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Distribution and Behavior of Tritium in the Coolant-Salt Technology Facility

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ABSTRACT

A 1000-MW(e) Molten-Salt Breeder Reactor (MSBR) is expected to produce 2420 Ci/day of tritium. As much as 60% of the tritium produced may be transported to the reactor steam system (assuming no retention by the secondary coolant salt), where it would be released to the environment. Such a release rate would be unacceptable.

Therefore, experiments were conducted in an engineering-scale facility — the Coolant-Salt Technology Facility (CSTF) — to examine the potential of sodium fluoroborate, the proposed coolant salt for an MSBR, for sequestering tritium. The salt was believed to contain chemical species capable of trapping tritium. A series of 5 experiments — 3 transient and 2 steady-state experiments — was conducted from July of 1975 through June of 1976 where tritium was added to the CSTF. The CSTF circulated sodium fluoroborate at temperatures and pressures typical of MSBR operating conditions.

Results from the experiments indicated that over 90% of tritium added at steady-state conditions was trapped by sodium fluoroborate and appeared in the off-gas system in a chemically combined (water-soluble) form and that a total of ∿98% of the tritium added at steady-state conditions was removed through the off-gas system overall.

Extrapolating to MSBR conditions based on a concentration ratio of ∿4000 for chemically combined tritium to elemental tritium in the salt observed at steady-state conditions, calculations indicated that less than 10 Ci/day of tritium would be transported to the reactor steam system. Such a release rate would be well within established guidelines for release of tritium to the environment.

Although a complete understanding of the behavior of tritium in sodium fluoroborate could not be developed from this series of experiments due to the termination of the Molten-Salt Reactor Program, the effectiveness of sodium fluoroborate to trap tritium was demonstrated. Furthermore, use of sodium fluoroborate as a secondary coolant in an MSBR would be expected to adequately limit the transport of tritium to the reactor steam system and environment.

1. INTRODUCTION

1.1 Tritium in MSBR

A 1000-MW(e) Molten-Salt Breeder Reactor (MSBR) operating at 2250 MW(t) is expected to produce tritium at a rate of 2420 Ci per full-power day.[1] The major source (Table 1) of tritium is the neutron reactions with lithium, an important constituent of the MSBR fuel salt, which contains uranium tetrafluoride and thorium tetrafluoride dissolved in a lithium fluoride—beryllium fluoride carrier salt. The composition of the fuel salt, expressed in mole percent of each constituent, is 71.7 LiF, 16 BeF_2, 12 ThF_4, and 0.3 UF_4.

Table 1. Sources and rates of
production of tritium in a
1000-MW(e) MSBR[a]

	Production rate (Ci/day)
Ternary fission	31
$^6Li(n,\alpha)^3H$	1210
$^7Li(n,n\alpha)^3H$	1170
$^{19}F(n,^{17}O)^2H$	9
Total	2420

[a]From Ref. 1.

At the operating temperatures, 700—977 K (800—1300°F), of an MSBR, tritium tends to diffuse through the metal walls of the various systems. In the migration process tritium is transferred from the primary system to the secondary coolant salt by diffusion through the walls of the primary heat exchanger tubes. Tritium in the secondary salt is in turn transferred through the steam generator tube walls into the steam system, where it would be converted to tritiated water and discharged to the environment in the steam system blowdown or the condenser cooling water.

Early calculations[2] indicated as much as 1425 Ci/day, or 60%, of the tritium produced would be transported to the reactor steam system assuming no retention of tritium by the secondary salt.

Release of the 1425 Ci/d of tritium would be unacceptably high. The MSBR design limit objective for release was set at 2 Ci/day. The resulting concentration of tritium in the water released to the environment would be well below established guidelines[3] for "as low as reasonably achievable" for release of radioactive material in effluents from light water reactors. It is assumed that an MSBR would have to meet similar guidelines.

1.2 Tritium in the MSRE

Some experience with tritium in a molten-salt system was gained from the Molten-Salt Reactor Experiment (MSRE). This reactor was operated from 1965 to 1969 at a full power of about 7.3 MW(t). It operated at a maximum temperature of 927 K (1210°F) with a fuel salt similar to the MSBR fuel salt. Heat was transferred to a lithium fluoride—beryllium fluoride coolant salt and removed from the secondary salt by blowing air over the tubes of a radiator, which was used in place of a steam generator—superheater, and discharging it up a stack to the atmosphere.

Tritium disposal from the MSRE never presented a significant problem. The only measurements made were of liquid wastes for health physics monitoring purposes. However, a growing concern for tritium production in a large molten-salt reactor initiated measurements for making a material balance on tritium in the MSRE.

The calculated production rate was 54 Ci/day, and the observed disposition of tritium, not including retention in the off-gas system, amounted to 80% of this production rate: 48% discharging from fuel off-gas system, 2% discharging from coolant off-gas system, 7% discharging in coolant radiator air, 9% appearing in cell atmosphere, and 14% going into the core graphite. Most of the remainder was probably held up in oil residues in the fuel off-gas systems.

The difference in tritium production between the MSRE at 7.4 Ci day^{-1} MW(t)$^{-1}$ and the MSBR at 1.1 Ci day^{-1} MW(t)$^{-1}$ is due mainly to the increased ^{6}Li concentration that was present in the MSRE fuel salt.

1.3 Proposal for Limitation of Tritium Transport

One method proposed for limiting tritium transport to the steam system in an MSBR is based on an isotopic exchange of tritium with a hydrogenous impurity in the reactor secondary coolant salt. Sodium fluoroborate, the proposed MSBR coolant salt, is an eutectic mixture containing 92 mole % $NaBF_4$ and 8 mole % NaF. Chemical analyses have shown that the fluoroborate salt normally contains a hydrogenous impurity produced by the reaction of water with the salt. Laboratory experiments[4] indicated that deuterium, on contacting the salt, is retained by the salt because of isotopic exchange with this impurity. Tritium would be expected to behave similarly. Another potential method for trapping tritium may involve the reaction of tritium with oxide-containing chemicals in the salt. Once in the chemically combined form, unlike the elemental form, tritium would not be available for transport to the steam system. With adjustment of the impurity level if required, the fluoroborate salt could then be processed for removal of tritium.

Experiments were then proposed for the Coolant-Salt Technology Facility (CSTF), an engineering-scale facility, to determine sodium fluoroborate's effectiveness in sequestering tritium. Information from the tritium experiments in the CSTF was to be used in extrapolating to MSBR conditions.

2. COOLANT-SALT TECHNOLOGY FACILITY (CSTF)

2.1 Primary Function and Capabilities

The primary function of the CSTF is to circulate the sodium fluoroborate coolant salt at temperatures and pressures typical of MSBR operating conditions. The facility was designed with the capability to supply coolant salt to a number of side loops for the purpose of (1) extending engineering-scale operating experience with the proposed MSBR coolant salt and its cover gas, (2) investigating on-line corrosion product traps, (3) investigating on-line salt monitoring by electrochemical means, and (4) monitoring the corrosion characteristics of the system by means of surveillance specimens. For the tritium experiments, the CSTF's function was to circulate sodium fluoroborate while several additions of tritium were made to determine if the coolant salt would inhibit tritium migration.

2.2 Description of Physical Parameters of CSTF

The CSTF consists of a Hastelloy N pump (the coolant salt pump which was used in the MSRE) and about 10.7 m (35 ft) of 5-in. IPS sched-40, 6.6-mm (0.258-in.) wall Hastelloy N pipe arranged in the form of a closed loop (Fig. 1). The system may be operated at a maximum flow of 54×10^{-3} m^3/s (850 gal/min) using the normal 60-Hz power supply, or at reduced flow rates using a variable-speed motor-generator set. The ratio of wetted surface to salt volume (including the pump tank inventory) is about 20:1 m^2/m^3. In comparison, the reference-design MSBR has a salt-circulating rate of 1 m^3/s (16,000 gal/min) for each of four cooling loops and a ratio of wetted surface to circulating salt volume of about 50:1 m^2/m^3.

The CSTF has two volumes of salt which are outside the main salt stream but which communicate with the main salt stream by means of side loops having relatively small salt flows.* These inventories of salt are in the bowl of the salt pump and in the salt monitoring vessel (SMV). Each of these regions is only partly filled with salt, there being a salt-gas interface and a gas space in each, and the gas spaces are intercon-nected. During normal operation, inert gas is fed into the pump bowl continuously by way of the drive shaft purge and cover gas connections. A small flow (about 70 cm^3/min) of BF$_3$, which is used to maintain the de-sired ratio of NaBF$_4$ to NaF in the salt, is also added to the pump bowl vapor space to compensate for the BF$_3$ that is removed from the circulating salt in the off-gas stream. This gas, together with volatile materials from the salt (e.g., BF$_3$ and H$_2$O reaction products, tritium, etc.), passes from the pump bowl gas space, through the SMV gas space, and then in se-quence through the salt mist trap, the cold trap (−80°C), the cover gas pressure control valve, and a mineral oil bubbler. Finally, the off-gas stream flows to the stack by way of the suction line of the containment system ventilation blower.

All of the salt-containing piping and components of the CSTF are enclosed in a steel containment enclosure equipped with an evacuation

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*In its original design, the CSTF had a third side loop passing through the salt mist trap. Prior to the tritium test, this third loop was disconnected and the loop-side openings were capped off.
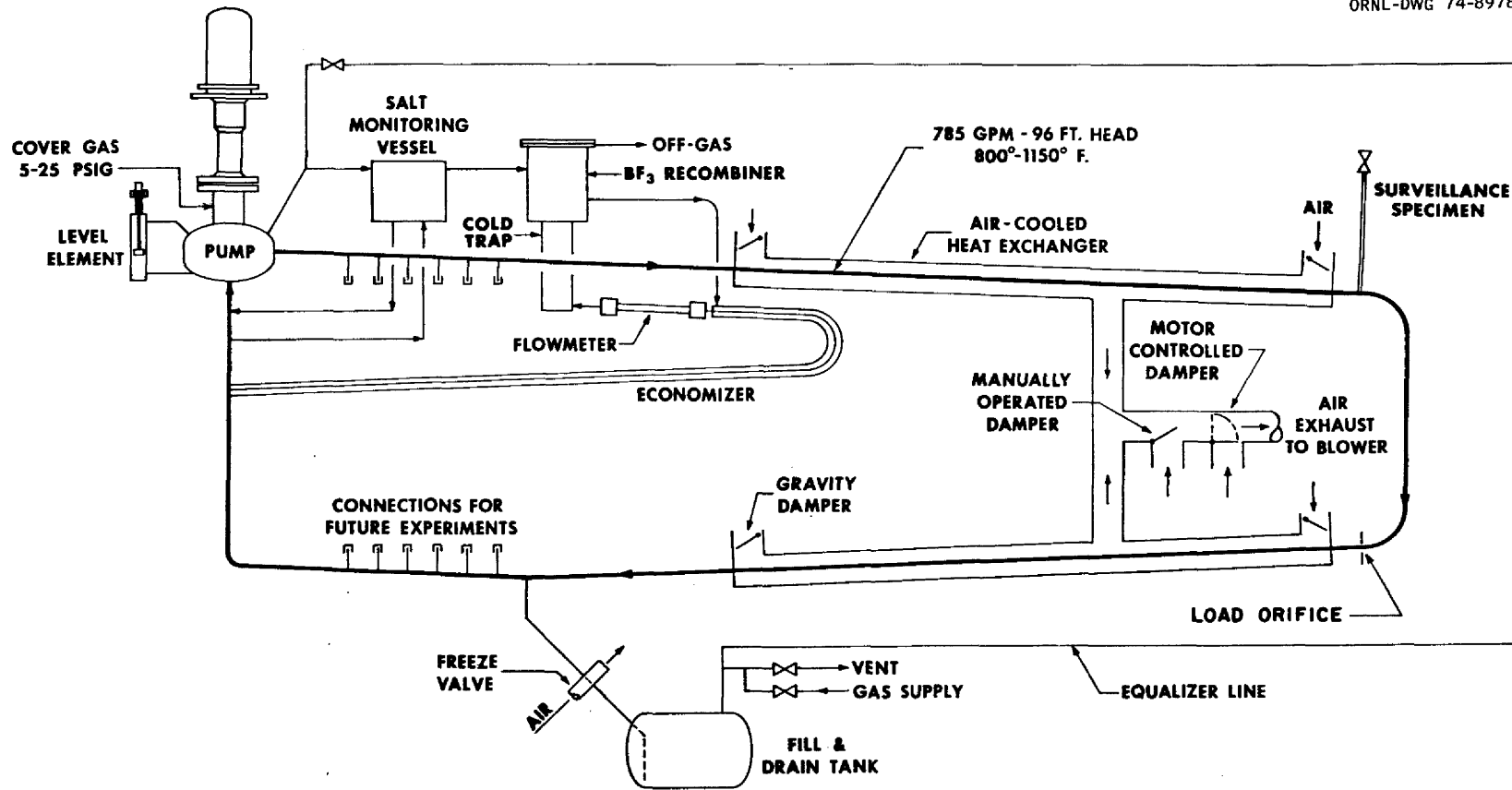
Fig. 1. CSTF schematic.

blower. The containment and ventilation system provides secondary containment for any salt leak and also provides for safe disposal of any gas released from the facility. The enclosure is maintained at a slightly negative pressure by the 1.4 m^3/s (3000 cfm) blower. The blower suction line is connected to parallel cooling ducts on the salt loop piping (Fig. 1) whereby more or less air can be drawn through the cooling ducts as dictated by the loop cooling requirements.

2.3 Operating History of CSTF

The CSTF became operational for the first time in October of 1972. Several runs[5] were made observing and measuring such things as cavitation at the load orifice (Fig. 1), BF_3 content of the BF_3-He off-gas stream, salt flow through the SMV, proton activity in the salt, and chemical composition of the salt.

In February of 1973, the CSTF was placed in standby because of the cancellation of the MSR program. From February 1973 through March 1974, the system was maintained in standby, namely at room temperature with a static pressure of 5 psig helium blanketing the salt-containing portions. In April 1974, the MSR program was restarted and work was begun on recommissioning the CSTF in preparation to study tritium behavior in sodium fluoroborate. Deuterium was originally to be added to the system as a stand-in for tritium; however, the necessary analytical equipment required for measuring the anticipated concentrations of deuterium would not have been operational at the time the experiments were to be conducted. Consequently, the decision was made to use tritium which could be measured with available radioactive counting techniques.

Once the CSTF was restarted, two important modifications were made. First, a second load orifice was installed in the main circulating loop. The two orifices in series permitted operation of the loop at maximum conditions of temperature [894 K (1150°F)] and pump speed without significant cavitation. Second, a salt mist trap was installed in the off-gas line at the outlet from the salt cold trap* to prevent plugging of the

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*The cold trap in Fig. 1 is a salt cold trap while the cold trap in Fig. 2 is an off-gas cold trap.

off-gas line by deposition of frozen salt mist. The salt mist droplets were generated in the pump bowl and were carried out with the off-gas stream and deposited at a point where the temperature fell below the freezing point of the salt. The salt lines (economizer in Fig. 1) from the salt mist trap to the pump suction line were also disconnected for the tritium tests.

