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IN

SNAP SYSTEMS

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ABSTRACT

Most of the materials and components in the SNAP reactors under development at Atomics International become exposed to hydrogen during reactor operation. The hydrogen, from the zirconium-uranium hydride fuel elements, diffuses and migrates throughout the system before it is expelled to the high vacuum of space. The effects of this hydrogen on materials, components, and overall system performance is the subject of this report. Existing information on the behavior of hydrogen on specific materials and reactor components under reactor service environments is presented. Observations of hydrogen influence on the performance of ground test reactors is cited. Current and planned analytical and experimental studies to further elucidate the behavior of hydrogen are outlined, and recommendations are made for further work.

It is concluded that hydrogen migration and accumulation presents no great threat to the successful operation of the SNAP reactors. Analytical studies do show some potential problem areas, particularly in the Mercury Rankine conversion systems. However, sufficient uncertainties exist in the input data so as to require experimental verification. If these problems are indeed real, it is felt that they can be solved by prudent materials selection and subsystem design.

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I. INTRODUCTION

The SNAP reactors under development at Atomics International all use zirconium-uranium hydride as the basic fuel material. This material has a significant, if not high, equilibrium hydrogen overpressure (dissociation pressure), which is a function of composition and design operating temperature. Consequently, each fuel element is a miniature hydrogen pressure vessel. SNAP 8 fuel elements, for example, operate at an internal hydrogen pressure in the vicinity of 2 atm abs.

No known material is completely impermeable to hydrogen; and, although great advances have been made in the development of hydrogen barriers under the SNAP fuel element development program, a certain predictable hydrogen flux will pass through the ceramic diffusion barrier and Hastelloy N cladding.

The subsequent disposition of this ex-fuel hydrogen has been the subject of considerable speculation and concern. The possibility of NaK-hydride formation causing plugging of orifices, material embrittlement by hydrogen, collection of noncondensibles in Rankine-cycle condensers, pump depriming or cavitation, and accelerated corrosion have been proposed, giving rise to the phrase, "the SNAP hydrogen problem." It must be mentioned, at the outset of this report, that none of these phenomena has been observed to be significant in tests performed to the date of this writing. This is not to say that the "problem" is fictitious, but rather that there is yet no direct, tangible evidence as to the nature and scope of the "hydrogen problem." It is the purpose of this report to present a thorough discussion of the "hydrogen problem" in hydride-fueled SNAP reactor systems.

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II. CONCLUSIONS AND RECOMMENDATIONS

It is the general conclusion, from this study, that hydrogen migration and accumulation presents no great threat to the successful operation of the SNAP reactors under development at Atomics International. Analytical studies do show some potential problem areas, but sufficient uncertainties exist in the input data so as to require experimental verification. If, indeed, these problems are real, it is felt that they can be solved by prudent materials selection and subsystem design. A large, concentrated hydrogen effort is not recommended.

In this study, the influence of hydrogen was considered with respect to materials, components, and overall systems. The following conclusions can be made, regarding each of the three groups:

A. MATERIALS

1) The mechanisms of hydrogen permeation through structural materials are quite well established at high temperatures and pressure differentials in the vicinity of 1 atm. More work is needed, before the influences of low temperature and pressure, surface films, and liquid-metal interfaces are understood.

2) Hydrogen dissociation pressures over NaK-hydrogen compositions are well established at pressure levels exceeding 1 atm. Further studies are required in the low-composition, low-pressure regions, to improve the accuracy of analytical models for hydrogen distribution throughout the systems.

3) NaK hydride precipitation conditions seem to be sufficiently well established. Refinement of the data in the low-temperature region would be beneficial, but is not urgently needed.

4) A review of the effects of hydrogen on mechanical behavior of primary structural materials indicates that there should be no problems, under SNAP operating conditions. The effects of space vacuum, liquid metals, and nuclear radiation are considered far more significant.

5) Hydrogen effects on NaK corrosion appear to be negligible; and, in some instances, they may be slightly beneficial.

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6) The effects of hydrogen on mercury corrosion are unknown, but are probably not significant. However, a "proof test" is considered advisable.

