

**TRITIUM PROCESSING AT THE SAVANNAH
RIVER SITE (SRS): PRESENT AND FUTURE (U)**

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Tritium Processing at the Savannah River Site (SRS): Present and Future (U)

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ABSTRACT

Tritium handling equipment and methods at the Savannah River Site Tritium Facilities have been continually improved since tritium processing operations began in 1955. Several new technologies were introduced into the Tritium Facilities in the 1980's. One of these is the use of fluidless, mechanical pumps (Normetex and Metal Bellows) to replace mercury pumps. A second is the use of metal hydride technology to store, purify, isotopically separate, pump, and compress hydrogen isotopes. Metal hydrides, such as La-Ni-Al alloys and Pd loaded on kieselguhr, offer significant flexibility and size advantages compared with conventional tritium handling technology, such as gas tanks, thermal diffusion columns, and mechanical compressors. Metal hydrides have been used in the Tritium Facilities since 1984 with the most important application of this technology being planned for the Replacement Tritium Facility, a \$140 million facility scheduled for completion in 1990 and startup in 1991.

I. INTRODUCTION

Tritium processing operations have been performed at the Savannah River Site Tritium Facilities in support of national defense programs since 1955. During this time improvements have been continually implemented in the process and the tritium technology base has been an evolving one. Current tritium processing operations are contained in two buildings:

- a **separations** building in which tritium is extracted from Li-Al targets, purified and enriched and
- a **loading** building in which tritium is loaded into reservoirs.

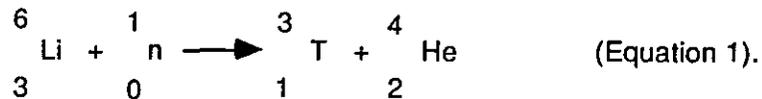
In 1987 construction was initiated on a new building, the Replacement Tritium Facility (RTF), to replace the current loading building. The RTF design builds on the last 30 years of tritium experience and incorporates many recent advances in tritium handling technology.

The emphasis in this paper will be placed on reviewing the experience gained by applying new technologies at the SRS Tritium Facilities in the 1980's. The existing process is reviewed in Section II. Background information and applications of metal hydride technology to the existing tritium process are given in Section III. The RTF project is described in Section IV. Future development efforts at SRS are presented in Section V.

II. EXISTING TRITIUM PROCESSING OPERATIONS AND CONVENTIONAL TECHNOLOGY

A. Overview

The flow of tritium at the Savannah River Site is shown in Figure 1. Lithium-aluminum alloy target and control rod assemblies are irradiated in nuclear reactors to produce tritium:



The target assemblies are then sent to the Tritium Facilities' Separations building where they are heated to melting in a crucible under vacuum conditions to release the tritium, helium and impurity gases such as protium, deuterium, water, air, and methane. This gas mixture is processed through a high temperature uranium decomposer to crack the tritiated water to oxygen and hydrogen isotopes. The hydrogen isotopes are then separated from helium mass 3 (produced by tritium decay) and 4 and impurity gases by permeation of the hydrogen isotopes through a palladium-silver alloy diffuser. The by-product waste gas is processed through catalytic strippers to remove residual tritium and other tritiated gases before the gas is stacked. Isotopic separation of the hydrogen isotopes purified by the palladium-silver diffuser is achieved by a batch cryogenic distillation column.(Section II.B.2). The purified tritium is pumped to the Loading building for mixing with deuterium, compression, and loading into reservoirs. The by-product gas from the cryogenic distillation column, if it is largely protium, is stacked.

Tritium also comes into the Tritium Facilities from reservoirs returned from the nuclear stockpile at the end of their lifetime. Reservoirs are received in the Loading building. The reservoir fill stems are mechanically sheared which releases the gas to the process. The tritium is then purified from decay helium by passing it through palladium-silver diffusers and is either reloaded into reservoirs or sent back to the Separations building for enrichment.

In addition to the preceding processing equipment, tritium storage and pumping capability is required at all points in the process. Tritium is stored in large stainless steel tanks as low pressure gas (< 3 atmospheres) to minimize potential for release to the environment. In the past, tritium pumps have generally been Sprengel falling mercury drop pumps or mercury diffusion pumps. Currently, the majority of the mercury pumps in the Tritium Facilities have been replaced with Normetex scroll, Metal Bellows, and the combination of Normetex scroll backed by Metal Bellows pumps. (Section II.B.1).

Stripping systems are used to recover tritium from by-product gases before they are sent to the stack. These stripper systems operate by pumping the gas over a heated Pt/alumina catalyst bed (Englehard Deoxo D) to oxidize the molecular hydrogen isotopic species to tritiated water. The tritiated water is then absorbed on zeolite beds (Linde 3A) before the gas is sent to the stack. All tritium absorbed on zeolite beds is recovered by physically transporting the beds to the Zeolite Bed Recovery System. The beds are regenerated by heating them under recirculating hydrogen gas which passes through heated magnesium beds to reduce the tritiated water to hydrogen isotopes. This mixture of hydrogen isotopes is then pumped to the cryogenic distillation columns for isotopic separation. In this way tritium is returned to the process and used rather than buried.

Many improvements have been made to the Tritium Facilities process during the 1980's. Some of the improvements include palladium-silver diffusers that are more compact for easier replacement, compressors that are more reliable, gaskets with improved resistance to radiation damage (EPDM and Ni vs. Buna N), pressure transducers that are higher accuracy, and an automated zeolite bed recovery system that has more than doubled the

zeolite bed recovery rate compared with the old manual recovery system. Other improvements in the areas of pumping and cryogenic distillation column operation which have had a large impact on the Tritium Facilities' operation are highlighted in the following section.

B. Recent Improvements

1. Pumps

For over a decade there has been an ongoing effort at the Tritium Facilities to develop and evaluate fluidless, all metal pumps to replace mercury diffusion pumps and Sprengel falling mercury drop pumps. Recent changes in environmental regulations have increased the emphasis on replacement of mercury pumps. Environmental concerns are also driving an effort to replace oil-lubricated pumps because waste oil must be disposed of as a "mixed waste". (A "mixed waste" is defined as one that contains both radioactive and hazardous metals contamination and requires special disposal procedures.)

Double-containment bellows-sealed pumps manufactured by Metal Bellows Corporation meet the above environmental constraints. They have been selected as a replacement for mercury pumps in applications which require suction pressures down to 20 torr and discharge pressures higher than 760 torr. The first Metal Bellows pumps were installed in 1975. Since then, the following different configurations of Metal Bellows pumps have been evaluated in tritium service: single-containment vs. double-containment pumps; 1-head vs. 2-head vs. 4-head pumps; fixed speed vs. variable speed drive pumps; and AM 350 stainless steel vs. AM 347 stainless steel vs. Inconel 626 bellows material.

The 26 Metal Bellows pumps currently in operation in the Tritium Facilities have accumulated about 51 pump-years of operating time in tritium service. Seventeen additional Metal Bellows pumps have been installed but have not yet been put into service. This large experience base has led to the selection of the MB151 as the Metal Bellows pump of choice. The MB151 pump has the following features:

- Double-containment: A pressure alarm switch monitoring the space between the 2 bellows indicates the failure of one level of containment so the pump can be

taken out of service before there is a possibility of a release of tritium to the environment.

- **Single-head:** In the event of pump failure, the whole pump is replaced. This is a much easier maintenance job than repair of a head on a multiple head pump that is contaminated with tritium. Since the pumps have about a 3.5:1 compression ratio, 3 single-head pumps are typically used in series to yield a compression ratio of approximately 40:1.
- **Fixed or variable speed:** The pump drive is available in fixed or variable speed models depending on the application.
- **AM350 stainless steel bellows material:** The AM350 heads are rated to 45 psi while the AM347 heads are only rated to 15 psi. In a process trial of Inconel 626, all 4 heads of a 4-head pump leaked after 2 weeks of service.

The many years of operating experience with Metal Bellows pumps have also led to the adoption of the following design and installation practices:

- **Outside bellows protection:** In one installation of 8 pumps, 6 bellows failed during cold tests and startup as a result of particles in the outer bellows folds from construction work above the pumps.
- **Inside bellows protection:** Particulates can also cause failure of the inner bellows. Stainless steel frit filters (35 micron nominal, 11 micron for gas service) provide adequate protection from particulates in process streams.
- **Rupture disk protection:** The pumps can generate pressures higher than the rating of some process equipment so most pumping systems are protected by 35 psi rupture disks.
- **Discharge pressure interlock:** The rupture disk is the primary means of pressure protection, but a high pressure interlock which shuts off pump power can prevent blown rupture disks and downtime for disk replacement.

The Tritium Facilities are also in the process of developing an experience base with scroll pumps. These are fluidless, all metal pumps manufactured in France by Normetex.

The gas is compressed between two interleaved vanes with spiral channels, one fixed and one moving. The vanes do not contact each other, so no lubricant is required.