During the initial operating period in 1972, salt was circulated for ∿1060 hr. Since the CSTF was recommissioned in 1974, salt has been circulated ∿8240 hr. On July 12, 1976, the loop was shut down following the conclusion of the final tritium experiment and work was begun to decommission the CSTF.

2.4 Equipment for Tritium Tests

The equipment for the tritium experiments consisted of (1) the Coolant-Salt Technology Facility (CSTF), (2) the equipment needed to add measured quantities of tritium to the circulating salt, (3) the sampling and analytical equipment needed to determine the distribution of the tritium between the various possible sinks.

2.4.1 CSTF physical parameters for tritium tests

A schematic of the CSTF as it was used in performing the tritium experiments is presented in Fig. 2. Table 2 presents the operating and geometrical parameters used for the CSTF tritium tests.

2.4.2 Addition of tritium to CSTF

The addition of tritium into the circulating salt stream was accomplished by means of a special addition tube assembly installed in the surveillance specimen access tube (Figs. 1 and 2) in place of the regular surveillance specimen holder. The surveillance specimen station was originally designed to permit exposure of Hastelloy N metal coupons to salt at normal velocities and temperatures of the loop. This location of the addition tube ensured that the tritium could not pass directly into the off-gas system without first coming in contact with the circulating salt. The inner part of the addition assembly was charged with a mixture of hydrogen and tritium at a desired pressure, the gas then permeated or
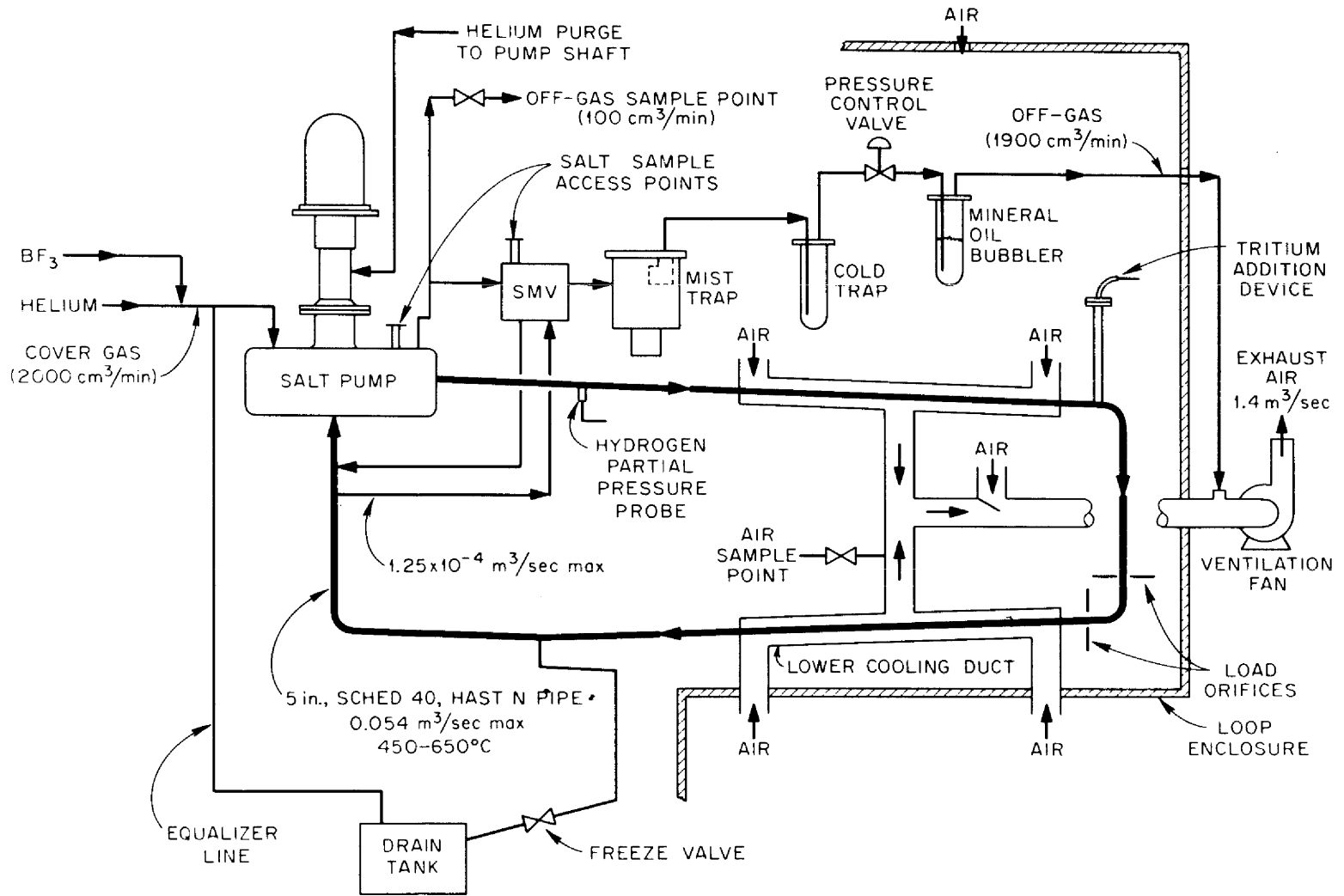
Fig. 2. CSTF schematic for tritium experiments.

Table 2. Operating and geometrical parameters
assumed for CSTF tritium tests

Main loop salt flow rate (pump speed = 1790 rpm)	540×10^{-4} m^3/s	850 gal/min
Bypass salt flow rates (pump speed = 1790 rpm)		
Pump bowl bypass flow rate	9.50×10^{-4} m^3/s	15 gal/min
Salt monitoring vessel flow rate	1.25×10^{-4} m^3/s	2 gal/min
Salt mist trap flow rate	0^a	0^a
Total bypass flow rate	10.75×10^{-4} m^3/s	17 gal/min
Main loop piping geometry		
Outside diameter	141 mm	5.56 in.
Inside diameter	128 mm	5.05 in.
Wall thickness	6.6 mm	0.26 in.
Wetted surface excluding pump bowl	4.5 m^2	48.4 ft^2
Wetted surface in pump bowl	1.0 m^2	10.8 ft^2
Pump bowl surface exposed to gas space	0.68 m^2	7.3 ft^2
Volumes		
Loop piping including SMV and salt mist trap, excluding pump bowl	150×10^{-3} m^3	5.30 ft^3
Circulating salt including pump bowl	270×10^{-3} m^3	9.53 ft^3
Pump bowl liquid	120×10^{-3} m^3	4.24 ft^3
SMV liquid	4.2×10^{-3} m^3	0.15 ft^3
Salt mist trap liquid	0^a	0^a
Pump bowl vapor space	57×10^{-3} m^3	2.01 ft^3
SMV vapor space	7.3×10^{-3} m^3	0.26 ft^3
Salt mist trap vapor space	2.8×10^{-3} m^3	0.10 ft^3

^{a}The salt lines were disconnected from the salt mist trap, so that during the tritium test there was no salt flow or salt inventory, other than accumulated salt mist, in the salt mist trap.

diffused through the wall of the Hastelloy N tube which formed the lower
end of the addition tube and was immersed in the circulating salt stream.
The Hastelloy N tube was about 120 mm (4.7 in.) long with an OD of 12.7 mm
(0.5 in.), and a wall thickness of 1.07 mm (0.04 in.), and the provision
was made to fasten metallurgical surveillance specimens to the upstream
face.
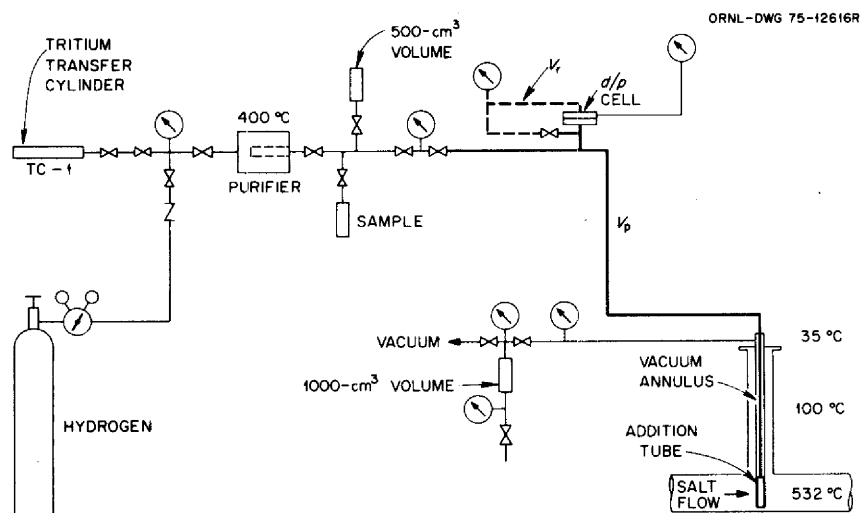
Fig. 3. Tritium addition system.

Connected to the tritium addition assembly was the equipment needed
to supply measured quantities of tritium to the CSTF (Fig. 3). The high-
pressure, tritium transfer cylinder was charged with tritium, and the
cylinder was connected to the addition system and charged with hydrogen
from the hydrogen supply bottle to a total pressure calculated to yield
the desired tritium isotope concentration. The tritium-hydrogen mixture
was fed from the cylinder through the purifier until the 500 cm^3 volume
was charged with purified gas to the desired pressure. Purified gas from
the 500 cm^3 volume was used to charge the addition tube and addition
assembly. A d/p cell was used to measure the resulting pressure drop
in the addition assembly due to diffusion of the mixture of tritium and
hydrogen into the salt. For a short-term experiment, the reference volume
(V_r) and addition tube volume (V_p) could be charged directly without using
the 500-cm^3 volume. A rupture disk was connected to the hydrogen supply

to minimize the probability of overpressurizing the system. The purifier was simply a heated palladium tube through which hydrogen isotopes diffuse more readily than heavier gases such as O_2, N_2, and H_2O. A vacuum pump was used to evacuate the annulus surrounding the addition tube in the high temperature zone adjacent to the salt piping (Fig. 3). Measurements of the pressure rise in the vacuum annulus were used to estimate the amount of stray leakage that occurred during the addition of tritium. A sampling point was provided to obtain samples for mass spectrometer analysis to determine the concentration of tritium in the addition gas.

2.4.3 Salt sampling

Salt samples for tritium analysis and for chemical analysis were taken from the salt pool in the bowl of the salt pump or in the SMV by inserting a copper tube through the salt sample access pipe (Fig. 2). The normal method was to use a "filter stick," wherein the salt was forced into the sample tube through a porous copper frit having a 10 µm mean pore size. An available alternate method was to use a "bucket sampler" which had slots in the sides of the lower end of the sample tube and functioned in the manner of a water dipper. The sample was dissolved in water and counted using scintillation counting techniques. Sample results of the tritium concentrations in the salt represented tritium in a chemically combined form since any elemental tritium present in the samples would have been released in preparing them for counting.

2.4.4 Off-gas sampling system

For water-soluble (combined) and elemental tritium in the off-gas stream, a 100-cm^3/min sample stream was taken from the 2-liter/min off-gas stream at a point just downstream of the pump bowl and was passed through a salt mist filter, a needle valve, a water trap to collect water-soluble (combined) tritium, a CuO furnace to convert elemental tritium to tritiated water, and a water trap and cold trap to collect the tritiated water (Fig. 4).

About 20 cm^3/min of hydrogen was added to the sample stream to promote efficient oxidation of the elemental tritium.
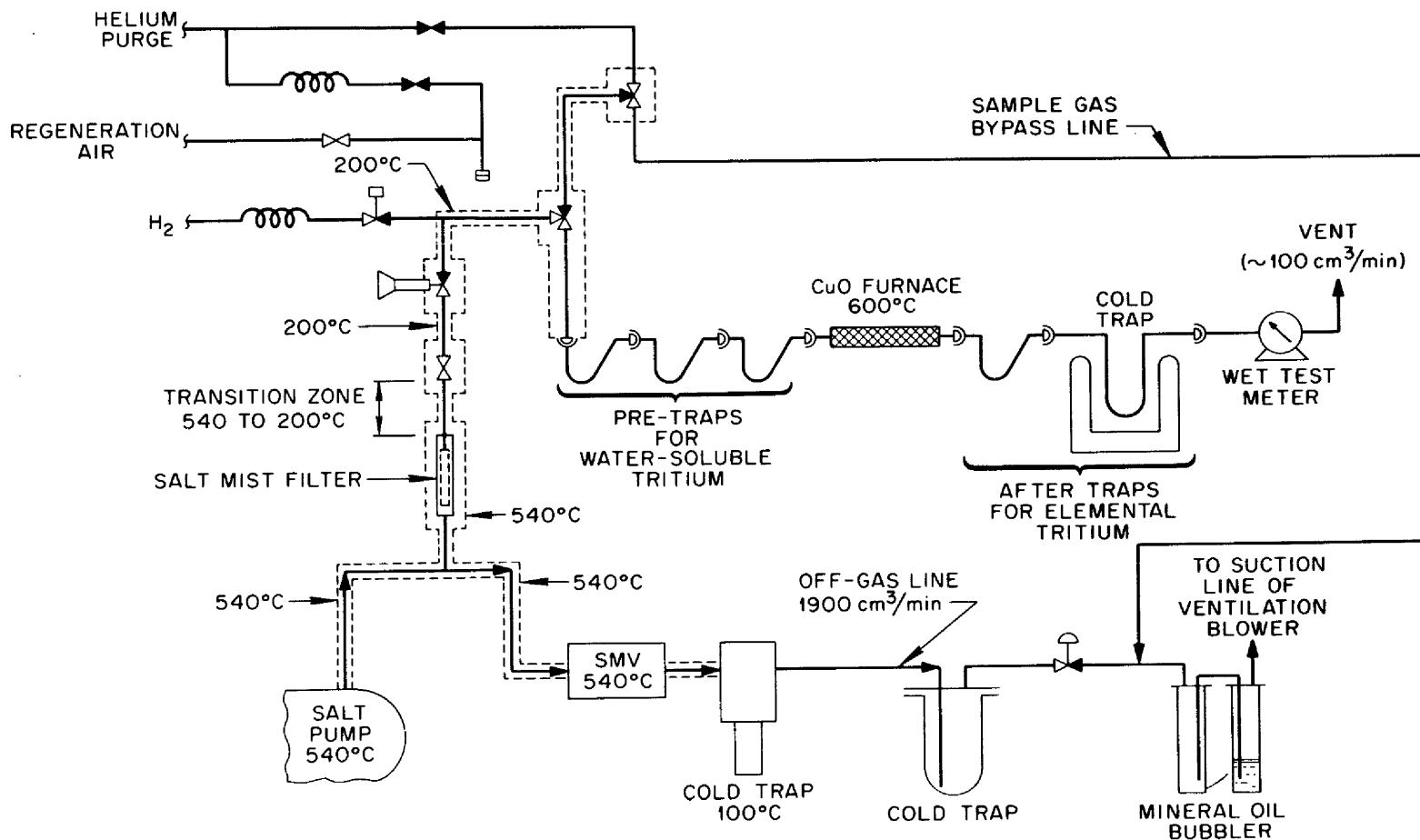
Fig. 4. Off-gas sampling system.