7) Hydrogen effects on mercury wetting are unknown, but may be significant. Experimental work is recommended.

8) The effect(s) of hydrogen on the significant properties of auxiliary materials cannot be generalized. Every material which is contiguous with a hydrogen source must be qualified on the basis of insensitivity to hydrogen.

B. COMPONENTS

1) Degradation of the SNAP 10A thermoelectric elements by hydrogen is considered very remote. cursory studies have shown good stability after exposure to hydrogen.

2) Hydrogen degradation of the thermoelectric radiator emittance coating is improbable, because of space and material barriers between the coating and the hydrogen source.

3) The influence of hydrogen on the stability of diagnostic and control temperature sensors requires further study, under hydrogen concentrations which are likely to be encountered in reactor operation.

4) No problems with thermoelectric NaK pump performance are anticipated, due to hydrogen.

5) The effects of hydrogen gas on the mercury Combined Rotating Unit (CRU) are being evaluated at this time. The CRU appears capable of handling hydrogen bubbles of maximum credible volume, contingent upon the use of a moderately permeable radiator-condenser tubing material.

6) The presence of hydrogen in the Radiator Condenser (R/C) of the Mercury Rankine Program poses several potential problems. Most prominent are the alteration of heat transfer characteristics and the loss of bond integrity between condenser tube and radiator fin due to brittle hydride formation. Both of these problems are receiving intensive study.

C. SYSTEMS

1) There are no serious systems problems in SNAP 10A associated with the presence of hydrogen.

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2) No deleterious systems effects in the primary loop of the Mercury Rankine Program (Interim SNAP 10A/2) due to fuel element hydrogen release are expected. Based on analytical models of hydrogen distribution, potential effects of hydrogen gas in the secondary (Hg) loop are foreseen. It may be advisable to limit the hydrogen flow into the secondary loop by a barrier, getter, or boiler redesign. These alternatives are presently under study. The choice of radiator-condenser tubing material has a pronounced effect on the rate of accumulation of hydrogen above the condensing interface in the mercury loop. The concern here is with an associated potential deterioration of radiator-condenser performance.

3) The SNAP 8 primary loop will not be subject to hydride precipitation, although a small side-stream (bearing coolant) loop may operate in a questionable temperature-hydrogen concentration regime. The effects of hydrogen on the performance of the secondary loop have not been analyzed at Atomics International; but, if a questionable situation is found, an order of magnitude reduction in hydrogen permeation through the boiler is possible by use of a 10-mil tungsten diffusion barrier. An alternate solution might be to place an enamel (glass) hydrogen barrier coating on the mercury boiler surface. Preliminary studies⁽⁴³⁾ indicate that the present SNAP fuel element hydrogen barrier materials could be used with slight modifications. The effects of hydrogen on the tertiary NaK loop have likewise not been analyzed; however, it is postulated that these effects will not be significant, due to the anticipated large NaK volume of this loop, and the previous loss of primary loop hydrogen to space.

D. RECOMMENDATIONS

As a result of this review, the following recommendations are made:

- 1) Continue, at an increase in effort, the study of the experimental and theoretical aspects of the permeation of hydrogen through metallic materials. Geometric, surface chemistry, low-temperature, and low-pressure effects require elucidation, if realistic analytical treatments of hydrogen distribution through SNAP reactor systems are to be derived.
- 2) Continue studies on hydrogen dissociation pressures in NaK-hydrogen compositions in the 10^{-3} to 10^{-5} atm range.

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3) Initiate studies to effect a reduction of hydrogen transport from the primary to secondary systems. Hydrogen getters and barriers should be considered.

4) Expand the experimental and analytical effort on hydrogen distribution through the Mercury Rankine and SNAP 8 systems.

5) Continue evaluation and qualification of reactor system primary and auxiliary materials, on the basis of their insensitivity to hydrogen.

6) Analytical predictions of hydrogen distribution should be verified experimentally. Modification of existing subsystem and system test facilities, as well as incorporation of the proper diagnostic equipment into planned facilities, is recommended, in preference to the establishment of additional engineering-scale loops having the sole purpose of determining hydrogen distribution.