Normetex scroll pumps are used in applications which require suction pressures down to 100 microns. Since the discharge pressure of a scroll pump is about 300 torr, scroll pumps are usually used in series with Metal Bellows pumps. The first Normetex scroll pump was installed in the Tritium Facilities in 1985 in series with Metal Bellows pumps. There are currently 4 Normetex scroll pumps in operation in the Tritium Facilities. They have accumulated a total of 4 pump-years of operating time in tritium service.

A 4-stage roots-blower pump manufactured by Stokes Vacuum, Inc. has been tested by the Savannah River Site's Equipment Engineering Section as a possible replacement for oil-lubricated stacking pumps. This 40 cfm pump has an ultimate suction pressure of 200 microns and is an excellent candidate for replacing the stacking pumps. The first in-process evaluation of the Stokes pump is currently scheduled for late 1989.

2. *Cryogenic Distillation Columns*

Originally, isotopic separation in the Tritium Facilities was performed using thermal diffusion columns. In 1967, a large, batch cryogenic distillation column manufactured by Arthur D. Little, Inc. became operational. In 1978, a second batch cryogenic distillation column was installed. Since that time cryogenic distillation has borne an increasingly large fraction of the isotopic separation burden. In the 1980's, several significant improvements in the operation of the cryogenic distillation columns made them the isotopic separation method of choice. It is now possible to make very high purity tritium and stackable raffinate containing ≤ 5 ppm tritium in a single batch run. Several of the improvements made in cryogenic distillation column operation are summarized below:

- **Process piping changes:** These changes include the minimization of dead volumes in drawoff lines and improved capability to flush lines.
- **Procedures:** Operating procedures have been clarified and streamlined. The pages of data sheets, calculations, and checklists that must be completed by distillation column operators during a typical week has been reduced from 122 to 22.

- Instrumentation: The major improvement in distillation column instrumentation is the computerized interpretation of the ion chamber used to determine product cutpoints. The computerized ion chamber display measures ion chamber current, temperature, and pressure and displays directly in percent tritium. Previously, operators made cutpoints based on a current output display at a specified pressure. Displaying the tritium concentration directly in percent tritium gives the operators a much better intuitive understanding of how the distillation column is operating. This has also aided the Technical Support group in adjusting drawoff rates and improving operating efficiency of the distillation columns.

III. METAL HYDRIDE TECHNOLOGY AND APPLICATIONS IN THE EXISTING TRITIUM PROCESS

A. Background

As described in Section II, the Tritium Facilities' processes have been continually improved and upgraded over the past three decades. These technological advances have allowed the Savannah River Site to reliably and efficiently meet all the nation's tritium requirements. This commitment to continual improvement of tritium handling operations led to a major program to develop metal hydride technology to handle hydrogen isotopes. The program was initiated in 1981 by the Savannah River Laboratory in cooperation with the Tritium Facilities (1). The goal was to implement this technology in the SRS Tritium Facilities. This program was initiated to take advantage of the discovery in 1969 of intermetallic compounds, such as LaNi_5 and FeTi , that would rapidly and reversibly absorb and desorb hydrogen under moderate conditions of temperature and pressure (2). Many other intermetallic hydride materials were discovered in the 1970's in support of potential applications in the "hydrogen economy" concept.

Metal hydrides, which react rapidly and reversibly with hydrogen at room temperature and atmospheric pressure to form metal hydride compounds, represent a technology ideally suited to the handling and processing of tritium. The hydriding/dehydriding reaction can be

used as a basis for the storage, pumping, compression, purification, and separation of hydrogen isotopes. One of the most important advantages of using hydride technology in tritium processes is the compact size of hydride equipment. This is due to the fact that the volumetric density of hydrogen in typical hydrides is greater even than that of liquid or solid hydrogen. The compact size of hydride beds allows installation in process hoods and gloveboxes at locations where only minimal space is available. In addition, extensive use of hydride technology in place of conventional tritium processing/storage equipment in the Replacement Tritium Facility (RTF) has led to cost savings of tens of millions of dollars by reducing the number of gloveboxes in the RTF and overall size of the RTF. Other benefits of using hydride technology for tritium handling applications are improved safety during storage of tritium in the hydride form at below atmospheric pressure and simple, reliable pumps and compressors with valves as the only moving parts.

It should be noted that metal hydrides had been used to process tritium at other Department of Energy sites prior to 1981. For example, uranium storage/purification beds were in use at Mound Laboratory (3) and Los Alamos National Laboratory (4), a vanadium compressor bed had been used at Los Alamos National Laboratory (5), and uranium beds were used at the Savannah River Laboratory for a short time in the 1950's to store and transport deuterium and tritium during experimental work. These hydride materials had drawbacks with respect to SRS Tritium Facilities' operation. High temperatures were required to desorb the tritium from the metal which leads to tritium permeation concerns and to process inefficiencies due to long heating/cooling times. In addition, the pyrophoric nature of uranium led to safety concerns with respect to its potential use in the SRS Tritium Facilities.

The details of the metal hydride systems at SRS will be described in Sections III.B and IV.B. However, in general a hydride system consists of a bed of hydride material which is cooled to absorb hydrogen isotopes at low pressure and heated to desorb hydrogen isotopes at elevated pressure. Frits contain the hydride material within the vessel. Three types of metal hydride materials have been used in the SRS Tritium Facilities in various applications since 1984: the $\text{LaNi}_{5-x}\text{Al}_x$ series of alloys, $\text{Ca}_{0.2}\text{M}_{0.8}\text{Ni}_5$, and palladium loaded on a

substrate material. The $\text{LaNi}_{5-x}\text{Al}_x$ alloys used at SRS are purchased from Ergenics, Inc. Alloys where $x=0.75$ and 0.85 are used for storage applications, whereas alloys where $x=0.3$ (HY-STOR 207) are used for storage/first-stage compressor applications. The $\text{LaNi}_{5-x}\text{Al}_x$ series of alloys are the hydride materials of choice for tritium storage at SRS owing to the following:

- The addition of aluminum to LaNi_5 results in a lowering of the equilibrium hydrogen overpressure. This is a safety advantage when working with tritium. The addition of aluminum may also make the metal lattice more resistant to tritium damage effects.
- The aluminum concentration can be varied over a wide range. This allows the alloy to be tailored to provide required absorption and discharge pressures at appropriate temperatures(1).
- This material has excellent resistance to disproportionation during cycling (1).
- This material is not pyrophoric.
- This material retains the decay helium in the lattice (Section III.B.1).

The hydride material that has been used for second stage compressor applications is $\text{Ca}_{0.2}\text{M}_{0.8}\text{Ni}_5$. This material is used chiefly because it was a readily available commercial alloy (Ergenics HY-STOR 203) in the required pressure region. It has performed satisfactorily in tritium service but other alloys, such as $\text{MNi}_{4.5}\text{Al}_{0.5}$ (HY-STOR 208) and $\text{MNi}_{4.15}\text{Fe}_{0.85}$ (HY-STOR 209), are under study as possible alternatives to $\text{Ca}_{0.2}\text{M}_{0.8}\text{Ni}_5$.

Palladium loaded on kieselguhr (a high surface area diatomaceous earth substrate) is the hydride material of choice for pumps and purifiers at SRS for the following reasons:

- Palladium loaded on a high surface area substrate yields rapid reaction rates, and the use of a substrate reduces pressure drop through the bed.
- The kieselguhr substrate is hydrophobic. Hence, there is little initial protium (in the form of H_2O) in the packing material to act via isotope exchange as a tritium sink.
- Palladium is inert to many poisons in process streams, especially air.

The first application of hydride technology to tritium processing at SRS was a small-scale research and development application that operated from 1984-1986(1). Since that time, there have been 8 additional applications of hydride technology - with several applications being full-scale production beds. All of the hydride applications have performed their design function - none have failed.

Several of the current applications of hydride technology are described in Section III.B. In addition to utilizing the advantages offered by metal hydrides for tritium processing, these applications have provided a wealth of information concerning the production scale use of metal hydrides for tritium service. Operating data collected from these applications is also providing input for the design of the metal hydride processes to be used in the RTF.

B. Metal Hydride Applications

1. Metal Hydride Tritium Storage Beds

In a recently constructed facility used for the production loading of tritium reservoirs, $\text{LaNi}_{4.15}\text{Al}_{0.85}$ is being used for the storage of tritium. These storage beds provide sufficient tritium storage capacity so that this process can function independently of other tritium supply operations for extended periods of time. In addition, these storage beds have met limited space requirements by providing tritium storage capacity in a small section of an existing glove box where tank storage of tritium would not have been feasible. In the storage beds, tritium is stored at subatmospheric pressures, thus there is little potential for loss of tritium to the environment.

In processes which require high purity helium-free tritium, storage for long periods in tanks is undesirable due to the accumulation of the helium mass 3 (^3He) decay product, which contaminates the tritium at a rate of about 0.03% per day. Tritium contaminated with ^3He must be passed through palladium-silver diffusers to be purified. The advantage of storing tritium in La-Ni-Al hydrides is that the ^3He decay product remains trapped in the metal lattice. Thus, tritium desorbed from these hydrides is free of ^3He . In a $\text{LaNi}_{4.25}\text{Al}_{0.75}$ storage bed used to store tritium for about 47 months in an experimental facility, tritium desorbed after the overpressure was evacuated contained no detectable ^3He (6).