The salt mist filter was installed in the off-gas sample line prior to the final two experiments to prevent salt mist droplets from being transported to cooler regions and subsequently freezing and plugging lines. The off-gas lines leading to the sampling equipment were maintained at 370 K (200°C) to prevent the water-soluble (combined) tritium from condensing in the lines. A flow of helium was passed through the sampling system after each sample was taken to purge out any remaining tritium to minimize any bias on subsequent samples. Air flow was also provided so that the depleted CuO in the furnace could be regenerated periodically. When the system was not in the sampling mode, the 100-cm^3/min sample flow was returned to the main off-gas flow via the sample gas bypass line. The tritium concentrations of the two species were determined by scintillation counting techniques.
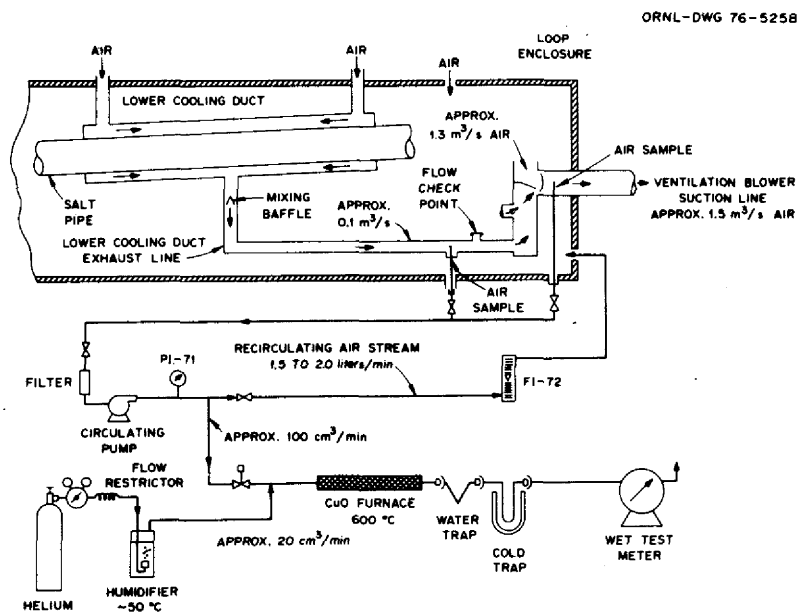
Fig. 5. Cooling duct air sampling system.

2.4.5 Cooling duct air sampling system

The rate of permeation of tritium through the walls of the loop was obtained by sampling the air stream at the exit from the lower cooling duct on the salt loop (Fig. 5). The surface area of loop piping shrouded by the lower cooling duct was approximately 20% of the total surface area of loop piping. A sample tap was installed in the air line coming from the lower

cooling duct. This tap was connected to a diaphragm pump that circulated sample gas at a rate of about 1700 cm^3/min and vented the gas into the loop enclosure. At the pump discharge, where the pressure was controlled at an absolute pressure of 140 kPa, a 100-cm^3/min side stream was taken off for sampling. The sample stream was mixed with 20 cm^3/min of humidified helium, and the combined streams were passed through a CuO furnace to convert the tritium to tritiated water and then through a water trap and cold trap to collect the tritiated water. The tritium concentration was measured by scintillation counting.

The modifications necessary for implementing this system involved extending the air intakes to the lower cooling duct so that the air was drawn from outside the loop enclosure to avoid contamination of the samples by extraneous tritium present in the enclosure. The air flow through the lower cooling duct was calibrated by adding a known flow of tritium to the air intake and sampling the air stream.

2.4.6 Hydrogen partial pressure probe

A probe was inserted in the main salt stream prior to experiment T4 at a point about 1.25 m downstream from the salt pump discharge (Fig. 2) to measure the partial pressure of elemental hydrogen and ultimately determine the dissolved elemental tritium concentration in the salt. The probe (similar in design to the addition tube) consisted of a sealed Hastelloy N tube, 12.7 mm OD × 1.1 mm wall, connected to the necessary valving and instrumentation to permit pressure readings inside the probe in the range of 0.01 to 100 Pa (0.1 to 1000 μm Hg).

3. GENERAL DESCRIPTION OF THE EXPERIMENTS

Hydrogen containing small amounts of tritium was added to the salt by allowing the mixture of gas to permeate or diffuse through the walls of the addition tube which was immersed in the circulating salt. Diffusion of tritium through the metal walls of the addition tube into the salt as opposed to bubbling tritium into the salt more nearly simulated MSBR conditions where tritium would be entering the secondary coolant system by diffusion through the primary heat exchanger.

The surface area of the addition probe was 50 cm^2 and the surface area of the MSBR primary heat exchanger would be 50×10^6 cm^2. The addition rate or transfer rate of gas in the experiment was about 10 times less than under MSBR conditions in terms of cm^3/hr. Therefore, the flux of gas in terms of cm^3 of gas per cm^2 of surface area per hr was about 10^5 times greater in the experiments than under MSBR conditions.

Tritium (hydrogen) added to the CSTF was distributed among several sinks and was considered to be in either the elemental or chemically combined form. The potential sinks for distribution and respective chemical forms were:

1. Dissolution in the salt in the elemental form.

2. Reaction with the salt to produce a chemically combined form.

3. Appearance in the off-gas system of the CSTF in both elemental and combined forms. The concentrations of both forms in the off-gas were proportional to their respective partial pressures over the salt that determined their respective concentrations in the salt in the pump bowl.

4. Dissolution in the metal of the loop walls and associated piping in the elemental form.

5. Permeation through the loop walls in the elemental form.

Samples were taken for analysis of the combined form of tritium in the salt, both forms of tritium in the off-gas, and elemental tritium in the cooling duct air. The cooling duct air sampling system for measuring the permeation rate of tritium through the pipe walls was available only for the final two experiments. Samples of the addition gas were taken periodically and analyzed by mass spectrometry to determine the tritium concentration and ultimately calculate the addition rate of tritium to the system.

A partial pressure probe for measuring the total hydrogen (elemental protium and elemental tritium) partial pressure in the salt was also operational only for the final two experiments, which were steady-state experiments. The pressure in the probe was permitted to build up over a period of two to three days in order to allow the partial pressure of hydrogen in the probe to be equilibrated with the partial pressure of hydrogen on the outside of the probe in the circulating salt. The initial rise in pressure

was due to the buildup of the hydrogen partial pressure in the probe. The gradual, constant increase in pressure over time was attributed to air in-leakage and was subtracted off by extrapolating a plot of the readings to time zero for each respective measurement (Fig. 6). The pressure obtained from the pressure gauges was corrected for (1) the difference between measurements for hydrogen and air since the gauges are calibrated for air and (2) thermal transpiration effects[6] which result since the partial pressure of interest was measured at 811 K (the operating temperature of the loop for the experiments) and the gauges recording the measurement were at room temperature.

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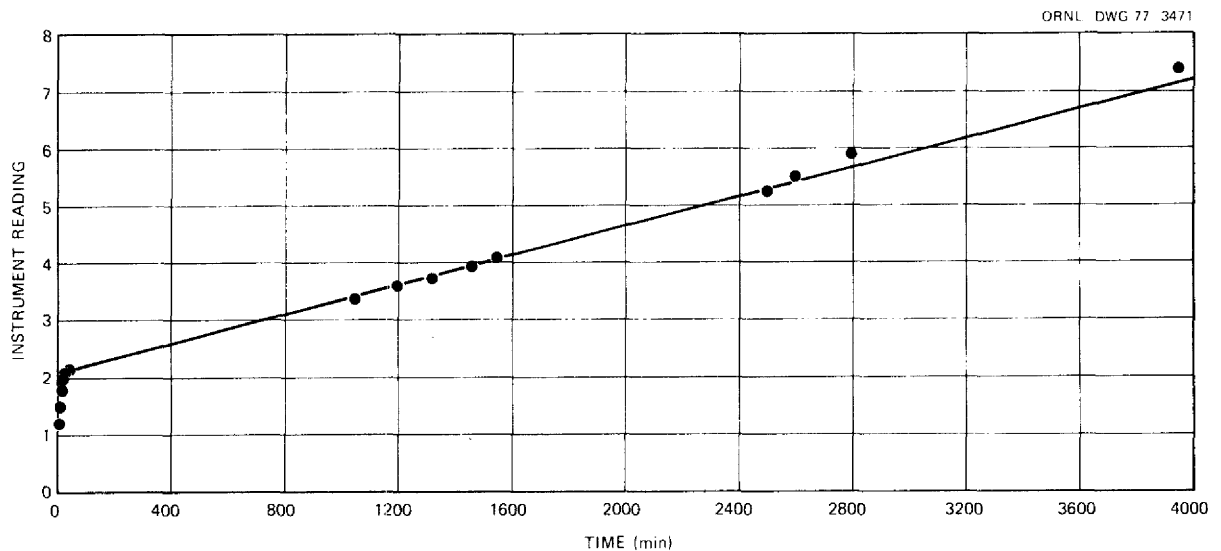
Fig. 6. Typical hydrogen partial pressure probe measurement.

A Henry's Law Constant[2] for hydrogen dissolved in sodium fluoroborate was used to convert the elemental hydrogen partial pressure to a concentration of elemental hydrogen dissolved in the salt. The dissolved elemental tritium concentration in the salt was then determined by assuming that the ratio of tritium to hydrogen in the salt was the same as that in the addition gas. The ratio of chemically combined tritium concentration (from salt samples extracted from the pump bowl or SMV) to the elemental tritium concentration in the salt (from the partial pressure probe measurements) becomes an important parameter in extrapolating results from the CSTF experiments to MSBR conditions.

The quantity of tritium stored in the metal walls was estimated using the following factors: (1) total hydrogen partial pressure, (2) isotopic ratio of tritium to total hydrogen, (3) solubility coefficient[7] of hydrogen in Hastelloy N, and (4) total volume of metal of the system.

Both transient and steady-state experiments were conducted in the CSTF. The three transient experiments — T1, T2, and T3 — were run during July, August, and September of 1975, respectively. The two steady-state experiments — T4 and T5 — were conducted for approximately 65 days from February through April of 1976 and for approximately 48 days from May through June of 1976, respectively.

Tritium was added for about 10 hr in each of the three transient experiments. The concentrations in the salt and off-gas did not become saturated. Sampling of tritium concentrations in the salt and off-gas was continued two to three weeks following the addition to observe the stripping or removal of tritium from the system.

In the steady-state experiments, tritium was added long enough to permit the tritium concentrations in the salt, off-gas, and cooling duct air to level out. Steady-state conditions were presumed to have been attained when the addition rate of tritium equaled the sum of the removal rates of (1) combined (water-soluble) tritium in the off-gas, (2) elemental tritium in the off-gas, and (3) tritium permeating the pipe walls of the CSTF. The stripping portions of experiments T4 and T5 were observed for considerably shorter periods of time than the transient experiments due to time limitations of the MSR program.

The three transient experiments were essentially scoping experiments in that they permitted

1. the acquisition of operational experience with the CSTF, both general and that required for operating the CSTF for the purpose of conducting tritium experiments;

2. an initial indication of sodium fluoroborate's effectiveness in trapping or retaining tritium;

3. a determination of what further measurments and samples would be required to better understand tritium behavior in sodium fluoroborate.

Subsequently, the cooling duct air sampling system and hydrogen partial pressure probe were installed and steady-state experiments T4 and T5 were run.

4. RESULTS OF TRANSIENT EXPERIMENTS

4.1 Experiment T1

In experiment T1 a total of 33.6 cm^3 of hydrogen at $\sim$1000 ppm tritium concentration was added to the CSTF during the 10.8-hr addition period. Thus, about 85 mCi of tritium were added to the loop at a rate of $\sim$7.9 mCi/hr. Samples of the salt and loop off-gas were taken during the addition and for 15 days following the addition. The apparent concentrations prior to the addition were:

1. Tritium in the salt: 1.7 nCi/g
2. Tritium in the off-gas, elemental: 1.0 pCi/cm^3
3. Tritium in the off-gas, water-soluble: 1.0 pCi/cm^3

The data for experiment T1 (Fig. 7) are presented as absolute concentrations without baseline corrections. The source for these initial concentrations was assumed to be tritium stored in the metal walls and/or from carbonaceous residues accumulated during the operation of the MSRE. The CSTF was constructed using portions of the MSRE piping. Presumably, the tritium diffused from the metal walls into the salt and subsequently appeared in the loop off-gas when operation of the CSTF was initiated.

During the addition period the concentration of tritium in the salt (open circles, Fig. 7) increased almost linearly to a maximum of about 100 nCi/g and then decreased approximately exponentially over the following three or four days to pretest concentration values. The apparent half-life for removal was between 9 and 12 hr, depending on how the data are extrapolated back to the end of the addition. Scatter in the sample results and lack of a sufficient number of sample measurements of the salt prevent a more accurate determination of the half-life for removal from the salt. If tritium removal from the salt is assumed to be a purely first-order process or combination of such processes, a time constant for removal from the salt is defined. The time constant may be the sum of several individual time constants, but the individual values would not be identifiable. Based on the time constant (or half-life), a trapping efficiency of the tritium by the salt can be calculated. A relatively

Fig. 7. Observed tritium concentrations in CSTF, experiment T1.

high trapping efficiency was calculated based on the 9-hr half life.
After the results from experiments T2 and T3 were analyzed where trapping
efficiencies of 50% and 55%, respectively, were determined, the trapping
efficiency of experiment T1 was re-evaluated. Based on the 12-hr half-
life, a trapping efficiency of 60% was determined. The 60% value for the
trapping efficiency appears to be more consistent with the values of ex-
periments T2 and T3.

The elemental tritium concentration in the off-gas (triangles, Fig.
7) rose to a maximum concentration of ∿830 pCi/cm^3 at the end of the addi-
tion and began to decrease as soon as the addition was stopped. The de-
crease in concentration with time was too irregular to justify any quanti-
tative evaluation.