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III. HYDROGEN PERMEATION AND ABSORPTION PROCESSES

A. PERMEATION

The permeation of a gas through a solid barrier or membrane is defined as the steady-state transport of the gas from one side of the membrane to a lower pressure region on the other side. While the term permeation is generally applied to the overall process, it is in reality a rather complex mechanism involving several interrelated processes. Norton⁽¹⁾ has defined these intermediate steps as:

- 1) Impact of gas atoms or molecules on the surface of the membrane
- 2) Surface adsorption
- 3) Possible dissociation of the gas molecule (as in the case of a metallic membrane)
- 4) Solution of the gas in the wall at the incoming surface
- 5) Diffusion of gas atoms within the membrane under a concentration gradient
- 6) Transfer of the gas to the exit surface layer, with possible recombination
- 7) Desorption of the gas and release to the low-pressure side of the membrane

Figure 1 illustrates the sequence of these permeation steps.

For a given condition of permeation, one of these mechanisms has such a strong influence on the overall permeation process that it is considered the rate-controlling step. Usually, the permeation of hydrogen through metals is diffusion controlled. However, if the metal possesses an oxide surface film, or if the hydrogen pressure is sufficiently low so that the metal surface is "starved" of dissociated hydrogen atoms, the permeation rate may be controlled by the surface adsorption process. Experimentally, it has been found that, if the diffusion step of the permeation process is rate controlling, the permeation rate is inversely proportional to the thickness of the membrane. In the cases where surface adsorption is rate controlling, the inverse thickness relationship does not hold.

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$$F = SD_0 \frac{A}{x} \sqrt{\Delta P} \exp(-Q/RT) \quad , \quad \dots (1)$$

where

F = quantity of permeating gas per unit time

S = solubility constant

D_0 = diffusion constant

A = area of membrane

x = thickness of membrane

ΔP = pressure differential across membrane

Q = activation energy for process

R = universal gas constant

T = absolute temperature

From this equation, it is apparent that the permeation rate of diatomic gases through metals varies exponentially as the reciprocal of the absolute temperature, inversely as the thickness, directly as the area, and as the square root of the pressure.

Because of the interrelated nature of these processes to the overall permeation, it is extremely difficult to discuss each separately. Therefore, only the diffusion process will be considered in detail, and an attempt will be made to show how the other processes influence diffusion.

1. Diffusion

The term, "diffusion in a solid," applies to the internal process by which an atom is transferred from one point to another in the lattice. With gas diffusion in a solid, the diffusion process is difficult to measure experimentally. The overall permeation process is much easier to study, and these experimental values can be applied to theoretical diffusion concepts. Fick's theoretical work, presented in 1855,⁽²⁾ still represents the best descriptive basis of diffusion theory. Fick's first law, which deals with homogeneous or steady-state diffusion, states that the quantity of a diffusing substance which passes per unit time through a unit area of a plane at right angles to the direction of diffusion is proportional to the concentration gradient,

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$$J = -D \frac{\partial C}{\partial x} \quad \dots(2)$$

The factor, D, known as the diffusion coefficient or diffusivity, is a proportionality factor, and has the dimensions of (length)²/(time). The negative sign emphasizes that J is positive if the concentration, C, decreases in the direction of increasing membrane thickness, x.

This law is similar in form to Fourier's equation, stating that the flow of heat is proportional to the temperature gradient,

$$J_T = -k \frac{\partial T}{\partial x} \quad \dots(3)$$

and to a form of Ohm's law, where the electric current density is proportional to the electrical potential gradient,

$$J_e = \sigma E \quad \dots(4)$$

When possible, in this report, electric circuit analogies will be used to portray hydrogen flows, especially in complex situations where the illustrative value of such analogies are believed to outweigh the technical weakness that will be apparent to the critical reader.