There are some precautions which need to be considered when storing tritium as a metal tritide. When attempting to absorb tritium which contains significant quantities of ^3He ($\geq 0.5\%$), or other inerts, the inerts accumulate in the free volume of the storage bed, causing a blanketing effect which drastically reduces the rate of absorption of tritium into the hydride. The ^3He overpressure must then be periodically evacuated and reprocessed. After evacuation, absorption can resume. Typically, high purity tritium obtained from cryogenic distillation columns (Section II.B.2) is not allowed to remain in tanks for more than 2-3 days before it is absorbed onto the storage beds to minimize the in-growth of decay ^3He .

Helium-3 generated from tritium decay in the lattice of the hydride material causes damage to the metal lattice structure, which results in a decrease in the desorption pressure, and a slight decrease in the tritium storage capacity (Section III.B.5). This must be taken into consideration in the design of metal hydride storage beds. The production loading facility storage beds, which have been in operation for about eighteen months, have experienced about a 10% decrease in storage capacity. Also, the beds must be heated to a slightly higher temperature to generate the same pressure. To date, no significant impact on operation can be attributed to these changes in the material properties.

Metal hydride materials to be used for tritium storage are typically first activated with deuterium and then subjected to 20 deuterium absorption/desorption cycles. Before introducing tritium to the material, a series of tritium flush and vacuum bakeout steps are performed to ensure that residual deuterium will not contaminate the high purity tritium placed on the bed. The deuterium removal process involves an initial vacuum bakeout at moderate temperature for several hours, absorption of a small amount of tritium (ca. 5% of the bed capacity) onto the bed, a second vacuum bakeout, a second absorption of a small amount of tritium, and a final vacuum bakeout. At this point, a full charge of tritium can be loaded onto the bed without concern of contamination with deuterium.

Due to the fact that the Department of Energy requires control of tritium, periodic inventories of tritium must be obtained for the entire Tritium Facilities. The significant decay heat generated by a tritium-loaded hydride bed (0.324 watt/gram of tritium) provides a

convenient technique for correlating the quantity of tritium stored on a hydride bed. Accordingly, the difference between the bed centerline temperature and the bed external surface temperature is correlated with the loading of the bed. The error associated with this type of correlation is in the range of 5-10% of the bed capacity.

2. Metal Hydride Compressors

In the production loading facility discussed above, metal hydrides are used for compression of tritium (Figure 2). In a first stage compressor, $\text{LaNi}_{4.7}\text{Al}_{0.3}$ is used for generating pressures up to 300 psia. A second stage compressor uses $\text{Ca}_{0.2}\text{M}_{0.8}\text{Ni}_5$ to generate pressures up to 2000 psia. Since startup of the facility, no effects attributable to tritium decay have caused any noticeable changes in the operation of the compressor system. Apparently, the short intermittent tritium exposure does not cause any noticeable effect on the behavior of the compressor hydride materials. The purity of tritium desorbed from the first and second stage compressors since startup of the facility is shown in Figure 3. Tritium desorbed from the first stage compressor has been relatively constant since startup. However, tritium desorbed from the second stage compressor has experienced some decrease in purity due to ^3He contamination after about 200 days. Thus, it appears that ^3He is retained in $\text{Ca}_{0.2}\text{M}_{0.8}\text{Ni}_5$ for a short time period (approximately 200 days), and then begins to release. Similar behavior for release of ^3He from erbium tritides has been observed by other investigators (7).

3. Metal Hydride Pump/Purifier

A large scale Pd/kieselguhr pump/purifier was recently installed in the Tritium Facilities. It has been used to purify hydrogen isotopes from inert impurities and may be used at some point in the future to pump purified, above atmospheric hydrogen isotopes to the cryogenic distillation columns. The pump/purifier consists of three separate vessels which are heated by electric cartridge heaters inserted in heater wells within the Pd/kieselguhr packing and are cooled by freon circulating through coils around the outside diameter of the Pd/kieselguhr-containing vessel. Each vessel is contained in a vacuum jacket, which provides insulation as well as secondary containment for tritium (Figure 4).

Unlike the case with the bulk metal hydrides, Pd/kieselguhr can absorb hydrogen isotopes from mixtures with high concentrations of non-absorbing gases because of the 80% gas void volume in a bed that is completely filled with Pd/kieselguhr. In a typical batch run of the pump/purifier, gas from storage tanks is absorbed into the Pd/kieselguhr bed at -40°C . The overpressure, which is concentrated in inerts, is pumped to an inerts tank. The bed is then heated and the purified hydrogen isotopes are desorbed to another tank. In a typical operation such as this, 98% of the hydrogen isotopes are recovered. About 2% of the hydrogen isotopes are lost during evacuation of the inerts from the pump (Figure 4). These hydrogen isotopes can be later recovered by processing the gas in the inerts tank through a palladium-silver diffuser. The smaller quantity of gas in the inerts tank is more easily processed by the diffusers. The results verify that the pump/purifier can be used to ease the load on the diffusers. However, the pump/purifier has had its greatest value to date simply in providing a full-scale demonstration of the usefulness of Pd/kieselguhr technology in a tritium environment.

4. Use of Metal Hydrides in an Experimental System

In support of the development of metal hydride technology for use in the SRS Tritium Facilities, the Savannah River Laboratory operates an experimental tritium gas handling manifold. The manifold uses a small $\text{LaNi}_{4.25}\text{Al}_{0.75}$ metal hydride storage bed to store about 10 grams of tritium for experimental work. As tritium is needed in the manifold, this storage bed is heated to deliver the tritium at the required pressures. When tritium is no longer needed, it is reabsorbed by cooling the storage bed. This minimizes the amount of tritium which must be pumped through mechanical vacuum pumps, thus prolonging the life of pumps. Tritium is received on the manifold storage bed from 50 liter gas containers which are charged from the cryogenic distillation column. The manifold storage bed has successfully provided high purity helium-free tritium for about 47 months of operation. In addition to these advantages, the storage bed provides storage in a minimal volume of costly experimental glove box space.

5. Metal Hydride Tritium Exposure Program

At the Savannah River Laboratory, a program is underway to investigate the fundamental aspects of the interaction of tritium with various metal hydride forming materials.

The tritium experimental manifold discussed in Section III.B.4 was installed in 1985 and twenty hydride samples ($\text{LaNi}_{5-x}\text{Al}_x$; $x=0.3, 0.75, 0.85$) in a controlled matrix study were charged with tritium and placed in storage in March/April 1987. The interaction of tritium with these samples is being investigated by collection of equilibrium desorption isotherms at time intervals generally on the order of several months. Typical desorption isotherms for a $\text{LaNi}_{4.7}\text{Al}_{0.3}$ sample are shown in Figure 5. The isotherm shown for 94 days tritium exposure represents the equilibrium behavior for a material with negligible tritium exposure. After 706 days of storage while loaded with tritium, the desorption pressures in the plateau region have decreased and the plateau region has greater slope than the initial isotherm. At low T/M values, the isotherm appears to have shifted towards the right, indicating a "heel", or a small quantity of tightly bound tritium. Subjecting the material to 20 tritium absorption/ desorption cycles increases the desorption pressures in the plateau region and decreases the quantity of tightly bound tritium. Thus, by cycling the material, the thermodynamic changes caused by tritium exposure have been partially reversed. The results of these investigations are discussed in greater detail elsewhere (8).

These effects are currently still under investigation at the Savannah River Laboratory. Other characterization techniques are being used to probe the changes induced to the metal lattice by the helium decay product. These techniques include X-ray diffraction, scanning and transmission electron microscopy, ^3He NMR, high temperature thermal desorption, and others.

IV. METAL HYDRIDE TECHNOLOGY AND APPLICATIONS IN THE REPLACEMENT TRITIUM FACILITY

A. Overview

As discussed earlier, the tritium processing facilities at SRS were built in the mid-1950's. Despite the many improvements made over the years to ensure safety of the operation, reduce tritium release to the environment, and maximize productivity, it became apparent in the mid-1980's that new facilities were required in order to meet increasingly

stringent safety and environmental requirements while maintaining high productivity. The Replacement Tritium Facility (RTF), a \$140 million project, is the first of these new facilities and will replace the existing Loading building (Figure 1).

The RTF will incorporate technological advances made at SRS over the past three decades. In particular, metal hydride technology will be used extensively to process hydrogen isotopes. The pumping of non-hydrogen gases will be accomplished by Normetex and Metal Bellows pumps. A distributed control system will control the process. All tritium handling equipment and processes will be installed in glove boxes which will have a recirculating nitrogen atmosphere. A tritium stripping system will maintain the tritium concentration in the glove boxes to below 10^{-2} micro Ci/cc. All zeolite beds will be regenerated in-place and not require transportation to a separate zeolite bed recovery system. The whole facility will be housed in a seismic and tornado resistant, underground structure. Construction of the RTF started in 1987 with mechanical completion currently scheduled for April 1990 and startup July 1991.