Although no measure of elemental tritium concentration in the salt is
available, a value can be inferred from the concentration of elemental
tritium in the off-gas by (1) assuming that the elemental tritium in the
off-gas samples represents release from the salt and only from the salt,
and (2) assigning reasonable values to gas stripping parameters in the
CSTF pump tank. Calculating the concentration of elemental tritium dis-
solved in the salt in this way indicated that the ratio of combined/ele-
mental tritium in the salt was about 50. It appears that chemical inter-
actions between the tritium-containing compound in the off-gas and the
new metal of the sample line may have been responsible for the high con-
centrations of elemental tritium in the off-gas samples in this experiment,
based on the ratio of the two forms of tritium in the off-gas observed in
later experiments. The actual ratio of combined to elemental tritium in
the salt may have been higher. The combined tritium released from the
salt possibly was reacting with the surface of the new metal to consume
the combined form and to produce the elemental form. Once the metal be-
came conditioned, the combined tritium concentrations in the off-gas began
increasing, thus explaining why the maximum concentration of combined tri-
tium in the off-gas occurred several days after the end of the addition.
The ratio of the concentration of combined tritium in the off-gas to that
of the elemental form was substantially greater in experiments T2 and T3
than in experiment T1. Also, the combined tritium concentrations in the

off-gas of experiments T2 and T3 rose to their maximum values at the end of the addition periods.

The combined or water-soluble tritium in the off-gas (closed circles, Fig. 7) did not increase significantly until after the addition was completed and then rose to ∿1750 pCi/cm³ before decreasing in an irregular manner. Again, due to the scatter in the data, no quantitative evaluation of results of the combined tritium in the off-gas was attempted.

Based on the results from experiment T1 it was apparent that the sampling frequency in later experiments would have to be increased, especially for the 24—36 hr following the addition, to reduce the scatter and uncertainty associated with some of the results in order to permit a meaningful evaluation of the experiment.

4.2 Experiment T2

In experiment T2 approximately 34.3 cm³ of hydrogen at ∿1100 ppm tritium concentration was added to the CSTF for 10.4 hr. Thus, about 97 mCi of tritium was added to the system at a rate of ∿9.3 mCi/hr. The indicated tritium concentrations prior to the addition were:

1. Tritium in the salt: 1.0 nCi/g
2. Tritium in the off-gas, elemental: 1.0 pCi/cm³
3. Tritium in the off-gas, water-soluble: 50 pCi/cm³

Samples of the salt and off-gas were taken during the addition period and the following 16 days. Again, no baseline corrections were applied to the data for experiment T2 (Fig. 8).

The tritium concentration in the salt (open circles, Fig. 8) rose to a maximum concentration of ∿70 nCi/g at the end of the addition and decreased with an apparent half-life of 12 hr. Assuming that the 12-hr half-life completely describes the processes for removal from the salt, a trapping efficiency of 50% was calculated. The sample results of the salt suggest possibly other mechanisms with longer time constants are present. However, because of scatter in the data at longer times, they were not extracted. Consequently, a single first-order process with the 12-hr half-life was used to describe both the removal of tritium from the salt and the initial buildup. If the longer time constant or constants could be
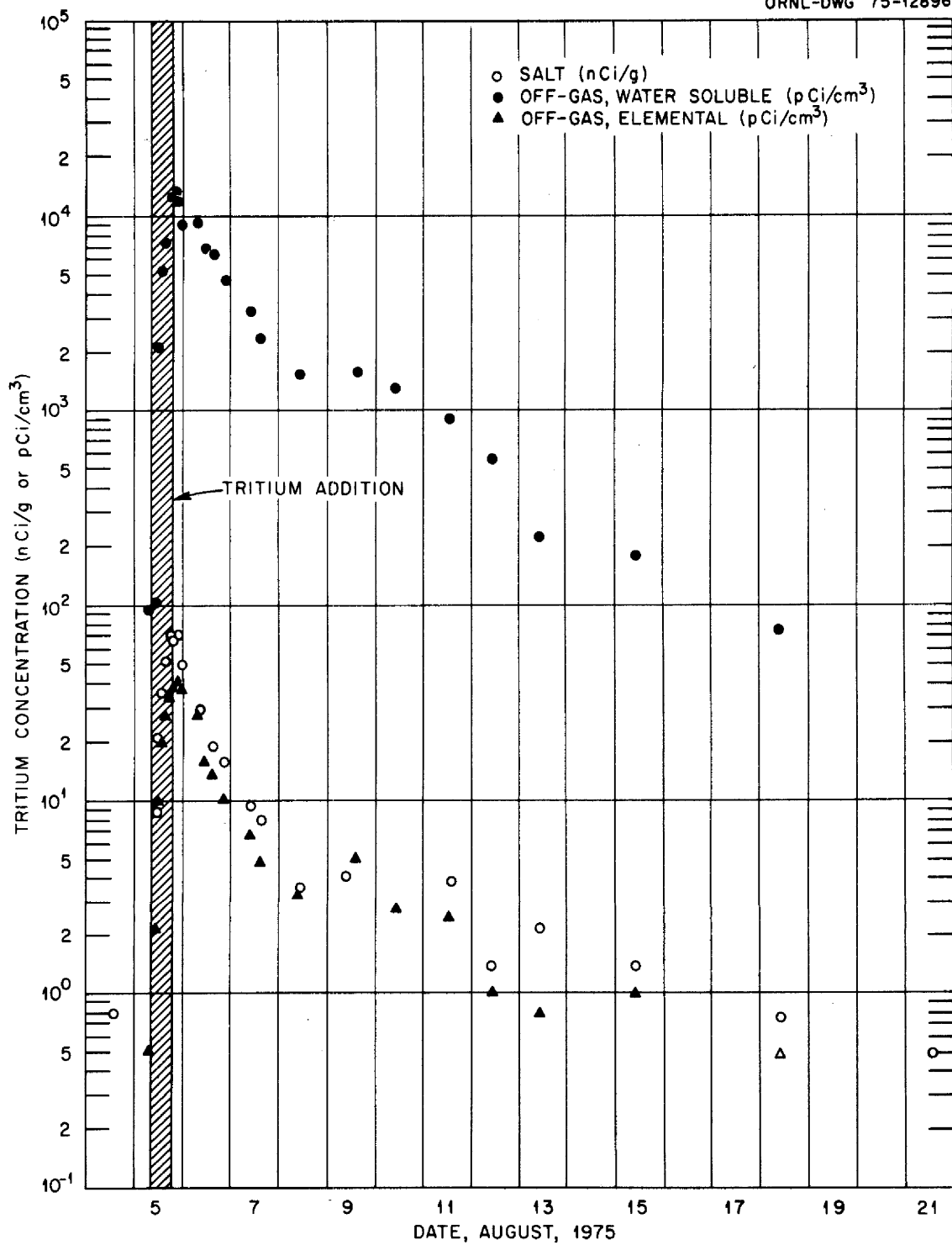
Fig. 8. Observed tritium concentrations in CSTF, experiment T2.

extracted, the half-life for the short-term process would be less than 12 hr. However, neglecting the longer time constant and using only the 12-hr half-life provide a reasonable basis for calculating the expected rate of tritium buildup in the salt. The comparison of calculated and observed inventories of tritium in the salt (Fig. 9) as functions of time during the addition period illustrate reasonable agreement. Improved agreement would be expected if additional time constants were factored into the calculation.
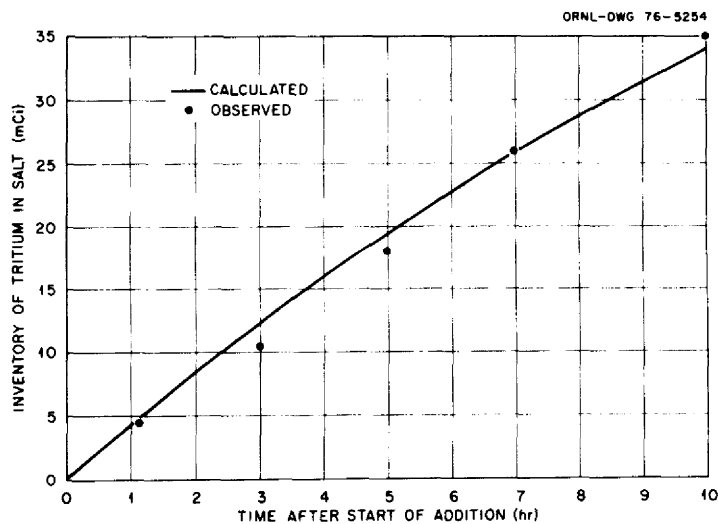
Fig. 9. Buildup of tritium concentration in salt, experiment T2.

The maximum concentration of elemental tritium (closed triangles, Fig. 8) in the off-gas was significantly lower than in the first experiment — 40 vs 830 pCi/cm3. A possible explanation for the marked difference between the two experiments was presented earlier in the discussion of experiment T1. Again assuming reasonable gas-stripping parameters for the CSTF pump, a concentration of dissolved elemental tritium in the salt was inferred. The ratio of combined tritium in the salt to elemental tritium in the salt was then determined to be 530.

The combined tritium concentration (closed circles, Fig. 8) in the off-gas increased rapidly during the addition and reached a maximum value of 13,100 pCi/cm^3 at the end of the addition. The ratio of the concentration of combined tritium in the off-gas to that of the elemental form was substantially greater in the second experiment than in the first. The initial decrease in concentration has an apparent half-life of 18 hr, but

the data again suggest the presence of other time constants. An attempt was made to separate the time constants by assuming that the decay curve was made up of two simple, first-order exponentials. This led to apparent half-lives of 9.3 and 37 hr for the two processes. Numerical integration of the water-soluble tritium data over ∿240 hr from the start of the addition yielded a total flow of 58 mCi through the off-gas line during the removal period and 7.5 mCi during the addition period. Thus, a total of 65.5 mCi or about 65% of the tritium added is accounted for as combined tritium in the off-gas stream during this test. (Numerical integration of the elemental off-gas data showed than an insignificant amount of tritium in this form had appeared in the off-gas system.) Calculations revealed that only ∿50 mCi of tritium had been released from the salt in the combined form. Thus, more tritium appeared in the off-gas system as combined tritium than could be accounted for through release from the salt. This discrepancy could conceivably be explained by a few apparently high off-gas sample results used in evaluating the integrated tritium off-gas flow. However, the magnitude of the discrepancy and evidence of long time constants for removal from the salt suggest that some of the tritium added accumulated in a reservoir other than the salt. The metal walls of the loop could possibly retain a portion of the remaining 35% unaccounted for. However, once the addition is stopped it would be expected that the removal of tritium dissolved in the metal walls would be as rapid as the build-up in the walls. Such was not the case as was observed, thus indicating a reservoir aside from the salt and metal walls.

4.3 Experiment T3

In experiment T3 approximately 30.5 cm^3 of hydrogen at ∿615 ppm tritium concentration was added to the CSTF for 9.9 hr. As a result, about 49 mCi of tritium was added to the system at a rate of 4.9 mCi/hr. Samples of the salt and off-gas before the addition indicated tritium concentrations were:

1. Tritium in the salt: 1.6 nCi/g
2. Tritium in the off-gas, elemental: 0.4 pCi/cm^3
3. Tritium in the off-gas, water-soluble: 38 pCi/cm^3

These concentrations are comparable to those obtained at the end of both the first and second experiments. Results from this third experiment (Fig. 10), which lasted for 24 days, again are presented uncorrected for any baseline concentrations.
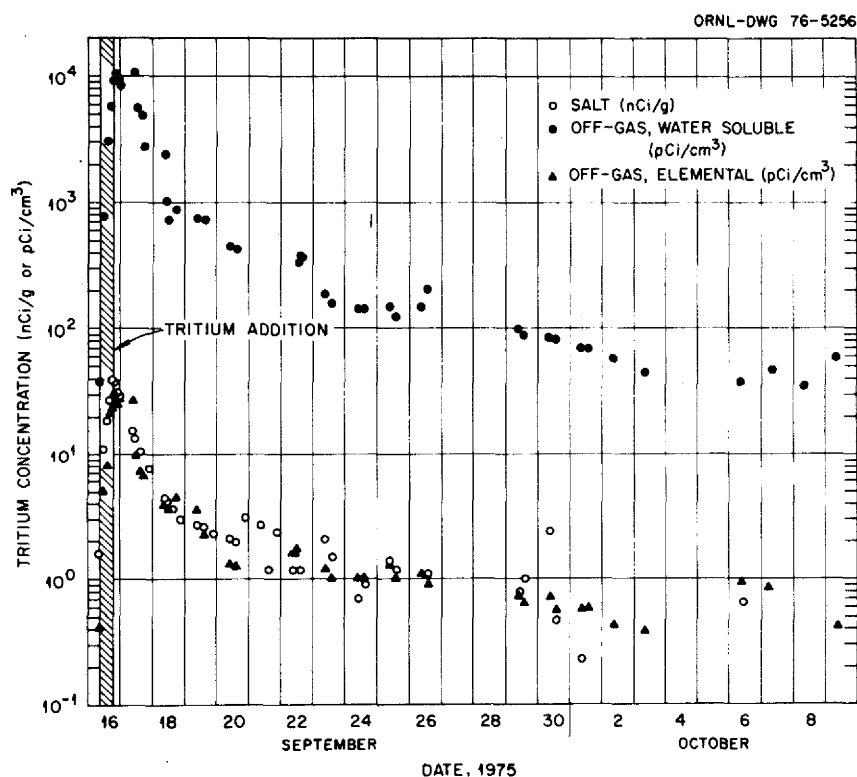
Fig. 10. Observed tritium concentrations in CSTF, experiment T3.

The tritium concentration in the salt peaked at ∿40 nCi/g at the end of the addition period and decreased in a manner similar to that observed in the previous two tests. If two first-order processes for removal of tritium from the salt are assumed, the apparent half-lives for the processes are 8.7 and 108 hr respectively. The tritium trapping efficiency of the salt determined by the time constants associated with the two half-lives was 55%. Recalling that the trapping efficiencies of experiments T1 and T2 were 60% and 50%, respectively, the trapping efficiencies then for the three experiments are reasonably consistent.

Using the 8.7- and 108-hr values for the half-lives, the same comparison as was made in experiment T2 was made between the calculated and observed inventories of tritium in the salt as functions of time during the

addition period (Fig. 11). Extracting a second half-life for removal from the salt as was done here in experiment T3 provides a somewhat better description of the buildup in the salt than using only one half-life for describing the buildup in the salt as was done in experiment T2.

Elemental tritium in the off-gas reached a maximum concentration of 30 pCi/cm^3, which was significantly higher than in experiment T2 relative to the tritium concentration in the salt. The elemental tritium concentration in the salt, which is inferred from the elemental tritium concentration in the off-gas, led to a combined/elemental tritium ratio in the salt of 380.