Under the conditions where a permeable membrane separates two gas regions of the same species but at different pressures, the gas on the high-pressure side will migrate to the low-pressure region by diffusion through the membrane (see Figure 1). After sufficient time lapse, the gas entering the membrane on the high-pressure side is equal to the amount which is leaving the low-pressure or downstream side. At this point, steady-state diffusion is said to exist. Under such conditions, the concentration of dissolved gas in the membrane is constant with time. If it is assumed that the diffusion coefficient, D, is also constant, then the flux, J, in Ficks law ($J = -D \partial C / \partial x$) is a constant, independent of time and position within the membrane. This constant of steady-state diffusion is called permeability, and is a fundamental property of the membrane material. The permeability is proportional to both diffusivity, D, and solubility, S; and, to determine steady-state diffusion, both terms must be considered.

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2. Solubility Effects

There is naturally a close relationship between solubility and diffusion. If a gas is not soluble in a solid, it will not diffuse through the solid. For example, the diffusion of a noble gas through a metal has never been observed. In general, there is close correlation between diffusion rates and solubilities, but notable exceptions do exist. For example, nickel has a high solubility for hydrogen, as compared to that of iron, but nickel has a slightly lower diffusion rate.

Experiments⁽³⁾ have shown that the solubility (and diffusion) of hydrogen in metals is generally proportional to the square root of pressure (see exceptions under Section III-A-4). This behavior is evidence that a metal-hydrogen solid solution is formed. That this solubility-pressure relationship exists can be demonstrated by considering the chemical equilibrium conditions. The diatomic hydrogen molecule must first dissociate before it can dissolve in the metal;

Then, by solving for the equilibrium constant, K_p , for this equation,

$$K_p = \frac{[\text{H}^+]^2}{P_{\text{H}_2}} \quad \dots (6)$$

it is apparent that the concentration of hydrogen in solution $[\text{H}^+]$ is proportional to $P_{\text{H}_2}^{1/2}$. This relationship is known as Sievert's Law. Thus, the general permeation equation (Equation 1) has a solubility constant term, S , and a $\sqrt{P}$ term.

In the case of non-metals, no chemical combination takes place with hydrogen, and the solubility is proportional to the first power of hydrogen pressure. In this case, Henry's law for dilute solutions governs the process,

$$S = KP \quad \dots (7)$$

where S is the solubility, P is the pressure, and K a temperature-dependent constant. A general equation for the permeation of hydrogen through non-metals

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has the form:

$$F = SD_0 \frac{A}{x} \Delta P \exp(-Q/RT) \quad \dots(8)$$

This equation is analogous to Equation 1 for metals.

3. Temperature Effects

Most diffusion processes are strongly influenced by temperature, and hydrogen diffusion in metals is no exception. Since the measured hydrogen permeation constant (permeability) of a material is strongly influenced by temperature, it follows that the two fundamental properties of permeation, the diffusion constant, D , and the solubility, S , would also be strongly temperature dependent. The temperature dependence of these two properties may be expressed, to a first approximation, by:

$$D_T = D_0 \exp(-Q_D/RT) \quad \dots(9)$$

and

$$S_T = S_0 \exp(-Q_S/RT) \quad \dots(10)$$

Since permeability, K , is equal to the product of D and S , the temperature dependence of permeability may be expressed as

$$K_T = K_0 \exp(-Q_K/RT) \quad \dots(11)$$

From these equations, it is apparent that the properties vary exponentially as the reciprocal temperature. A plot of $\log K$ vs $1/T$ will yield a straight line. The slope of this line represents the activation energy for permeation. Such plots are presented, for a number of SNAP materials, in Figures 2 and 3. These plots are valuable, not only as a comparison of the permeation characteristics of various materials, but they also provide a means of extrapolating to temperatures beyond the experimental values. Caution should be exercised, however, in such extrapolations. It should be realized that, in large extrapolations, any experimental error is greatly magnified. Also, the metallurgical characteristics of the material must be known and understood, to insure that a phase transformation does not exist in the extrapolated region.