B. Description of the RTF Hydride Processes

Metal hydride technology is used in the hydrogen isotope purification system, the hydrogen isotope separation system, and the storage/pump units, vacuum pumps, and compressors (Figure 6). The hydrogen isotope purification system is designed to purify the hydrogen isotopes recovered from recycled reservoirs. It consists of a flow-through absorption column with a heating/cooling jacket, and a set of Normetex-Metal Bellows pumps. The column is filled with Pd/kieselguhr. In a typical operating cycle, the column is first cooled to a predetermined temperature. The gas mixture to be purified is fed into the inlet end of the column. The hydrogen isotopes are absorbed rapidly by the Pd while the inert gases are drawn through the bed by mechanical pumps located downstream of the bed. When the column is saturated with hydrogen isotopes, the feed is stopped and all the inerts are removed by continuing evacuation for a few more minutes. The column is then heated to desorb the isotopes and to produce a pressure sufficient to deliver the gas to the hydride storage beds. Pilot-scale laboratory tests have demonstrated hydrogen isotope purities better than 99.99%

can be achieved by this process. The inert gas by-product contains less than 1% hydrogen isotopes which can easily be reduced to less than 0.05% by the use of palladium-silver diffusers similar to ones in use in the existing Tritium Facilities.

Storage and pumping of hydrogen isotopes are accomplished by using $\text{LaNi}_{4.25}\text{Al}_{0.75}$ hydride beds (9). The beds are of a special "inverted T" design (Figure 7). Each bed comprises a horizontal container and a vertical inlet/outlet port. The horizontal container is no more than 3 inches in diameter. Hydride powder occupies about 70% of the container volume. The vertical inlet/outlet port is fitted with a porous sintered stainless steel filter (5 micron nominal, 0.1 micron for gas service) through which the gas can pass but not the hydride particles. A heat transfer medium passing through the jacket provides the heating and cooling as required.

This design has two important features which overcome two of the most commonly encountered problems in hydride storage applications. First, the hydride material in the container is shallow with a void space on top so that the hydride powder can expand and contract without stressing the container wall. Second, the porous filter is in a vertical position and clear of the hydride bed and serves as both the gas inlet and outlet so that clogging of the filter is avoided.

Hydride storage beds, when cooled, can take in hydrogen gas at a pressure as low as several psia. When heated, they can deliver the gas at pressures up to several atmospheres. Their storage capacity is about 300 STP liter per liter of container volume, with an over pressure of less than one atmosphere at room temperature.

The construction of the hydride vacuum pump and the compressors are similar to the storage beds, except that heavier wall containers are required for the compressor beds. Pd/kieselguhr packing material is used in the vacuum beds. When cooled, these vacuum beds absorb hydrogen at a rapid rate and provide a vacuum of less than 20 torr for the operation of the palladium-silver diffusers (Figure 8). $\text{LaNi}_{4.7}\text{Al}_{0.3}$ alloys and $\text{Ca}_{0.2}\text{M}_{0.8}\text{Ni}$ are used in the hydride compressor beds to achieve pressures in the hundreds and the thousands of psia range, respectively.

The separation of tritium from deuterium and protium is accomplished by the use of a Thermal Cycling Absorption Process (TCAP) (10). TCAP is a semi-continuous chromatographic separation process, using Pd/kieselguhr as the packing material. Palladium is known to have a very large hydrogen isotope effect. It preferentially absorbs the lighter protium compared to deuterium and tritium. This effect increases as the temperature decreases. The use of Pd to separate hydrogen isotopes is not new to SRS. A batch fractional absorption process, which used columns of Pd black mixed with asbestos and stainless steel coils, was used in the Tritium Facilities from 1964 until 1968. Two advantages of TCAP over the old fractional absorption process are:

- It is a semi-continuous rather than a batch process. This results in much higher
- The column packing, Pd/kieselguhr, has much better gas flow characteristics than did the Pd black/asbestos/SS coil packing.

The key attractive feature of TCAP with respect to other separation technologies is its compact size. A unit with separative capacity comparable to a 2-story cryogenic distillation column or to ten 2-story thermal diffusion columns is roughly the size of a large suitcase. Without TCAP, it would have been cost prohibitive to have designed isotope separation capability into RTF, and it would have made it necessary to use the existing Separations building to perform all isotope separations work.

TCAP consists of a Pd/kieselguhr packed column which can be heated and cooled and an empty column with plug flow characteristics. The top end of the Pd/kieselguhr column is connected in series with the empty column (termed the plug flow reverser). Raffinate, consisting of the light isotopes, is withdrawn from the top end of the Pd/kieselguhr column and product from the bottom end (Figure 9).

In operation, the Pd/kieselguhr column undergoes a cooling half-cycle and a heating half-cycle. During the cooling half-cycle, due to the absorption of hydrogen by the palladium, the mixture of isotopes moves from the plug flow reverser column through the raffinate end and toward the product end. Due to the preferential absorption of the lighter isotope, by Pd, the heavier tritium is effectively traveling much faster than the lighter deuterium or

protium. As a result, a concentration profile develops along the length of the Pd/kieselguhr column, with tritium concentrated at the product end. During the heating half-cycle, the gas is desorbed from the Pd and is moved from the product end through the raffinate end and to the plug flow reverser column. Again, due to the isotopic effect, the heavier tritium is traveling faster than the lighter deuterium or protium which partially negates the separation gained in the cooling half-cycle. However, the heating half-cycle does not completely negate the separation gained in the cooling half-cycle since the preferential absorption of lighter isotopes by Pd is significantly reduced at high temperatures. As a result the concentration profile is reduced somewhat but is still present at the end of the heating half-cycle. Therefore, a net gain in separation is realized after each full cycle. In this way, high purity of product and raffinate are produced after repeated cycling.

To maintain semi-continuous operation, small portions of the column inventory are withdrawn from the product end and the raffinate end, respectively, at the beginning of each heating half-cycle. At the beginning of each cooling half-cycle, an equal amount of feed is sent into the mid point of the Pd/K column to keep the column inventory constant. The production rate depends on the desired purities of the product and raffinate.

C. Development Effort

Development of hydride technology at the Savannah River Laboratory began in 1981. Since then the processes discussed above have gone through bench scale, pilot scale and, in some cases, full scale testing. Most of the development work has been done "cold" with protium and deuterium. The metal hydride applications in the existing Tritium Facilities discussed in Section III.B have provided confidence that "cold" laboratory work will translate to successful operation in a tritium production environment.

Presently, development efforts are concentrated in the following three areas:

- **Advanced Hydride Laboratory:** The Advanced Hydride Laboratory is a \$3.2 million "cold" pilot plant constructed in support of the RTF project and started up in November 1987 (11). The main purpose of the Advanced Hydride Laboratory is to demonstrate the RTF's metal hydride technology by integrating the various unit

operations into an overall process. Similar to RTF, there is a central nitrogen heating/cooling system for the hydride units and a computer control and data acquisition system to evaluate process control and operating strategies.

- Tritium accountability on hydride beds: When tritium is stored in tanks, its quantity is measured by pressure, volume, temperature and composition (P-V-T-C). However, the P-V-T-C method is not practical for tritium stored on hydride beds. It would require complete desorption of the tritium to a tank and the reabsorption of the gas onto the bed - a very time consuming procedure. In addition, the tritium heel which builds into $\text{LaNi}_{5-x}\text{Al}_x$ storage beds with time would not be accounted for by desorption of the gas to a tank. For these reasons, a new "in-bed" accountability method is being developed in which the nitrogen stream flowing through the hydride bed jacket is set at a constant rate and a constant inlet temperature. After roughly 8-10 hours, the outlet temperature of the nitrogen reaches a steady state temperature. The temperature rise of the outlet versus the inlet nitrogen gas is proportional to the amount of tritium on the bed. Initial tests on this "flowing nitrogen calorimetric" method with an internal heater to simulate tritium decay heat have indicated that this method can be expected to measure the tritium in the hydride beds to an accuracy comparable to that achieved in the existing facilities.
- Tritium exposure program: This program has been discussed in Section III.B.5. Basically, data to date have shown that RTF hydrides will perform satisfactorily for a minimum of 2 years. A 2 year bed lifetime is considered acceptable, though longer service time is desired. It is expected that, as the tritium exposure effects on hydrides are better understood, bed lifetimes considerably in excess of 2 years will be achieved.

