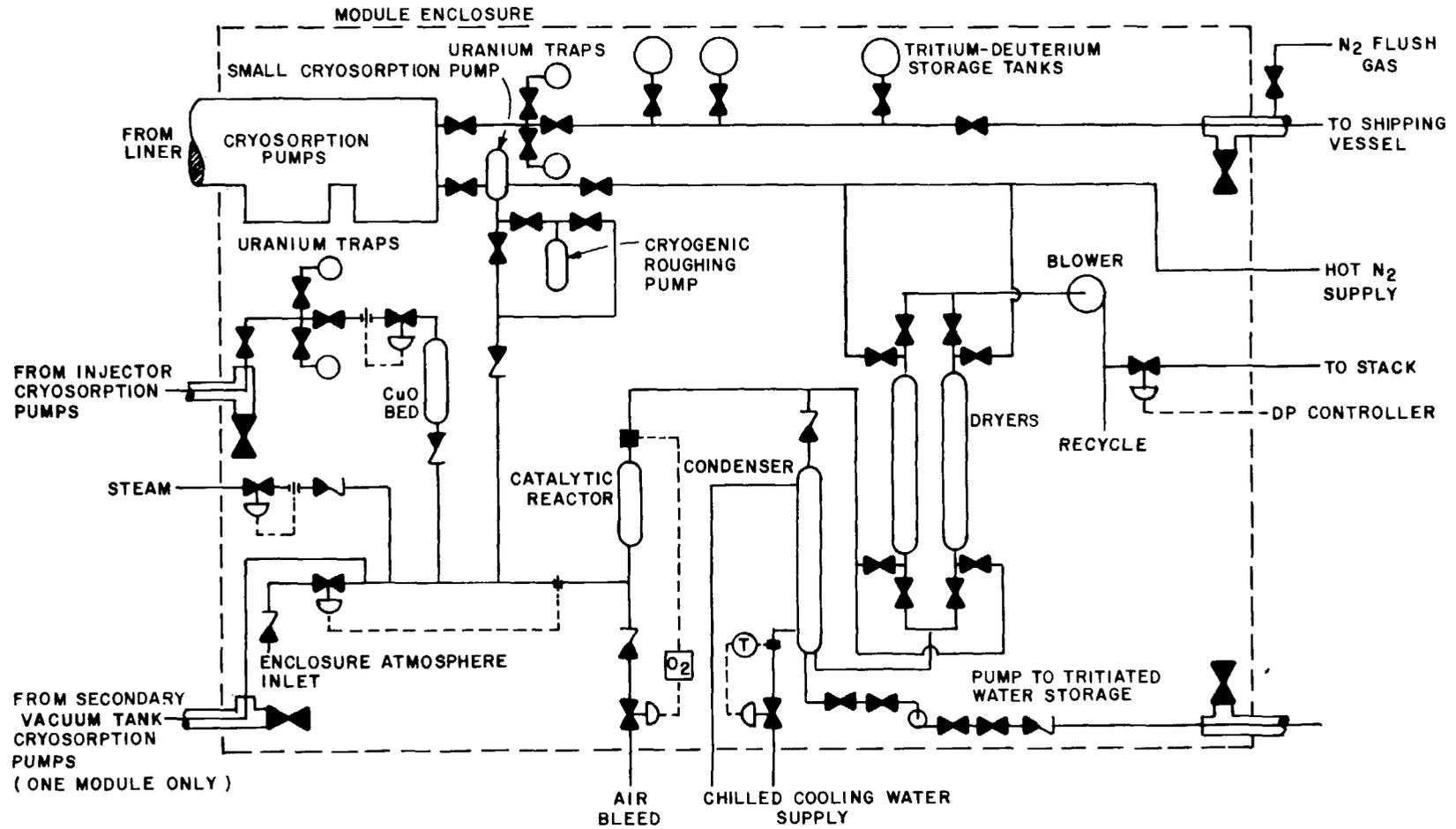


Figure 3. Tritium processing module flowsheet. (ORMAK-F/BX)

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CHAIRMAN'S SUMMATION:

A few closing comments are in order. We have had three papers which hit upon three different classes of facilities that either now exist or will come into being in the next couple of decades and I would like to make a few comments about each.

With respect to the nuclear power economy coming on line, I think most people realize that if you really want to control your effluents, you have to go to low air flow ventilation systems and try for dry incinerator systems. You must bottle up your entire liquid process stream by using water recycle systems. You should do that with some cost analysis in mind. With respect to research and development facilities, the Atomic Energy Commission has some 30 major sites through the nation. Several of them handle tritium and most of them are 20 to 30 years old. Effluent control was not well enforced 20 or 30 years ago and we had facilities, such as production reactors, that handled large amounts of tritium where the principal concern was to protect the people who were working with it. And so, we designed them with hundreds of thousands of CFM ventilation systems and high stacks. Therefore, we do have some problems in terms of air cleaning at those facilities. If a simple criterion is to clean up all you can, we do that. However, most of our sites are located on or in areas with site boundaries of five to ten miles, such as the Idaho plant and the Hanford reservation. As a result of that large site size, compared to other licensed facilities, all of the AEC-owned facilities now meet 10 CFR criteria at the site boundary. In terms of this demand, we don't look bad. I hope, as the concern for noble gas and tritium cleanup evolves, that people will make intelligent cost-benefit analyses and start looking at the real impact of large capacity and operating costs for providing cleanup systems. We have to make a realistic and profitable tradeoff and I hope many people in this room will play a responsible role in that regard. I don't want to say too much about CTR except that the current budget is quite large and AEC is spending in excess of a hundred million dollars a year during the current fiscal year. This is projected to grow to perhaps half a billion dollars per year by year 2000 in order to develop a thermonuclear energy program. The nation is beginning to get rather heavily committed to this and certainly tritium will be in the forefront. I will close by emphasizing that the Agency made a decision this last year to attempt a break-through in fusion reactors at Princeton and, hopefully, the machine will handle tritium and yield as much fusion power as it takes to contain it.