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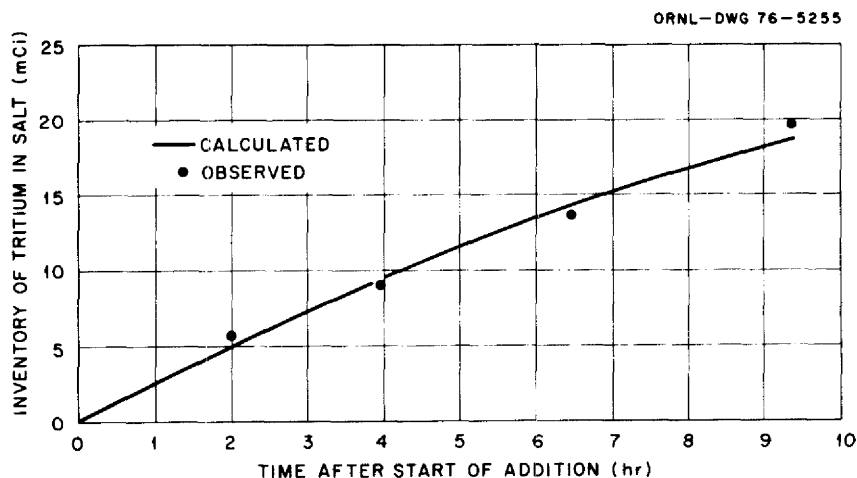
Fig. 11. Buildup of tritium concentration in salt, experiment T3.

The combined tritium concentration in the off-gas system at the end of the addition was ∿10,200 pCi/cm^3. (A slightly larger value was recorded the day after the completion of the addition, but it was believed to be anomalously high.) This result also was significantly higher in relation to the tritium concentration in the salt than in the second test. The time behavior of the concentration of tritium in the off-gas was examined even though there was a substantial amount of scatter in the data. As in the second test, two first-order time constants were apparent. The half-life of the more rapid process ranged from 7—15 hr, while the half-life for the longer process was about 70 hr.

A similar treatment of this data as was done in the second experiment indicated that after 150 hr from the start of the addition of experiment T3, about 25 mCi of tritium had been removed from the salt and that about

37 mCi of tritium had passed through the off-gas line. As in the second experiment, more combined tritium was appearing in the off-gas system than was being removed from the salt.

Measurements of the tritium concentration in the exhaust air from the loop enclosure of the CSTF were made shortly after the end of the addition period in an attempt to determine the rate of tritium permeation through the loop walls. These measurements were invalidated by simultaneous operations to dispose of excess tritium from the addition station by venting to the loop enclosure at the end of the third addition. When the loop sample results had reached previous baseline values, the loop sampling frequency was reduced and several tests were made to develop a method for determining the rate of permeation of tritium through the loop walls. Tritium was added to the loop enclosure and to one of the cooling shrouds on the loop piping while samples of the ventilation air were analyzed for tritium content. These tests led to the use of an air-sample tap in the discharge line from one of the coolers and to modification of the cooler inlets to supply fresh air (instead of air from within the enclosure) to that cooler. The results indicated that the tritium concentration in the air leaving the cooler would be readily and accurately measurable if anticipated loop-wall permeation rates were experienced.

Immediately after the end of the third tritium addition, some preliminary data were obtained to determine if the addition tube (or a similar device immersed in the main salt stream) could be used to measure the partial pressure of elemental hydrogen in the circulating salt. The addition tube was evacuated several times and then "isolated"; it was expected that any pressure rise within the isolated tube would be due to hydrogen diffusion from the salt into the tube. After each evacuation the pressure in the tube increased at a rate roughly consistent with the expected hydrogen partial pressure in the salt, but the pressure did not reach a steady value. It was subsequently determined that stray inleakage (presumably of air) was occurring and that the rate of inleakage was not sufficiently consistent to permit the extraction of meaningful data about the hydrogen partial pressure. However, it appeared that a sufficiently leak-tight device could be used to measure hydrogen partial pressure. Subsequently, such a device,

the hydrogen partial pressure probe, was constructed and installed in the CSTF for the steady-state experiments.

4.4 Summary of Transient Experiments T1, T2, and T3

Table 3 summarizes the various measured parameters and analyses for the tritium experiments T1, T2, and T3 performed in the CSTF.

The maximum concentrations of tritium in the salt for the three experiments were consistent considering the reduced addition rate for experiment T3. The ratios of water-soluble to elemental tritium in the off-gas for experiments T2 and T3 are comparable. Conditioning of new sample lines was believed to have altered the distribution of the two forms in the off-gas in experiment T1 which would also affect the ratio of combined to elemental in the salt since the elemental concentration in the salt was inferred from the elemental off-gas concentration. The ratios of the concentrations of the two species in the salt for experiments T2 and T3 are of the same order, and a larger value for T1 similar to those obtained in T2 and T3 would have been expected if the aforementioned conditioning phenomena had not occurred. The trapping efficiencies (60, 50, and 55%) determined for the three experiments are quite consistent. The sodium fluoroborate salt demonstrated that it could retain a substantial fraction of the tritium added.

The amount of tritium added that was not accounted for through removal by the off-gas and accumulation in the salt is assumed to (1) have been stored in the metal walls of the loop, (2) have diffused through the walls, or (3) have been stored in the undefined reservoir mentioned earlier.

Thus, it was decided to perform steady-state experiments using the cooling duct air sampling system and hydrogen partial pressure probe developed after the completion of the transient experiments to (1) define the distribution of tritium among the various sinks, (2) attempt to complete the material balance on tritium added to the system, and (3) observe a change, if any, in trapping efficiency at steady-state conditions as compared to transient conditions.

Table 3. Summary of tritium addition experiments
T1, T2, and T3 in the CSTF

Parameter	T1	T2	T3
1. Length of addition (hr)	10.8	10.4	9.9
2. Total gas added (cm^3)	33.6	34.3	30.5
3. Total tritium added (mCi)	86	97	49
4. Average tritium addition rate (mCi/hr)	7.9	9.3	4.9
5. T_2 concentration in H_2 (ppm)	1000	1100	615
6. T_2 concentration in salt at end of addition (nCi/g)	74	71	40
7. T_2 concentration in off-gas at end of addition (pCi/cm^3)			
Water soluble	1750	13,100	10,000
Elemental	820	40	30
8. Trapping efficiency (%)	60	50	55
9. Half-life for removal of tritium from salt (hr)	10.5	12	8.7
10. Half-life for tritium in combined form in off-gas (hr)		9	7–15
11. Ratio of combined to elemental in salt[a]	50	530	380

[a]See section 7 for further discussion.

5. RESULTS OF STEADY-STATE EXPERIMENT T4

Experiment T4 — the first steady-state experiment — was started on
February 3, 1976, and was completed on April 9, 1976. An attempt was made
to start this experiment on January 27, 1976, using an addition tube pres-
sure of 560 kPa (80 psia) to obtain an addition rate of 6 cm^3/hr. This
attempt was discontinued when the bypass rate of tritiated hydrogen into
the vacuum guard chamber surrounding the addition probe was found to be
significantly greater than had been observed during previous tritium tests.
This bypass rate was ∿14 times the rate at which tritium was reaching the
circulating salt. Measurements were made of the bypass leak rate as a
function of addition-tube pressure. Based on the results of those tests,
the addition-tube pressure was adjusted to 35 kPa (5 psia) in order to

keep the bypass leakage at an acceptable value (1.5 cm^3/hr). The tritium
concentration of the addition gas was increased to compensate for the re-
duced gas addition rate ($\sim$1.5 cm^3/hr).

Prior to the attempted addition on January 27, samples from the CSTF
showed the following tritium concentrations:

tritium in the salt:	<1—8 nCi/g
combined (water-soluble) tritium on off-gas:	20—50 pCi/cm^3
elemental tritium in off-gas:	5—17 pCi/cm^3
elemental tritium in cooling-duct air:	$\sim$Background[*]

Those pre-test samples taken on February 3, prior to actual start of the
test, were biased by the tritium added on the January 27 attempt.

5.1   Buildup and Attainment of Steady-State Conditions

The tritium concentration in the salt (open circles, Fig. 12) rose
in a manner similar to the transient tests to $\sim$500 nCi/g in about 2.5 days
following the start of the addition. It then gradually increased to a
steady-state value of 600—700 nCi/g over a three week period.

Several anomalously high concentrations of tritium in the salt were
observed during February and early March 1976. The location for salt
sampling was changed from the pump bowl to the salt-monitoring vessel (SMV)
on February 27, 1976, to permit an examination of the effects of sampling
procedure on the salt-sample results. The design of the SMV eliminates any
material that may tend to collect on the salt surface (and accumulate tri-
tium), so that "bucket" samples were taken and compared with "filter-stick"
samples which involve cover-gas flow through the sampling device. The
bucket samples from the SMV (both single and double) indicated tritium of
concentrations of 600 nCi/g ±5% in the salt. Filter-stick samples taken
from the SMV utilizing the same sample method employed in the pump bowl
indicated tritium concentrations comparable to those obtained in the pump
bowl, along with several high results. Consequently, the method using the
filter stick was modified on March 16, 1976, to eliminate possible contam-
ination of the samples by material in the gas lines connected to the filter

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[*]No detectable radioactivity by comparison with blank sample.
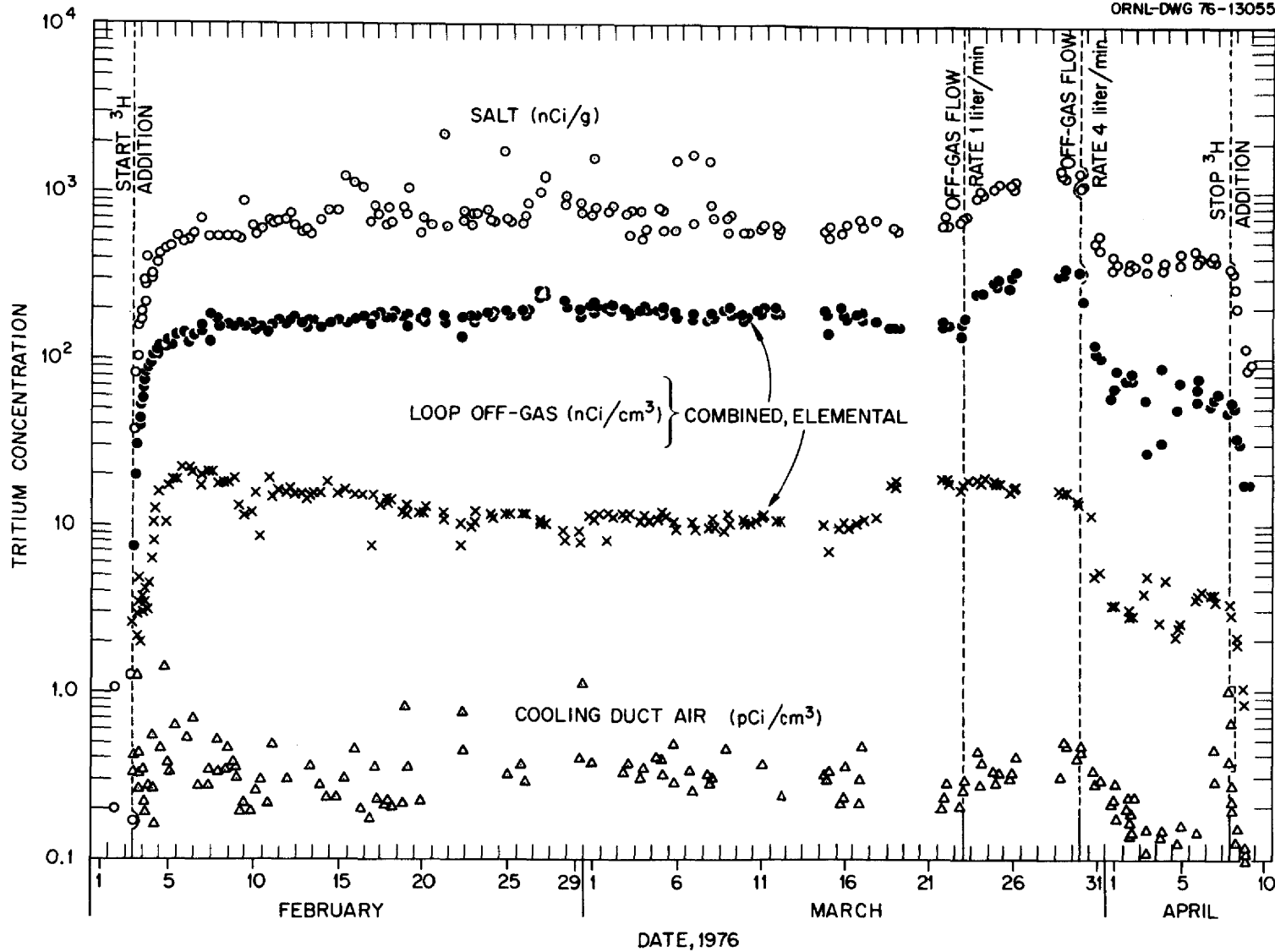
Fig. 12. Observed tritium concentrations in CSTF, experiment T4.

stick. The amount of scatter associated with samples of the salt following the modification of the procedure was greatly reduced.

The concentration of water-soluble (combined) tritium (closed circles, Fig. 12) in the off-gas increased from the pre-addition level to a value of 150 nCi/cm^3 in about 4 days from the start of the addition. Subsequently, it gradually rose to a steady-state value of 190 nCi/cm^3. At a 33-cm^3/s (2-liter/min) off-gas flow rate the 190 nCi/cm^3 concentration corresponds to 22.8 mCi/hr of tritium that was appearing in the loop off-gas system in the water-soluble (combined) form. An analysis of the data for combined tritium (hydrogen) in the off-gas indicates a hydrogen partial pressure of 8.3 Pa (62 μm Hg) in the gas phase, assuming ideal-gas behavior and one atom of tritium or hydrogen per molecule of compound. If this value represents equilibrium between the liquid and gas phases, the solubility coefficient for the water-soluble hydrogen form is 1.7×10^{-20} atm (molecule/cm^3 salt)$^{-1}$. This is close to the value of 1.1×10^{-20} estimated for the solubility of HF, which is one possible form of the water-soluble compound.

The elemental tritium concentration in the off-gas (x's, Fig. 12) showed irregular behavior and scatter for about 1 day following the start of the addition before increasing in an orderly fashion to a value of ∿22 nCi/cm^3. This irregular behavior was not entirely unexpected and may have been due to conditioning of new piping in the off-gas system that had been installed prior to this experiment. A somewhat similar phenomenon was observed during the first tritium addition experiment (T1). The concentration of elemental tritium in the off-gas subsequently decreased to a steady-state value of ∿10 nCi/cm^3. Thus, elemental tritium was appearing in the loop off-gas system at a rate of 1.2 mCi/hr. The gradual decrease may have also been related to the conditioning of surfaces.