V. FUTURE DIRECTIONS

As discussed in Sections III and IV, metal hydride technology is already having a significant impact on tritium handling operations at SRS. However, several areas of growth for hydride applications remain:

- Diffuser replacement: Work is currently underway to develop flow-through hydride beds that will reduce the hydrogen isotope concentration to levels comparable to that of palladium-silver diffusers.
- Stackable hydrogen isotope raffinate: Work is in progress to replace the TCAP plug flow reverser column with a column of hydride material having an isotope effect inverse to that of Pd. This would allow stackable deuterium (≤ 5 ppm tritium) to be made in RTF rather than having to send deuterium gas containing low levels of tritium to the Separations building for processing by the cryogenic distillation columns.
- Compressors for hydrogen isotope mixtures: The RTF compressors consist of metal hydride beds for compressing pure isotopes to high pressures and conventional, mechanical compressors for compressing isotopic mixtures to high pressures. It is possible that a metal hydride compressor could be developed that would compress isotopic mixtures without fractionating them, and this is an area that may warrant further investigation in the future.

There are many benefits to metal hydride technology. Metal hydride technology, coupled with Normetex and Metal Bellows pumps for handling inert gases, is a compact technology making it cost effective for installation into expensive glovebox space. This combination of technologies is also clean with no pumping fluids to contaminate process gas. Hydride technology itself is extremely flexible with a single bed serving several processing functions, such as storage/pumping, pumping/purification, or storage/compression. The retention of ^3He in the lattice by $\text{LaNi}_{5-x}\text{Al}_x$ alloys give metal hydride storage beds added value. In summary, metal hydride technology appears to be the tritium handling technology of the future at SRS.

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Figure Captions

- Figure 1: Schematic of the flow of tritium into and out of the Savannah River Site Tritium Facilities.
- Figure 2: Storage and compressor bed arrangement in the production loading facility.
- Figure 3: Purities of tritium desorbed from the first and second stage compressor beds.
- Figure 4: Schematics of the tanks used for a metal hydride pump/purifier test run and of a hydride pump/purifier vessel. Typical results obtained during the operation of the hydride pump/purifier are also given, where $H=H_2, D_2, T_2$ and $I = \text{Inerts}$.
- Figure 5: Typical tritium desorption isotherms for a $\text{LaNi}_{4.7}\text{Al}_{0.3}$ sample as a function of time of exposure to tritium.
- Figure 6: Schematic of the process gas flow in the Replacement Tritium Facility.
- Figure 7: Schematic of a metal hydride storage/pump/compressor unit.
- Figure 8: Schematic of a metal hydride vacuum pump unit. Pilot-scale performance data are also shown. The beds operate in tandem - one is cooled and is absorbing (pumping) hydrogen isotopes while the other one is heated and is desorbing (discharging) hydrogen isotopes.
- Figure 9: Schematic of the Thermal Cycling Absorption Process (TCAP) columns.

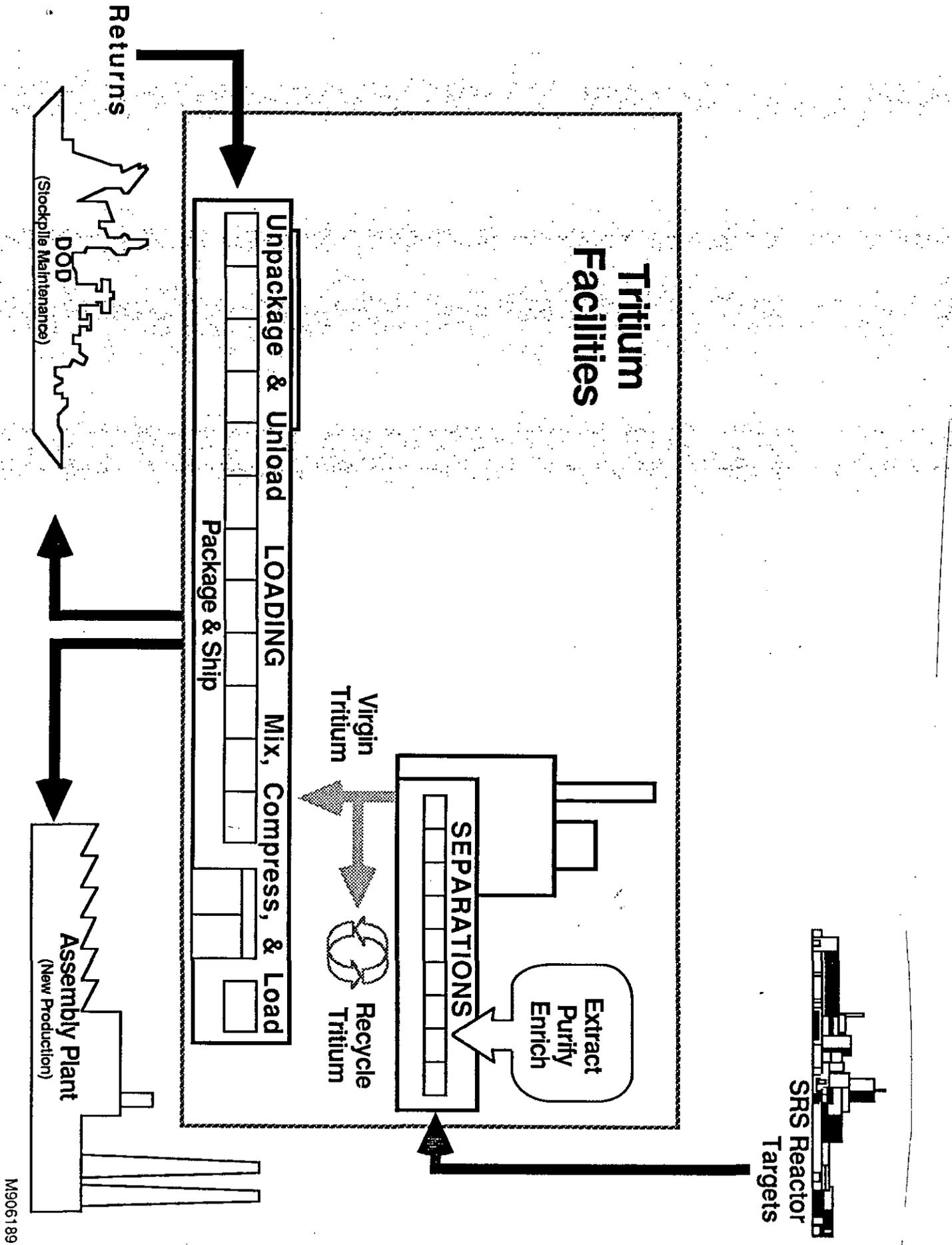


Figure 1

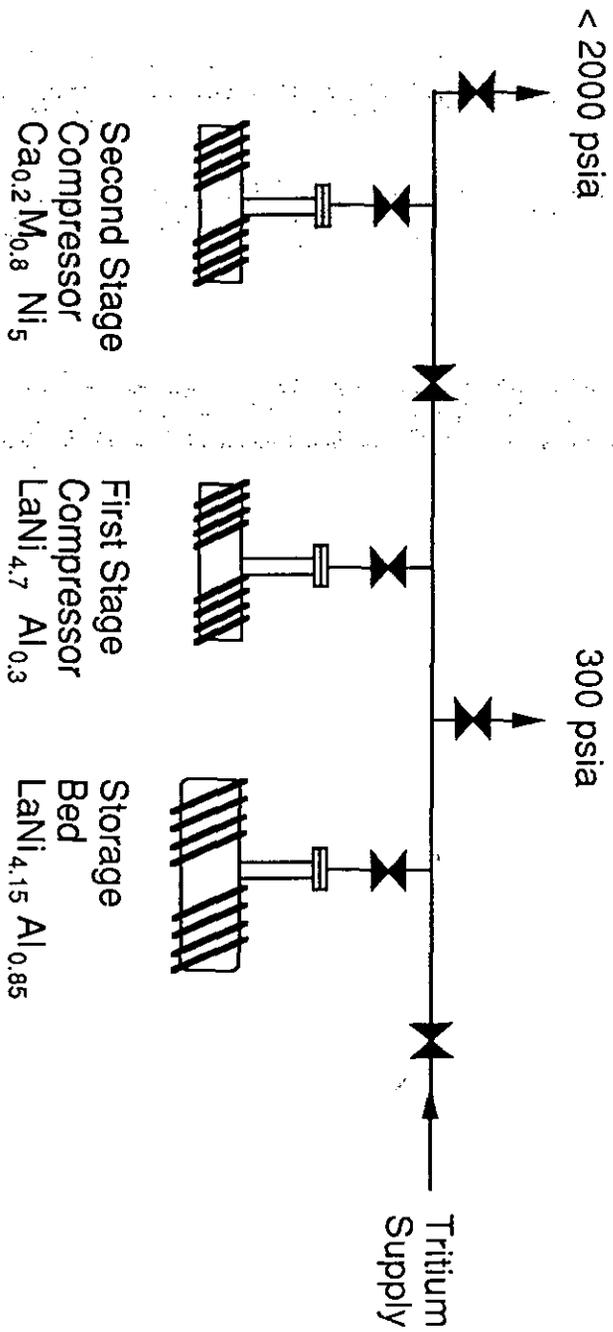


Figure 2

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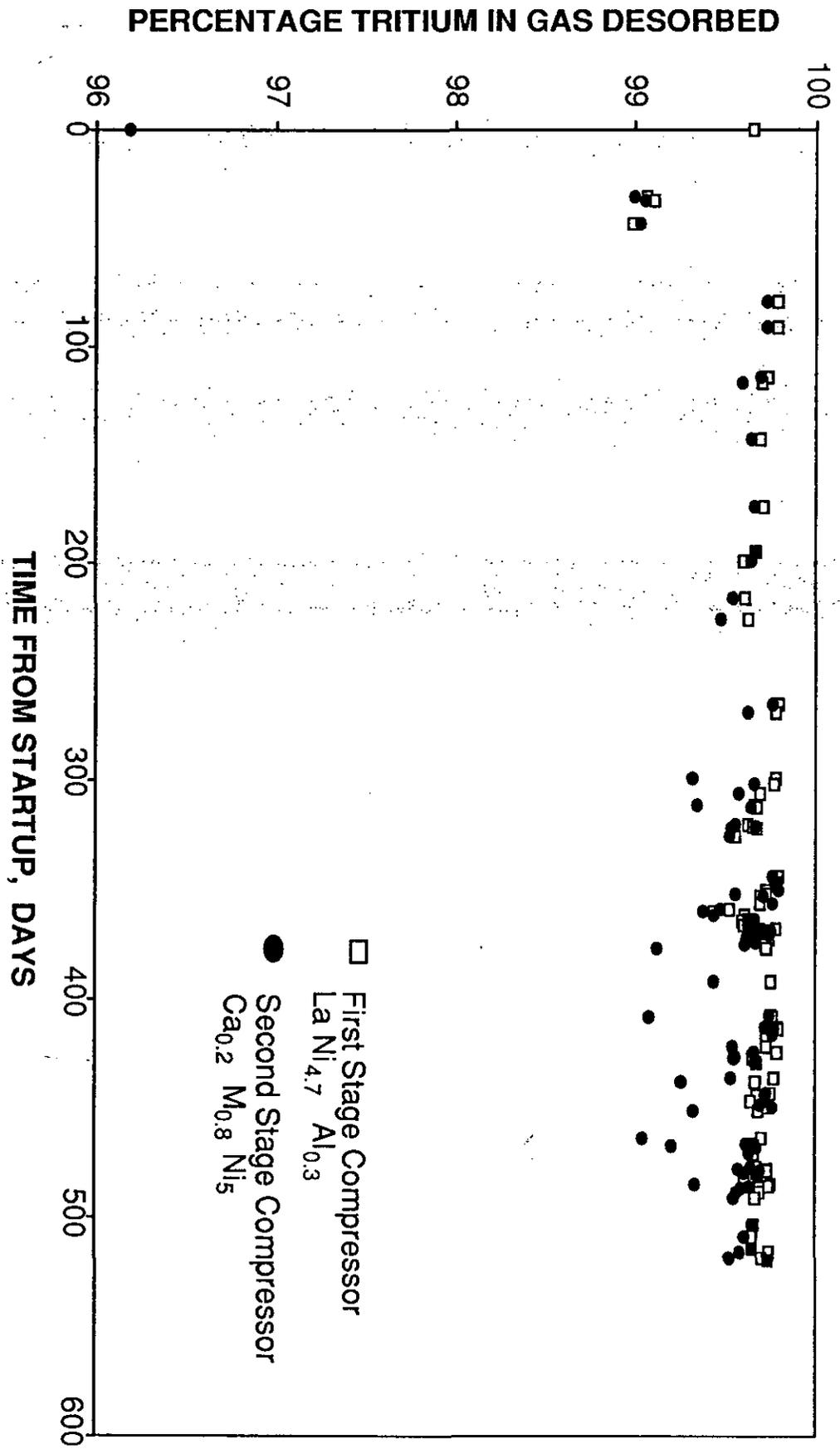