Measurable concentrations of tritium were observed in the first sample taken from the cooling duct air only 2 hr after the start of the experiment. These concentrations varied from 0.2—0.8 pCi/cm^3. A value of 0.3 pCi/cm^3 was assumed for steady-state conditions. This was the current value at which time the concentrations of tritium in the off-gas were presumed to have reached steady-state concentration levels (early to mid March, 1976). Consequently, approximately 0.3 mCi/hr of tritium was permeating the walls of the CSTF. The apparent rate of hydrogen permeation through the loop

walls, based on the observed tritium concentrations in the loop cooling duct, was between 0.7 and 2.7 × 10^{-6} $cm^3(STP)/m^2 \cdot s$. If the hydrogen partial pressure in the salt is 0.4 Pa (discussed later in this section), this rate requires the effective permeability of the loop piping to be between 10 and 50 times lower than that of bare metal. A reduction of this magnitude would be consistent with the presence of an oxide film on the exterior metal surfaces.

With an addition rate of 1.65 cm^3/hr of tritiated hydrogen at 5775 ppm tritium or 24.5 mCi/hr, the following material balance at steady-state conditions was made (Table 4). Therefore, at steady-state conditions the material balance was 99% complete. Approximately 98% of the material that was being added appeared in the loop off-gas system. The trapping efficiency at steady-state conditions was assumed to be the ratio of the rate at which the water-soluble tritium was appearing in the off-gas system to the addition rate of tritium. The trapping efficiency for experiment T4 therefore was ∿93%.

Table 4. Steady-state material
balance for experiment T4

	(mCi/hr)
Addition rate	24.5
Removal rates	
Off-gas, water soluble	22.8
Off-gas, elemental	1.2
Permeation of loop walls	0.3
	24.3

As mentioned earlier there was a significant bypass of tritiated hydrogen into the vacuum guard chamber surrounding the addition probe during experiment T4. Therefore, an attempt at making an overall system material balance at steady-state conditions was made (Table 5). An addition rate of tritium was determined from the pressure drop of tritiated hydrogen in the tritium transfer (supply) cylinder. There were several removal rate terms associated with the addition system besides losses through the off-

Table 5. Overall system material balance at
steady-state for experiment T4

	(mCi/hr)
Addition rate — as determined by pressure drop of tritiated hydrogen in tritium transfer cylinder	42.0
Removal rates	
1. Off-gas	
Water-soluble (combined)	22.8
Elemental	1.2
2. Permeation of loop walls	0.3
3. Average removal rate for taking samples of the addition gas to determine the tritium concentration	2.4
4. Bypass rate into vacuum guard chamber surrounding the addition tube	12.0
5. Loss by permeation through walls of hydrogen purifier	3.0
	41.7

gas system and loop walls. Again, a material balance of 99% at steady-state conditions was determined.

In Table 6 are presented those hydrogen partial pressure probe measurements which were considered representative during experiment T4. The higher readings during the earlier part of the experiment were probably the result of extraneous hydrogen introduced into the loop when installing the probe. A value of ∿0.4 Pa (3 μm Hg) for total hydrogen partial pressure was consistent once the steady-state conditions were attained. This partial pressure of total hydrogen may be converted to a concentration of dissolved elemental tritium in the salt using a Henry's Law Constant for hydrogen dissolved in sodium fluoroborate and knowing the concentration ratio of tritium to hydrogen. The ratio of the concentration of the combined tritium in the salt to the concentration of elemental tritium in the salt at steady state was about 4300, based on a 650-nCi/g concentration of combined tritium in the salt and the 0.4 Pa partial pressure of total hydrogen.

Those measurements following March 12, 1976, were biased when extra-
neous hydrogen was introduced into the probe when a helium leak detector
was used in an attempt to measure the flow rate of mass 4 species — presum-
ably the same mass as an HT molecule formed once the hydrogen atoms and
tritium atoms had permeated the walls of the probe. (See Section 6.1 and
6.4 for further discussion of the helium leak detector.) The helium leak
detector measurements were intended to serve as a check on the partial
pressure probe readings, but no conclusive results were obtained.

Table 6. Representative hydrogen partial
pressure probe measurements for
experiment T4

Date	H_2 partial pressure	
	Pa	μm Hg
February 7—10	0.7	5
10—13	0.7	5
13—17	0.5	4
17—20	0.5	4
20—24	0.4	3
24—27	0.4	3
February 27 — March 1	0.4	3
5—9	0.4	3
8—12	0.4	3

Assuming a half-power dependence on pressure and the same tritium to
hydrogen ratio as was present in the addition gas, an inventory of ∿0.5 Ci
of tritium was stored in the metal walls of the CSTF at steady-state con-
ditions based on the 0.4-Pa partial pressure of hydrogen. Using these
same assumptions and 0.4 Pa partial pressure, the observed permeation rate
through the metal walls indicated a reduction in metal wall permeability
by a factor of ∿30 from reference values.

5.2 Change in Off-Gas Flow Rate

Once steady-state conditions were established, tests were conducted to obtain data on gas-liquid equilibria in the pump bowl. If equilibrium conditions had existed, decreasing the flow rate of gas in the off-gas system would have resulted in increased concentrations of both the combined and elemental forms of tritium in the salt and off-gas. Conversely, increasing the flow rate of gas in the off-gas system would have decreased the concentrations. If conditions in the pump bowl were mass-transfer limited on the gas side of the gas-liquid interface, changing the flow rate of gas through the pump bowl would cause different concentration changes. Similarly, if the mass-transfer limit were on the salt side of the interface, changes in salt flow would provide data on the nature of the limitation. On March 23, the flow rate of gas was lowered by a factor of 2, to 17 cm^3/s (1 liter/min). The concentrations of combined tritium in the salt and off-gas increased to about 1350 nCi/g and 340 nCi/cm^3, respectively. Changes in the elemental concentrations in the off-gas system and cooling duct air would be expected to occur less rapidly because of dissolution of element tritium in the loop piping. Concentrations of elemental tritium in the cooling-duct air increased to 0.4—0.5 pCi/cm^3 compared to 0.2—0.3 pCi/cm^3 concentrations prior to the change of off-gas flow rate. The concentration of elemental tritium in the off-gas was perturbed by a valve replacement in the gas-sampling system shortly before the gas flow was changed. Consequently, the effect of this flow rate change on the concentration of elemental tritium in the off-gas is not well defined. The elemental tritium concentration in the off-gas still, however, leveled out at about 16 nCi/cm^3. Thus, the various concentrations increased approximately a factor of 2 as would have been expected if equilibrium conditions existed. The tritium material balance on the system was reasonably complete, but true steady-state concentrations were not established with the reduced flow rate of purge gas.

When the purge-gas flow rate was increased to 68 cm^3/s (4 liters/min) on March 30, the concentrations of tritium in the off-gas decreased by more than the expected factor of 2 from the original steady-state condition. With the higher flow rate of purge gas the tritium material balance on the

system was only about 50% complete. This suggests that, at the $68\text{-cm}^3/s$ purge-gas flow rate, the gas stripping efficiency in the pump bowl is substantially reduced. The results also suggest that additional hydrogen (tritium) stripping may have been occurring as the purge gas flowed through the salt-monitoring vessel (SMV).

5.3 Stripping Period

After the addition of tritium to the CSTF was stopped, sampling was continued for only 24 hr into the stripping portion of the experiment so as to have ample time to prepare and conduct another steady-state experiment before having to shut the loop down. The initial half-lives for removal during this period as indicated by the sample results were:

11.8 hr for the water-soluble (combined) form in the salt,

7.5 hr for the water-soluble (combined) form in the off-gas, and

12.3 hr for the elemental form in the off-gas.

The values for the water-soluble form in the salt and off-gas were consistent with the values obtained for the transient experiments (Table 3). No values for removal of elemental tritium were extracted from the data of the transient experiments.

5.4 Tests for Tritium Concentration in Addition Gas

Tests were conducted after shutdown of the loop to independently measure the tritium concentration in the addition gas used in experiment T4 for comparison with results obtained from mass spectrometer analyses. The sampling system used for measuring tritium concentrations in the cooling-air duct was utilized for these tests. From mass spectrometer analyses of 14 samples of the addition gas taken during experiment T4, the average concentration of tritium in hydrogen in the addition gas was 5775 ppm. The average tritium concentration in 5 samples taken throught the cooling-air sampler was 5785 ppm.

6. RESULTS OF STEADY-STATE EXPERIMENT T5

Experiment T5 — the second steady-state experiment — was started on May 4, 1976, and was completed on June 30, 1976. (Sampling of the loop

off-gas was continued from July 1 — July 9, 1976, while helium was being circulated in the loop to reduce the level of radioactivity in the CSTF in preparation for the decommissioning of the loop.) The basic plan for T5 was to establish steady-state conditions and then make chemical additions to the salt to determine any resulting effect on tritium behavior.

After the completion of experiment T4, a new addition probe was installed to replace the original probe, which had developed a large leak between the addition gas chamber and the vacuum guard chamber. The new addition probe was essentially identical to the original one with respect to the material and geometry of the parts exposed to the circulating salt. The two tubes differed in that the new tube did not have corrosion specimens attached to the upstream face and the internal design was modified to reduce the potential for leakage to the vacuum guard chamber.

Results from experiment T4 indicated about 93% of the tritium added to the system at steady-state conditions was trapped in the salt and appeared in the off-gas system in the combined form. Since such a large fraction of the total amount of tritium was present in the combined form, any change imposed on the system to enhance the trapping capability of the salt might be difficult to monitor by observing the combined concentrations in the salt and off-gas. Also, with such a relatively low partial pressure of dissolved elemental hydrogen (tritium) in the salt in experiment T4, an increase in trapping efficiency might lower the partial pressure below the limits of the measurement capability with the present setup of the partial pressure probe.

The addition rate of total hydrogen for experiment T5 was to be comparable to the addition rate for experiment T4 but with an increase in tritium concentration in the addition gas by a factor of ~3. The objective was to increase the tritium concentration in the loop cooling air, which would provide a wider range of sensitivity to possible changes in the rate of tritium permeation through the loop walls that might result from any increase in trapping efficiency due to chemical additions to the salt. Also, a helium leak detector was to be connected to the partial pressure probe to measure the flow rate of tritium through the probe. Elemental tritium permeating the walls of the probe would be expected to form HT molecules (of mass 4) and produce a signal on the helium leak

detector. The partial pressure probe could be used in this manner should the partial pressure of total hydrogen fall below the limits of the measurement capability with the original setup.

The tritium concentrations in the system prior to the start of the addition for this experiment had not reached baseline values because only a minimal amount of time was involved in the stripping portion of experiment T4 (∿1 day) and startup of the loop (∿5 days) in preparation for experiment T5. However, the tritium concentration levels were judged to be low enough (∿10% of steady-state values obtained in experiment T4) to start experiment T5.

6.1 Buildup and Attainment of Steady-State Conditions

The tritium concentration in the salt (open circles, Fig. 13) rose rapidly for about 2.5 days following the start of the addition and attained an apparent steady-state concentration of approximately 2000 nCi/g. This concentration level was very consistent for ∿3 weeks as no anomalously high or low concentrations were recorded. The steady-state tritium concentration in the salt for experiment T4 was about 650 nCi/g, suggesting that T5 was much like T4 except for a factor of 3 in the concentration of addition gas.

The water-soluble (closed circles, Fig. 13) and elemental (x's, Fig. 13) forms of tritium in the off-gas increased rapidly for 2—3 days following the start of the addition and then approached their respective steady-state values more slowly. From May 10 through May 19, difficulties were encountered in obtaining meaningful off-gas sample results due to problems with a valve in the off-gas sampling system. On May 19, 1976, the valve was replaced and a conditioning period of ∿2 days followed before the tritium concentrations in the off-gas became consistent. This conditioning of new metal in the off-gas system also had occurred in experiments T1 and T4 previously when new lines or valves were installed. The apparent steady-state concentrations of tritium in the off-gas prior to the NaBO$_2$ addition were 655 and 20 nCi/cm^3 for the water-soluble and elemental forms, respectively.

Representative samples of the air from the loop cooling duct (triangles, Fig. 13) were not obtained until a week after the start of the
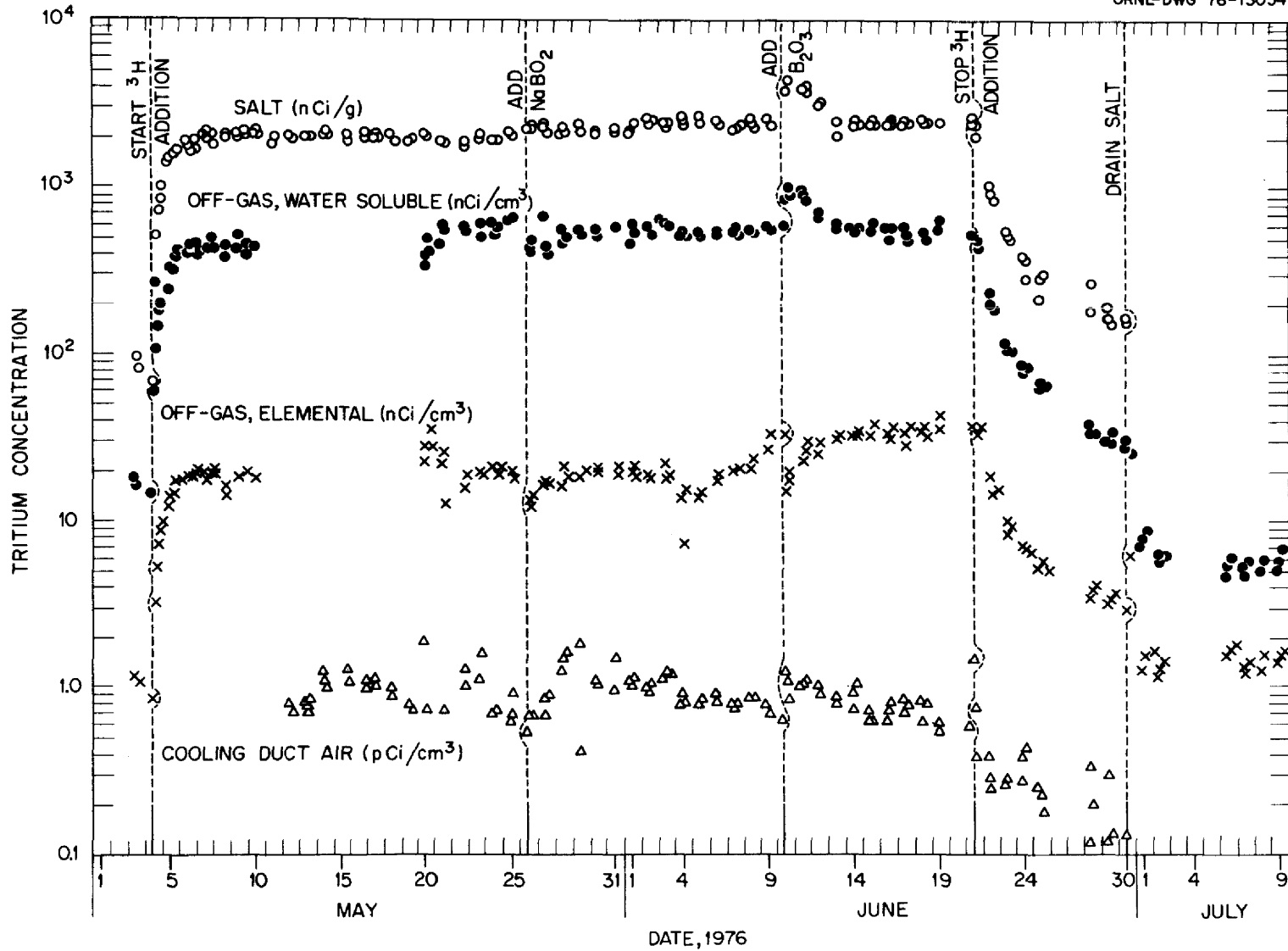
Fig. 13. Observed tritium concentrations in CSTF, experiment T5.

tritium addition. The system had been contaminated from the tests conducted to determine the tritium concentration in the addition gas after the completion of experiment T4. After correction of this condition, the tritium concentrations varied from 0.7—1.2 pCi/cm^3. A value of 1.0 pCi/cm^3 was assumed for steady-state conditions.