Figure 3

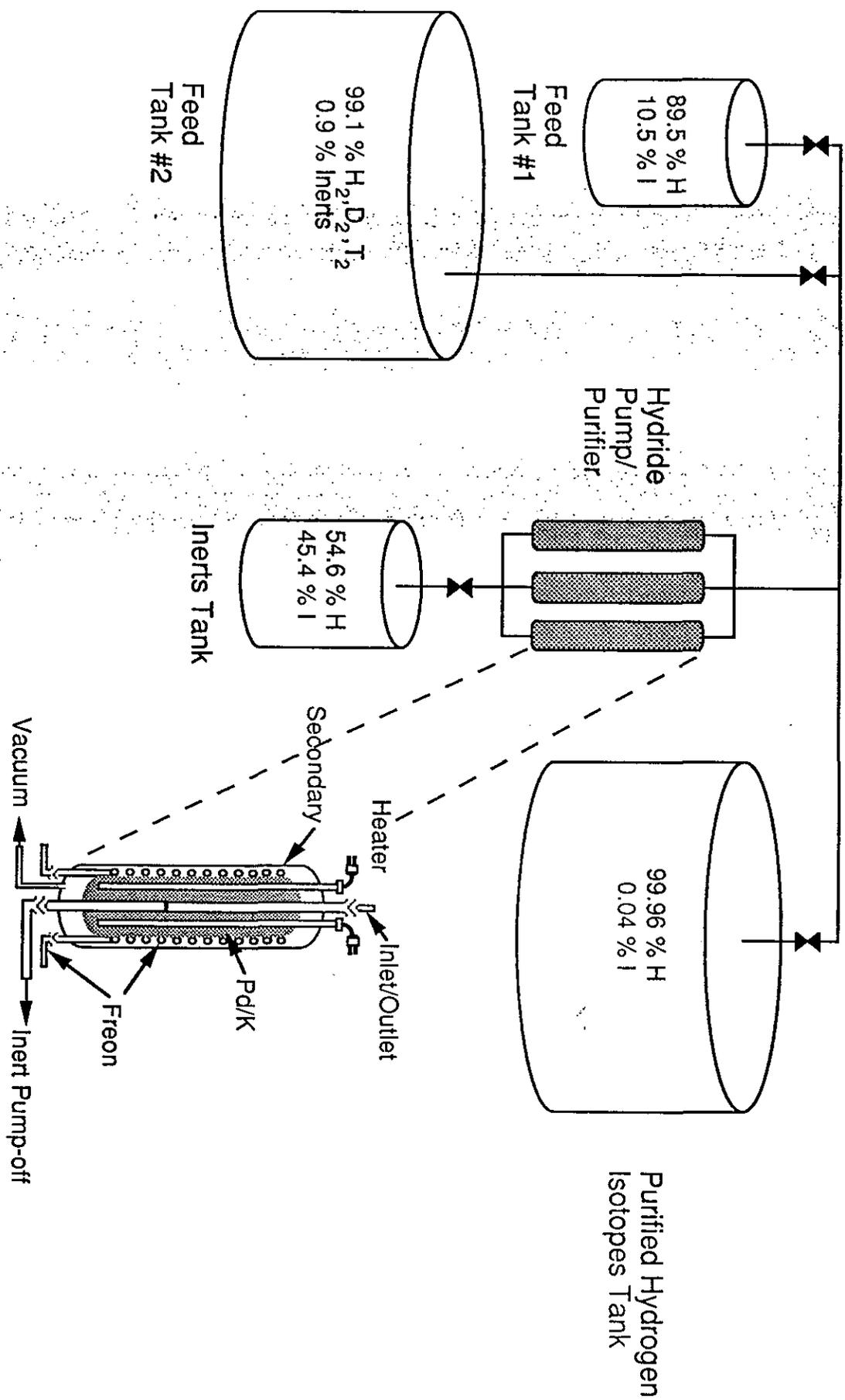


Figure 4

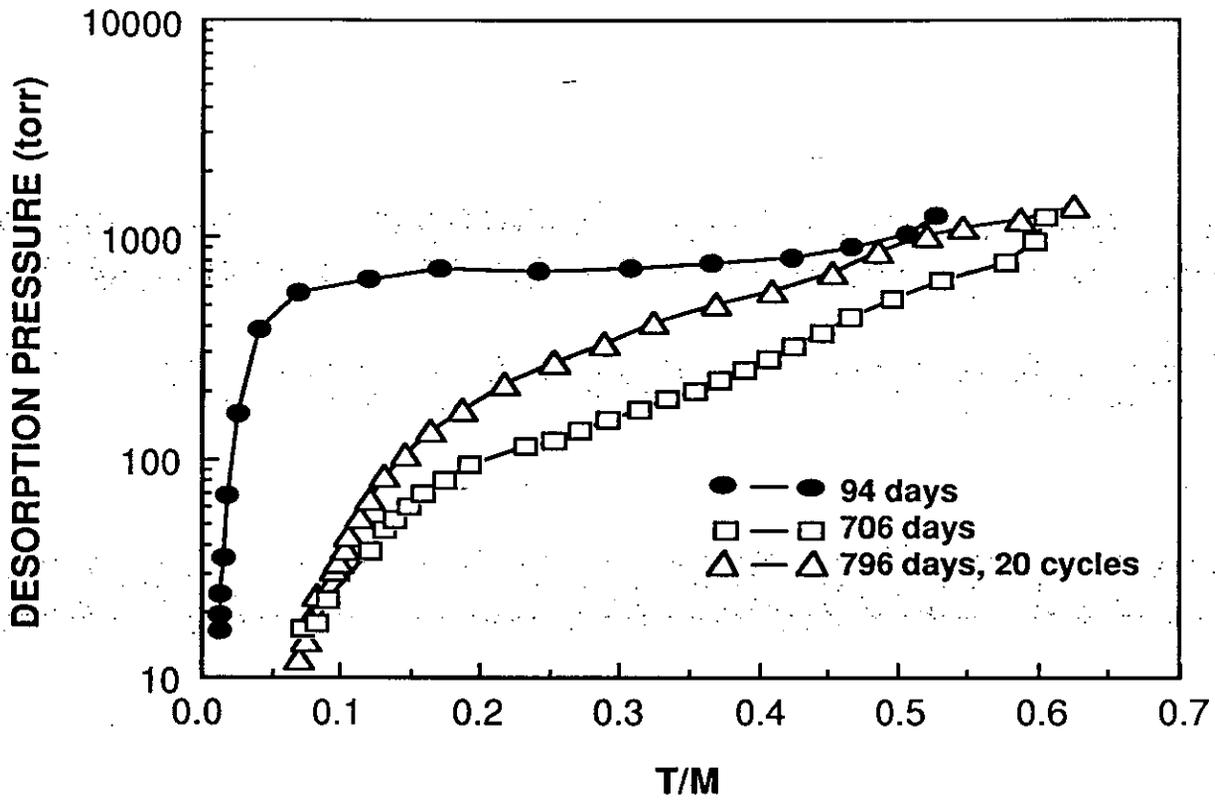


Figure 5

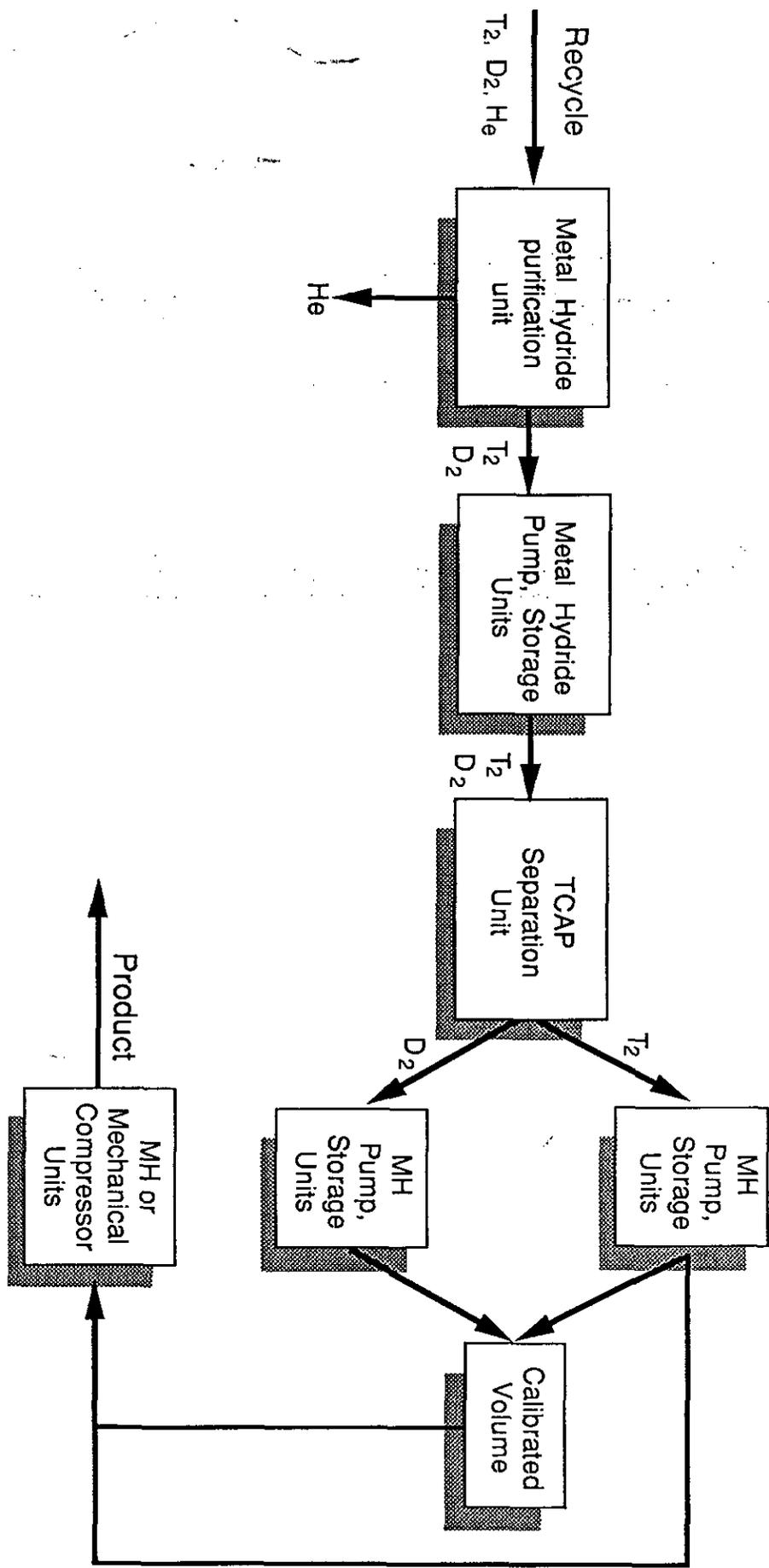
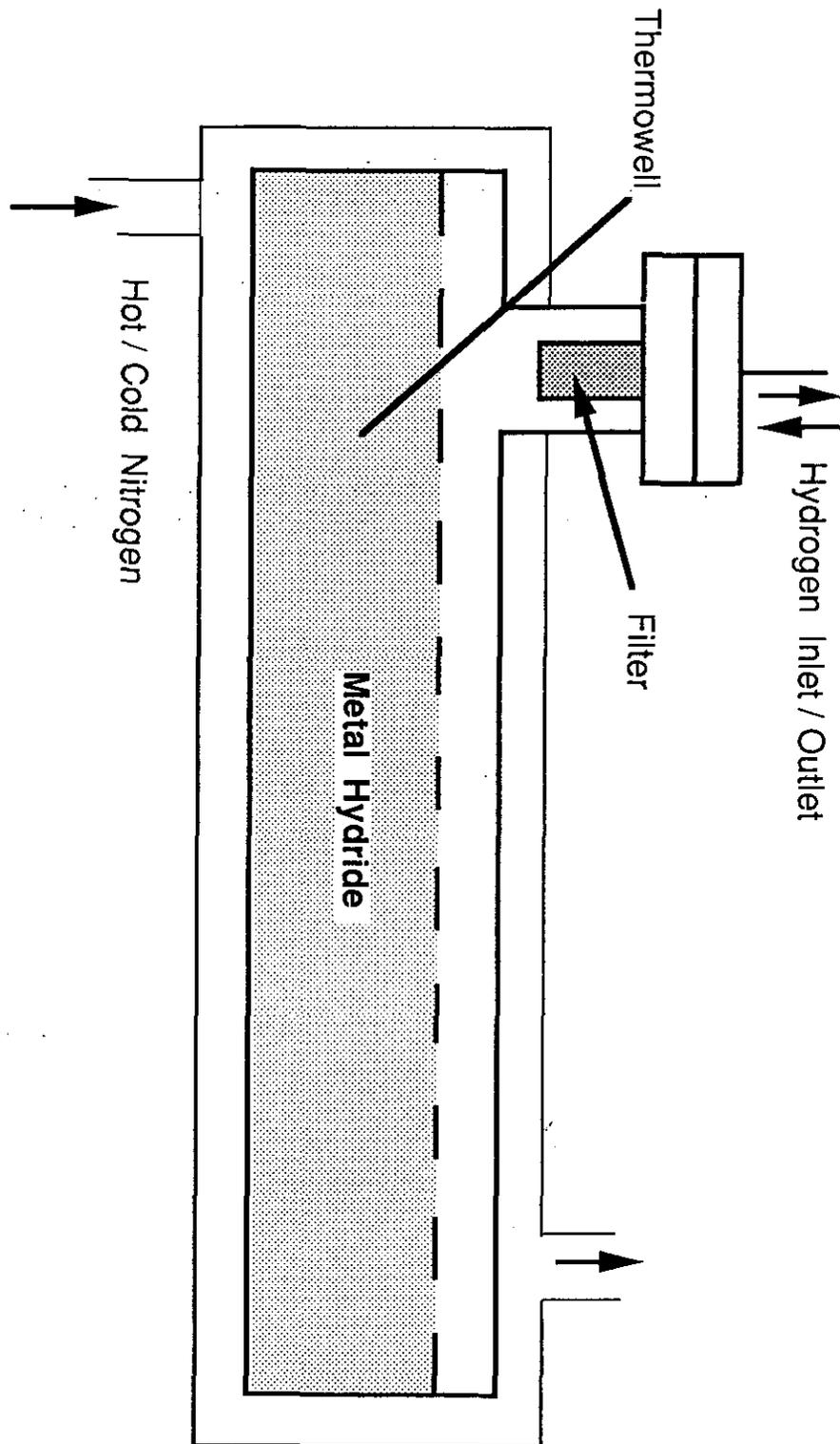
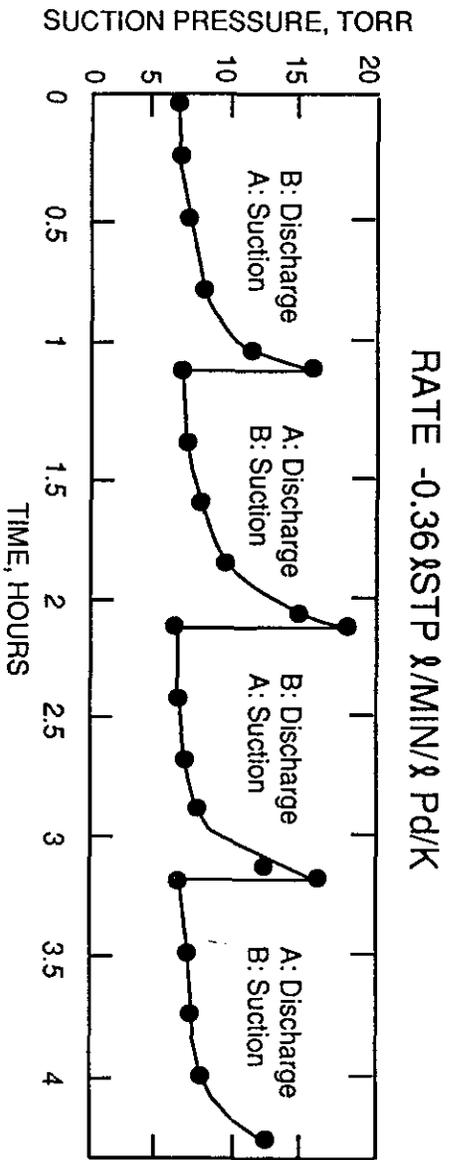
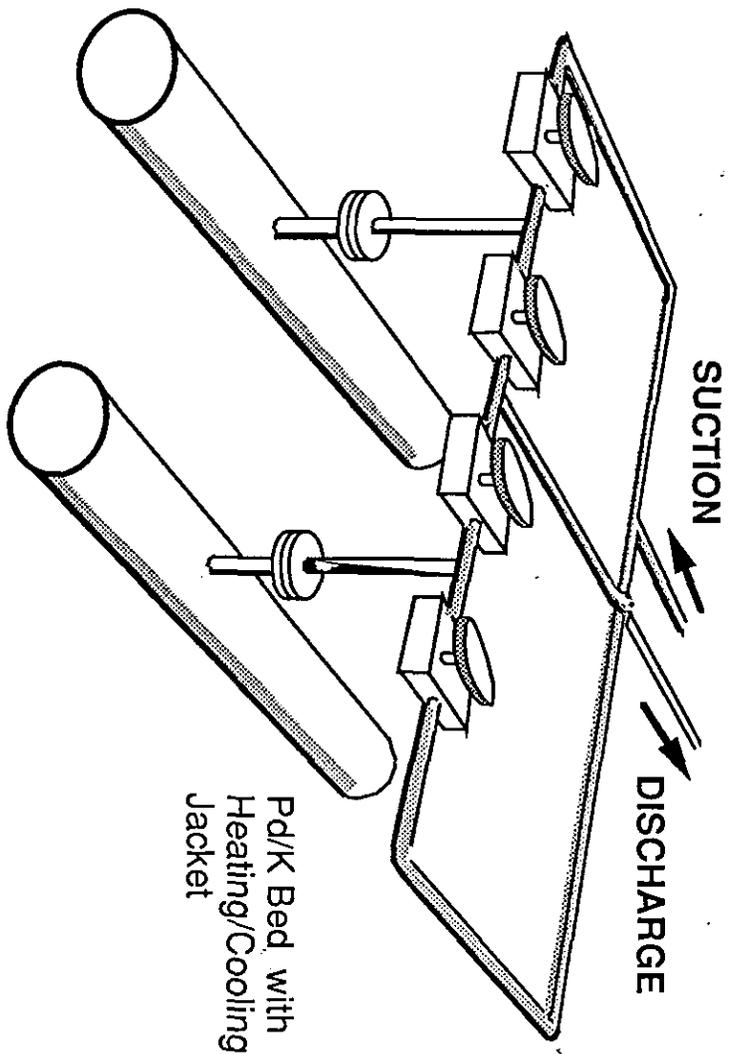


Figure 6



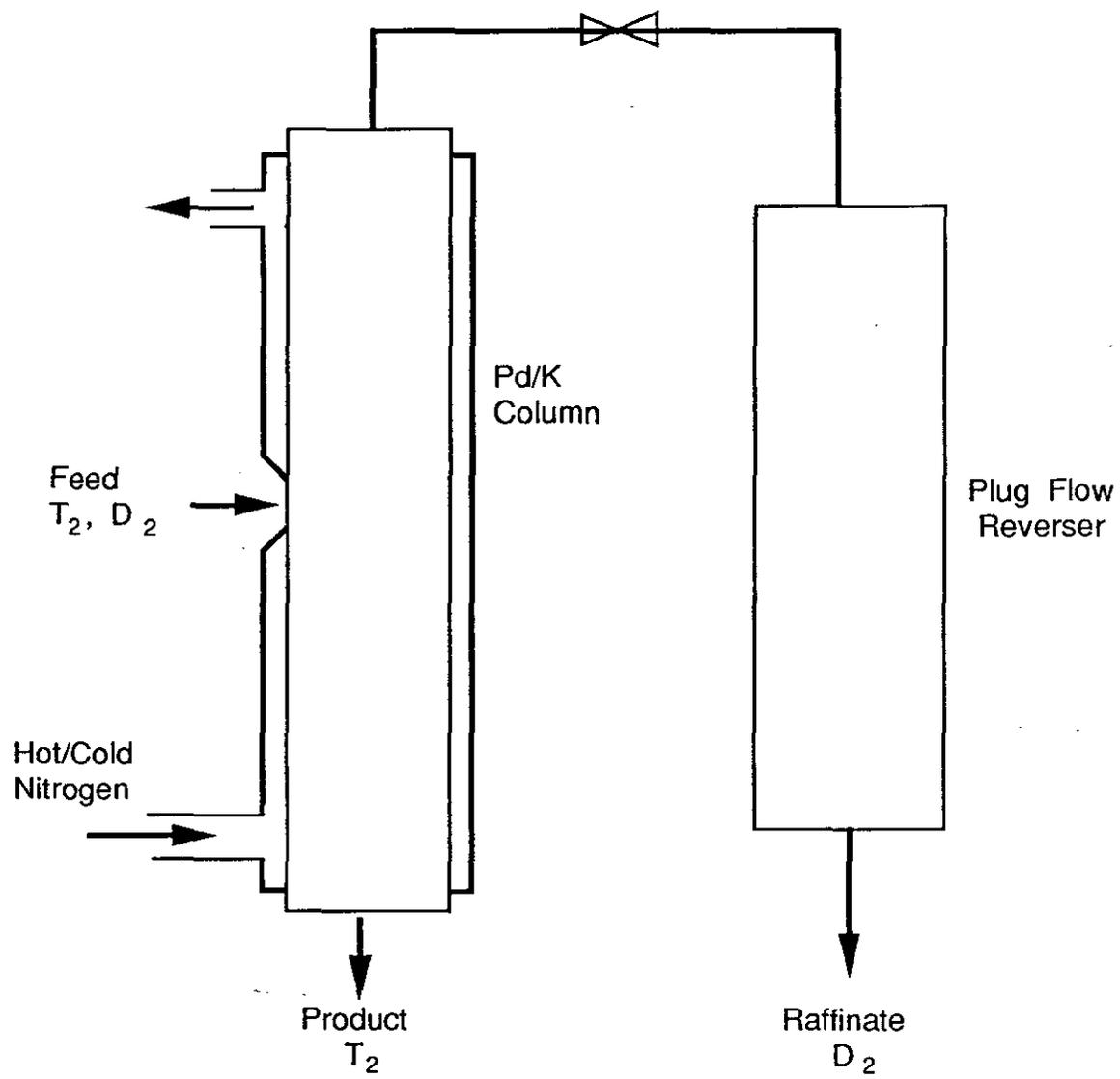
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Figure 7



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Figure 8



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Figure 9