Table 7. Steady-state material
balance for experiment T5

	(mCi/hr)
Addition rate	83.0
Removal rates	
Off-gas, water soluble	78.6
Off-gas, elemental	2.4
Permeation of loop walls	1.0
	82.0

Prior to the start of experiment T5 the new addition probe was installed in the CSTF. The bypass rate of tritiated hydrogen into the vacuum guard chamber for experiment T5 was neglible whereas in experiment T4 with the original probe the bypass rate was significant, thus complicating the calculation of the addition rate of gas to the salt. Based on an addition rate of 1.68 cm^3/hr of hydrogen at 19,000 ppm tritium or 83 mCi/hr, the material balance for experiment T5 at steady-state conditions is as presented in Table 7. At steady-state conditions the material balance for experiment T5 was 99% complete as in experiment T4. Approximately 98% of the tritium that was being added appeared in the off-gas system as in experiment T4. The trapping efficiency for experiment T5 was 95% as compared to 93% for experiment T4. The rate at which elemental tritium appeared in the off-gas was 2% lower in experiment T5 than in experiment T4. This 2% of tritium appeared as combined tritium in experiment T5 since the percentage of tritium permeating the loop walls was the same (1.2%) for both steady-state experiments.

The difference in trapping efficiencies for the two steady-state experiments could be the result of the limitation of measurement capabilities

of the sampling systems since such a large fraction of the tritium added
appeared in the off-gas system in the water-soluble (combined) form.
However, examining the ratio of the concentrations of water-soluble tritium
in the off-gas to elemental tritium in the off-gas over the duration of
the two experiments seems to indicate that some equilibrium distribution
between the two forms was being approached. During the early part of
experiment T4 the ratio of the two species (water soluble/elemental) was
∿10 and increased eventually to ∿20 prior to the change in off-gas flow
rate (Fig. 11). In experiment T5, once steady-state conditions were estab-
lished, the ratio further increased to 30. Conceivably, in the early
phases of the experiment a small amount of tritium being released from the
salt in the water-soluble form was reacting in the off-gas system to liber-
ate the elemental tritium. As equilibrium conditions in the off-gas system
were approached, the distribution or ratio of the two forms in the off-gas
system was approximating the actual ratio of the two forms as they were
released from the salt.

In Table 8 are presented those hydrogen partial pressure probe mea-
surements which were considered representative for experiment T5. From
May 10, 1976, until the addition of $NaBO_2$ to the loop where steady-state
or near steady-state conditions existed, the indicated partial pressure
of hydrogen was again 0.4 Pa (3 μm Hg). The ratio of the concentration
of combined tritium in the salt (2000 nCi/g) to the dissolved elemental
tritium in the salt as determined by the 0.4-Pa partial pressure of hydro-
gen was ∿4270 as compared to ∿4300 for experiment T4.

Based on the 0.4-Pa partial pressure of hydrogen and assumptions made
for similar calculations for experiment T4 discussed in Section 5.1,
approximately 1.7 Ci of tritium was stored in the metal walls and a reduc-
tion in metal wall permeability by a factor of ∿30 from reference values
was again indicated.

Those measurements taken after May 21, 1976, are somewhat questionable.
On May 24, 1976, an attempt was made to obtain a reading from the partial
pressure probe using a helium leak detector. Apparently, a leak had de-
veloped at the connection between the probe and the leak detector. Sub-
sequently measurements (those in June, 1976) with the probe showed that
the rate of pressure rise in the probe was considerably more rapid than

previously observed. Consequently, no results could be extracted from some of the measurements, and those measurements during June of 1976, that are presented in Table 8 may have been biased. Therefore, not much significance should be attached to these partial pressure probe measurements in connection with the chemical additions made to the salt during this same time period.

Table 8. Representative hydrogen
partial pressure probe
measurements for
experiment T5

Date	H_2 partial pressure	
	Pa	μm Hg
May 5	0.5	4
6—7	0.7	5
10—11	0.4	3
12—14	0.4	3
17—19	0.5	4
20—21	0.4	3
June 1—3	0.7	5
4—7	0.8	6
11—12	0.7	5
15—16	0.7	5
17—18	0.5	4

6.2 NaBO$_2$ Addition to CSTF

A total of 120 g of sodium metaborate (NaBO$_2$) was added to the CSTF on May 26, 1976. The purpose of this addition was to increase the free oxide (total amount of oxide less that bound as hydroxide) content of the salt by about 100 ppm and to determine any effect on the trapping efficiency of the salt since oxide species in the salt were believed to be involved with the trapping process. The free oxide content of the salt prior to the NaBO$_2$ addition was between 410 and 450 ppm. Chemical analyses of the salt after the NaBO$_2$ addition showed a free oxide concentration of

∿570 ppm. (The hydroxide concentrations for these samples were in the few-ppm range such that the free oxide concentration was representative of the total oxide concentration also.)

The tritium concentration in the salt increased from a preaddition level of 2000 nCi/g to about 2200–2300 nCi/g. The tritium concentration subsequently leveled out at about 2500 nCi/g and maintained this level until the addition was stopped, being interrupted only by the transient effects of the B_2O_3 addition. The concentrations of both forms of tritium in the off-gas decreased after the addition. No noticeable change from preaddition levels occured in the tritium concentrations in the cooling duct air immediately after the addition was made. The establishment of the new, increased steady-state concentration of tritium in the salt with respect to the tritium concentrations in the off-gas indicate an improvement in the trapping capability of the salt. The off-gas concentrations returned to their preaddition steady-state levels ∿2 days later.

During the period of time after the $NaBO_2$ addition and before the B_2O_3 addition, changes in tritium concentrations in the system occurred. These changes may or may not have been associated with the $NaBO_2$ addition. However, the cause or causes of these changes could not be conclusively identified and were not investigated further because of time limitations associated with the MSR program.

The tritium concentration in the salt increased from ∿2200 to 2500 nCi/g about June 1, 1976. The elemental tritium concentration in the off-gas on June 4, 1976, decreased and subsequently increased to a concentration ∿1.5 times higher than the 20-nCi/cm^3 concentration observed at steady-state conditions and after the $NaBO_2$ addition. The behavior of the cooling duct air samples was not consistent with the behavior of the elemental tritium in the off-gas system as might have been anticipated since the tritium in the cooling duct air was also elemental in form. This implies that the behavior of elemental tritium in the off-gas system was not necessarily indicative of the behavior of elemental tritium elsewhere in the loop.

6.3 B_2O_3 Addition to CSTF

On June 10, 1976, ∿55 g of boron oxide (B_2O_3) was added to the CSTF. The purpose of the B_2O_3 addition was to further increase the oxide level of the salt. Also, the B_2O_3 was not completely anhydrous and, as a result, a small amount of water was added with the B_2O_3. The oxide level of the salt after the B_2O_3 addition was ∿710 ppm compared to ∿570 ppm before the B_2O_3 addition.

The tritium concentration in the salt increased from 2500 to ∿4000 nCi/g immediately after the B_2O_3 addition. The water-soluble tritium in the off-gas increased (from ∿600 to ∿1000 nCi/cm^3) in a similar manner as the salt did, while after the $NaBO_2$ addition it decreased. The elemental tritium concentration in the off-gas decreased (from ∿30 to ∿15 nCi/cm^3) immediately after the B_2O_3 addition, as it had done after the $NaBO_2$ addition. (Apparently, the B_2O_3 addition interrupted the establishment of a new concentration level of elemental tritium in the off-gas which had begun just before the B_2O_3 addition.) The tritium concentrations in the cooling duct air increased from ∿0.7 to 1.0 pCi/cm^3 after the B_2O_3 addition. The magnitude of the transient effect associated with the B_2O_3 addition was greater than that resulting from the $NaBO_2$ addition. Some 3–4 days were required for the concentrations to return to their pre-B_2O_3 addition levels.

The inventory of tritium in the salt before the B_2O_3 addition associated with the 2000 nCi/g concentration was ∿1 Ci of tritium, and correspondingly for the 4000 nCi/g concentration resulting after the addition of B_2O_3 the inventory of tritium in the salt was 2 Ci. The addition rate for experiment T5 was only ∿83 mCi/hr. In order to compensate for such a rapid increase in the inventory of tritium in the salt (and ultimately increased concentration in the water-soluble form in the off-gas), the B_2O_3 and water addition must have brought about the release of elemental tritium from another reservoir, making more tritium available for trapping by the salt.

The inventory of dissolved elemental tritium stored in the metal walls of the loop piping would have been enough to account for the observed increase in tritium inventory in the salt. Approximately 1.7 Ci of tritium (as noted in Section 6.1) could have been stored in the metal

of the loop piping. However, for the metal walls to act as such a reservoir would require a significant decrease in the partial pressure of total hydrogen in the salt such that hydrogen (tritium) dissolved at a higher partial pressure in the metal walls would have diffused from the walls into the salt. No such decrease of partial pressure of total hydrogen in the salt was observed from the partial pressure probe measurements. Also, no decrease in the tritium concentration in the cooling duct air samples was noted which would be expected to accompany a decrease in the total hydrogen partial pressure — the driving force for hydrogen (tritium) transport through the loop walls. (This undefined reservoir is discussed further in Section 7.)

The decrease in the elemental tritium concentration in the off-gas indicates an apparent increase in the trapping capability of the salt as a result of the B_2O_3 addition. The water-soluble concentration of tritium in the off-gas would have been expected to decrease as a result of increased trapping efficiency as was observed after the $NaBO_2$ addition. However, the resulting increases in the concentrations of tritium in the off-gas and in the salt obscured any change in trapping efficiency that may have been discernible by observing these two tritium concentrations.

6.4 Helium Leak Detector Measurements

The helium leak detector, as mentioned earlier, was connected to the hydrogen partial pressure probe for flow rate measurements of mass 4 species — presumably the mass of an HT molecule after hydrogen and tritium atoms permeated the walls of the probe. The helium leak detector was to provide a check on the hydrogen partial pressure probe readings. Based on the rate of pressure rise observed from the partial pressure probe readings, a flow rate of HT molecules was determined (assuming each tritium atom permeating the walls of the partial pressure probe combined with a hydrogen atom) to compare with the helium leak detector reading. The helium leak detector was also to provide an alternate method for determining the partial pressure of hydrogen in the event the chemical additions lowered the partial pressure of elemental hydrogen below the limits of the probe. This was not the case, however, as significant partial pressures of total hydrogen were observed after the two chemical additions (Table 8, p. 44).

Some difficulty was encountered initially in obtaining a reading on the helium leak detector. Finally, after increasing the sensitivity of the machine, two representative readings were obtained.

On June 7, 1976, a flow rate of 5.0×10^{-10} cm^3/s of mass 4 species was recorded with the helium leak detector. Based on the hydrogen partial pressure probe measurement for the three days preceding this helium leak detector reading, a flow rate of 6.0×10^{-10} cm^3/s was calculated. Similarly, on June 18, 1976, a helium leak detector reading of 2.2×10^{-10} cm^3/s compared favorably with a flow rate of 4.0×10^{-10} cm^3 determined from the probe measurement made during June 14—16, 1976.

Thus, the probe appeared to be a reliable measure of hydrogen partial pressure in the loop. Even though the partial pressure of total hydrogen may have been artificially high at the time the measurements with the two devices were made (due to a leak in the connection between the helium leak detector and hydrogen partial probe discussed earlier in Section 6.3), the agreement obtained with the measurements by the two devices serves to substantiate the 0.4-Pa (3 μm Hg) total hydrogen partial pressure obtained at steady-state conditions during experiments T4 and T5.

6.5 Extraneous Source of Hydrogen in Off-Gas System

After the early failure of the helium leak detector to measure the anticipated flow rate of HT molecules, a decision was made to determine the concentration of hydrogen in helium in the off-gas in the event that an extraneous source of hydrogen was present. By increasing the sensitivity of the helium leak detector, reasonable measurements were obtained; but the results from mass spectrometer analysis of the off-gas showed that there was ∿30 ppm elemental hydrogen in helium. Assuming an elemental tritium concentration in the off-gas system of 20 nCi/cm^3 and 19,000 ppm tritium in hydrogen from analysis of the addition gas, the elemental hydrogen concentration in helium should have been only 0.4 ppm or a factor of 75 less than that observed. The extraneous hydrogen could have been supplied from the decomposition of oil vapors resulting from an oil leak from the pump of the CSTF. A leak of only ∿0.1 cm^3/day of oil could account for enough hydrogen to increase the hydrogen concentration in helium from 0.4 to 30 ppm.

This extraneous source of hydrogen could explain some of the peculiar behavior observed in the samples of the off-gas and the gradual increase in ratio between the water-soluble and elemental forms of tritium in the off-gas noted during experiments T4 and T5. The extraneous hydrogen could have been exchanged with some of the tritium in the water-soluble form in the off-gas system. As equilibrium conditions in the off-gas system were established, a more representative value for the distribution between the two forms was being approached.

If extraneous hydrogen were present in the loop, the measurement of the flow rate of HT molecules with the helium leak detector would have been significantly lower (due to the diluent effect of the extraneous hydrogen) than that predicted by calculations using the partial pressure probe measurements, which were based on a tritium to hydrogen ratio assumed to be the same as that of the addition gas. Since reasonable agreement was obtained from measurements using the hydrogen partial pressure probe and the helium leak detector, the indication is that if the extraneous hydrogen was present in the off-gas system, the behavior observed in the off-gas and pump bowl was not necessarily representative of behavior in the rest of the loop.

However, assume the extraneous hydrogen were present in the rest of the loop. Consider the potential effects on three of the parameters, separately, discussed thus far: (1) The amount of tritium permeating the loop walls of the CSTF would be greater if the extraneous hydrogen were not present. The partial pressure of total hydrogen in the salt would be lower by a factor of ∿100 (a factor of 100 is used here for discussion purposes rather than the apparent factor of 75 mentioned earlier). Assuming a half-power dependence on pressure for permeation of the metal walls, the total hydrogen (and hence tritium) diffusing through the metal walls of the system then would be decreased only by a factor of 10. But, the tritium concentration in the hydrogen passing through the walls of the loop would be increased by a factor of 100. The net result would be an increase by a factor of 10 in tritium permeating the metal walls of the CSTF. (2) The trapping efficiency of the salt could be expected to be higher than noted in experiments T4 and T5 if the extraneous hydrogen were not present. Since both forms of hydrogen (tritium and protium) are presumed to behave similarly, an increase in tritium concentration in the total

hydrogen available for trapping by the salt would result in an improved trapping efficiency. (3) The ratio of the chemically combined tritium in the salt to elemental tritium dissolved in the salt would be greater than observed if the additional hydrogen were not present. The partial pressure of total hydrogen in the salt would be less and hence the elemental tritium concentration in the salt which is derived from the total hydrogen partial pressure would be less also, thus increasing the ratio of combined to elemental forms in the salt.

Since the combined to elemental ratio was used for extrapolating to MSBR conditions, the ratios determined for experiments T4 and T5 then represent conservative values because they were based on the same tritium concentration in hydrogen as that present in the addition gas.

6.6 Stripping Period

The stripping portion of experiment T5 was monitored for ∿9 days following the termination of the addition of tritium before draining the salt from the CSTF in preparation for decommissioning the loop. The data for the salt and both forms in the off-gas were resolved in two components as was done in experiment T3. The following half-lives were extracted from the data:

> 11.1 and 112 hr for the water-soluble (combined) form in the salt,
>
> 12.7 and 105 hr for the water-soluble (combined) form in the off-gas,
>
> 12.6 and 137 hr for the elemental form in the off-gas.

Again, the half-lives for removal for experiment T5 are comparable to those obtained from experiments T1–T4.

During the stripping period more tritium was appearing in the off-gas system than could have been supplied by the salt. This suggests the presence of the previously mentioned reservoir that apparently had built up an inventory of tritium, and once the partial pressure of hydrogen (tritium) in the salt began to decrease after the addition was stopped, the elemental hydrogen (tritium) was transferred from the reservoir to the salt where it was trapped and eventually appeared in the off-gas system.

Helium was circulated in the loop after the salt was drained from the loop on June 30, 1976, until July 9, 1976. Off-gas and cooling duct air samples were taken during this period. The cooling duct air samples were

Table 9. Summary of tritium addition experiments
T4 and T5 in the CSTF

	Parameter	T4	T5
1.	Length of experiment (days)	66	58
2.	Average addition rate of gas (cm^3/hr)	1.65	1.68
3.	Average tritium concentration in addition gas (ppm)	5775	19,000
4.	Average tritium addition rate (mCi/hr)	24.5	83.0
5.	Steady-state concentrations		
	Salt (nCi/g)	650	2000
	Off-gas, water soluble (nCi/cm^3)	190	655
	Off-gas, elemental (nCi/cm^3)	10	20
	Cooling duct air, elemental (pCi/cm^3)	0.3	1.0
6.	Trapping efficiency (%)	93	95
7.	Ratio of chemically combined to elemental in salt	4300	4270
8.	Half-lives for removal (hr)		
	Salt	11.8	11.1; 112
	Off-gas, water soluble	7.5	12.7; 105
	Off-gas, elemental	12.3	12.6; 137

negligible and thus are not shown in Fig. 12. The water-soluble tritium concentration in the off-gas was between 5–6 nCi/cm^3 and for the elemental tritium concentration in the off-gas was ∿1.5 nCi/cm^3.

7. INTERCOMPARISON AND INTERPRETATION OF EXPERIMENTAL RESULTS

Experiments T4 and T5 are summarized in Table 9. Analysis of data from the two experiments indicate reasonable agreement and reproducibility for such parameters as trapping efficiency, ratios of chemically combined tritium in the salt to elemental tritium in the salt, and half-lives for removal from the salt and off-gas. The material balance at steady-state conditions for both experiments was essentially complete.

For both experiments approximately 3 weeks were required to obtain steady-state conditions. Apparently, the reservoir discussed earlier required saturating before steady-state conditions could be established. This would explain why lower trapping efficiencies were determined for the

transient experiments T1—T3. The reservoir acted as another sink for the tritium added during these short-term transient experiments. However, once the system was at steady state as in experiments T4 and T5, a more accurate evaluation of sodium fluoroborate's trapping efficiency could be made. After the addition of tritium was stopped, the reservoir released tritium to the salt, thus explaining the discrepancy between the amount of tritium that appeared in the off-gas system as water-soluble and that released from the salt during the stripping periods as noted in experiments T2, T3, and T5.

It is thought that this reservoir may have been carbonaceous deposits on the surfaces of the pump and pump tank resulting from the decomposition of oil. After completion of the experiments, the pump was disassembled. A black carbon-like residue was observed on the shield plug and bearing housing of the pump and on the volute support cylinder in the pump tank. These and other surfaces exposed to the off-gas, when smeared, indicated appreciable levels ($1 \times 10^5 - 1 \times 10^7$ dis/min) of tritium contamination. The tritium was probably chemisorbed on the carbon. Those surfaces such as the pump impeller, exposed only to the salt were free of the black film and were not as highly contaminated with tritium.

In experiment T5, the additions of $NaBO_2$ and B_2O_3 appeared to enhance the trapping ability of sodium fluoroborate for a short period of time following the additions. The anticipated effects from the additions on the tritium concentration in the cooling duct air and on the partial pressure probe measurements did not materialize. However, the decrease in the elemental tritium concentration in the off-gas and increase in tritium concentration in the salt following the additions indicated improvement in trapping efficiency.

The ratio of combined tritium in the salt to elemental in the salt of ∿4300 determined for experiments T4 and T5 was the result of a more direct measurement than those ratios obtained for the transient experiments (Table 3), which were significantly lower. The values for the transient experiments were inferred from elemental off-gas concentrations. Since the results from the transient experiments after having conducted the steady-state experiments revealed that these experiments were not completely

representative of the trapping effectiveness of sodium fluoroborate, the ratios of combined tritium in the salt to elemental tritium in the salt obtained for the steady-state experiments were used to extrapolate to MSBR conditions.

8. EXTRAPOLATION TO MSBR CONDITIONS

Based on a value of ∿4000 for the combined to elemental ratio of tritium in sodium fluoroborate observed in CSTF tritium addition experiments T4 and T5, calculations were performed to examine the resulting behavior and distribution of tritium in an MSBR assuming this same ratio were established in the secondary salt of an MSBR. The same computer program[8] was used for this calculation as was used for earlier calculations that indicated as much as 1425 Ci/day of tritium could be transported to the steam system of an MSBR.

Presented in Table 10 are the results of the calculated distribution of tritium at steady-state conditions for the reference design[9] MSBR:

Case 1. Reference case where no special preventive measures are taken to mitigate the transport of tritium to the reactor steam system.

Case 2. Modified case where a value of ∿4000 for the concentration ratio of combined to elemental tritium in the salt was established in the reactor secondary or coolant system.

The following conditions were assumed for both cases:

1. No sorption of HT or HF (TF) on the core graphite.
2. Reference value of 10^2 for the U^{4+}/U^{3+} ratio in the fuel salt.
3. Bare-metal permeability for the steam tubes (no oxide film).

Furthermore, for the modified case, an 80% efficiency was assumed for removal of the chemically combined form (water-soluble form in off-gas of CSTF) on a 10% salt bypass stream ($0.5 \text{ m}^3/\text{s}$ — MSBR reference value).

The distribution of tritium in the primary or fuel system for the two cases is essentially the same, but in case 2 most of the tritium entering the secondary system is removed in the secondary system purge

Table 10. Extrapolation of results from CSTF tritium experiments to MSBR conditions

Calculated distribution of tritium in an MSBR^a for

Case 1. Reference case where no special preventive measures are taken to mitigate the transport of tritium to the reactor steam system.

Case 2. Modified case where a value of ∿4000 for the concentration ratio of combined to elemental tritium in the salt as determined from CSTF tritium experiments was established in the reactor secondary or coolant system.

	Distribution of the 2420 Ci/day produced in an MSBR (percentages)							
	Primary system			Secondary system			Steam system	
Case	Purge		Permeation of system piping	Purge		Permeation of system piping	T released	
	Elemental	TF		Elemental	TX^b		%	Ci/day
1	17.1	2.1	1.2	1.6		19.0	58.9	1425
2	16.4	2.1	1.2	0.004	80.1	0.05	0.16	4

^{a}MSBR conditions assumed for both cases: (1) no sorption of HT of HF (TF) on core graphite; (2) reference value of 10^2 for the U^{4+}/U^{3+} ratio in the fuel salt; (3) bare-metal permeability for the steam tubes (no oxide films).

^{b}For case 2, an 80% efficiency for removal of chemically combined form from a 10% salt bypass steam (0.5 m^3/s) is assumed.

in the chemically combined form. Tritium permeating the walls of the
primary and secondary system could be processed for removal from the
atmosphere of the primary and secondary cells and thus these cells are
considered to be sinks for tritium. In case 2, representing the extrapo-
lation from results obtained from the CSTF tritium experiments to MSBR
conditions, only 0.16% (4 Ci/day) of the 2420 Ci/day of tritium produced
in an MSBR was transported to the reactor steam system compared with 1425
Ci/day of tritium reaching the reactor steam system in the reference case.
This release rate of tritium to the environment would be within the range
of release rates from pressurized-water reactors (PWRs) currently oper-
ating. The release rate of tritium for the MSBR includes the entire fuel
cycle, while that for PWRs would be about 80 Ci/day if releases associated
with fuel reprocessing were included.

9. CHEMISTRY OF TRAPPING PROCESS IN SODIUM FLUOROBORATE

Although it was not possible to specifically identify the mechanisms
and chemistry by which tritium was retained by sodium fluoroborate,
studies[10] in the laboratory led to the postulation of several plausible
reactions involving species known to exist in the salt along with hydrogen
(tritium) and dissolved metal fluoride.

The trapping process can be described through two equations which
actually are the net result of several reactions. First,

$$2H_2 + 2MF_2 + \frac{1}{3} Na_3B_3F_6O_3 \rightleftarrows 3HF + 2M^0 + NaBF_3OH. \tag{1}$$
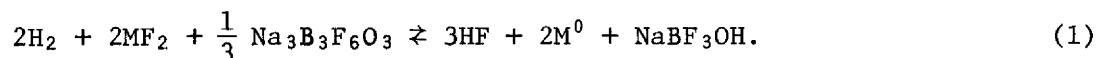
The equilibrium constant for this reaction is

$$K_1 = \frac{P_{HF}^3 \ (NaBF_3OH)}{(Na_3B_3F_6O_3)^{1/3} \ (MF_2)^2 \ P_{H_2}^2}.$$

The above expression is not entirely representative of the system since
HF and $NaBF_3OH$ can react according to:

$$HF + NaBF_3OH \rightleftarrows H_2O + NaBF_4. \tag{2}$$

This equilibrium constant for this reaction is

$$K_2 = \frac{P_{H_2O}}{P_{HF}(NaBF_3OH)} \cdot$$

NaBF$_4$ is not incorporated in the expression since it is the solvent. Finally, the system could be represented by combining K_1 and K_2 into the following expression:

$$K_3 = \frac{P_{HF}^4 (NaBF_3OH)^2}{(Na_3B_3F_6O_3)^{1/3} (MF_2)^2 P_{H_2}^2 P_{H_2O}} \cdot \tag{3}$$

Evaluation of the constant K_3 would lead to a quantitative description of the system. A more practical qualitative observation based on this expression is that tritium trapping would be favored by relatively high concentrations of oxide and/or metal fluoride in the salt along with a relatively high value for the partial pressure of water.

10. FURTHER EXPERIMENTATION REQUIRED

The tritium addition experiments conducted in the CSTF demonstrated sodium fluoroborate's effectiveness for sequestering tritium. However, further experimentation and research would be required to yield a better understanding of tritium behavior in sodium fluoroborate, to better define basic parameters, and to explain some of the observed phenomena as a result of conducting the experiments in the CSTF.

If the MSR program were to be continued, further investigation relating to the following would be desirable:

1. The chemistry of sodium fluoroborate and the trapping process by which tritium is retained by the salt.

2. Permeability values for Hastelloy N.

3. Solubility data for the dissolution of elemental hydrogen (tritium) in sodium fluoroborate.

4. Data on gas-liquid equilibria in the pump bowl in an effort to explain behavior such as that observed in experiment T4 when, upon increasing the off-gas flow rate to 4 liters/min, equilibrium conditions in the pump bowl between the gas and liquid were altered drastically.

5. Identification of the sink that required saturating before steady-state conditions could be established.

6. Determination of the existence of an extraneous source of hydrogen in the off-gas system and its effect (if present) on the behavior and distribution of tritium in the CSTF.

11. CONCLUSION

Originally, this group of tritium experiments conducted in the CSTF was to have been the first of several possible series of experiments to examine the potential of sodium fluoroborate for limiting tritium transport to the steam system of an MSBR. If favorable results were obtained from these experiments, namely that sodium fluoroborate would retain tritium, then further experiments and research were to be conducted to provide a complete description of the behavior of tritium in sodium fluoroborate. However, shortly after this series of experiments was begun, funding for the MSR program was withdrawn, effective at the end of fiscal year 1976. Thus, the results from these experiments could not provide a complete description or understanding of tritium behavior in sodium fluoroborate.

However, the results from these experiments, particularly experiments T4 and T5, have in fact demonstrated in an engineering-scale facility the effectiveness of sodium fluoroborate for trapping tritium. More than 90% of tritium added to the CSTF at steady-state conditions appeared in the off-gas system in a chemically combined (water-soluble) form. No chemical additions were made to the salt under these conditions. When chemical additions were made to the salt in experiment T5, increasing the oxide level in the salt, the trapping efficiency of the salt appeared to be further enhanced.

Calculations performed to extrapolate from the results obtained from the CSTF tritium experiments to MSBR conditions indicate that the release of tritium to the environment from an MSBR would be well within established guidelines.

Therefore, sodium fluoroborate is considered the leading candidate[11] as a secondary coolant for an MSBR and would be expected to adequately limit the transport of tritium to the reactor steam system and subsequent release to the environment.

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