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Figure 2. Permeation Constants for Primary Loop Materials (Figure Unclassified)

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Figure 3. Permeation Constants for Secondary and Tertiary Loop Materials (Figure Unclassified)

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4. Pressure Effects

Experimental work on the diffusion of hydrogen through metals has mostly been conducted at hydrogen partial pressures between 0.5 and 3 atm. Most investigators have used a 1-atm pressure differential. As mentioned previously, the permeation of hydrogen through metals under these conditions has been found to be proportional to the square root of the partial pressure (Sievert's law).

At low pressures, however, there is a deviation from a square root relation toward a more linear relationship. This is because the steps of adsorption, dissociation, recombination, and desorption of hydrogen on the metal membrane surfaces assume a more influencing role. At low pressures, there is not an adequate supply of dissociated hydrogen at the surface of the membrane to satisfy the solubility requirements. It is postulated that, under this condition, the permeation is controlled by the metal-surface activity (adsorption), rather than by solubility and diffusion; therefore, the rate assumes a nearly linear relationship with pressure.

This deviation from Sievert's law at low pressures has been reported by several investigators.^(3, 4, 12) Recent work conducted at Atomics International⁽⁷⁾ also supports these findings. As shown in Figure 4, the hydrogen flow rate through Hastelloy N (0.010 in. wall) deviates from the square root of pressure relationship at pressures below 10 mm Hg.

5. Thickness Effects

In the diffusion of hydrogen through metals, where diffusivity and solubility are rate governing, the diffusion is inversely proportional to thickness. This has been experimentally verified by many investigators.^(8, 9) If, however, the surface absorption process is dominant, as in the case of low-pressure metal permeation and the permeation through non-metals, one would expect increased thickness to produce a lesser decrease in rate than predicted by the inverse thickness rule.⁽¹⁰⁾

6. Surface and Structure Effects

Surface processes strongly influence the hydrogen permeation process and, at times, represent the rate-controlling step in the overall process. On a metallic surface, the hydrogen is absorbed as the molecule; but, due to the surface activity, the molecule dissociates and diffuses through the metal lattice in the

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Figure 4. Low-Pressure Hydrogen Permeation Through Hastelloy N
[Showing deviation from Sievert's Law
($J \propto P^{1/2}$)]
(Figure Unclassified)

atomic or protonic form. On a non-metallic surface, no dissociation of the molecule occurs, and the hydrogen permeates in molecular form.

The condition of the surface has a considerable effect on permeation rate. Smithells and Ransley⁽¹²⁾ have shown as much as a ten-fold increase on an etched iron specimen over a polished specimen of the same material. Presumably, the increased surface area of the etched sample, together with the removal or disruption of any surface films, contributed substantially to this marked increase. Oxide films on metals have been found to have a marked effect on diffusion. With the surface no longer having sufficient activity to dissociate the hydrogen molecule, it must diffuse through the film lattice in molecular form. Because of the size difference between the atom and the molecule, the molecular diffusion is a much slower and more tortuous process.

Internal structure in a metal has been found to have only a limited effect on hydrogen diffusion. Edwards⁽¹³⁾ and Smithell and Ransley's⁽¹²⁾ studies on single crystal and polycrystalline iron have demonstrated that diffusion occurs through the metal lattice, and that grain boundaries and crystal size have negligible effect. Cold working apparently enhances hydrogen diffusion, possibly due to an increase in dislocation density. As would be expected, alloy additions of elements possessing high permeabilities will usually increase the diffusion rate through the alloy. However, any alloy addition which leads to a phase change may alter the diffusion rate considerably.

B. ABSORPTION

During the operation of the SNAP reactors, there is a slow but continual loss of hydrogen from the zirconium-uranium hydride fuel elements. This hydrogen, which permeates through the fuel element cladding, becomes exposed directly to the hot flowing NaK coolant. The NaK, in turn, acts as a "distributor," to move hydrogen through the primary system and to allow exposure of other components to this "core hydrogen." To predict the magnitude of this hydrogen distribution, one must understand the mechanisms of hydrogen absorption in NaK.

Both Na and K react with hydrogen at elevated temperatures. These metals can absorb large quantities of hydrogen, with ultimate formation of a hydride compound. The eutectic alloy of these two metals, NaK-78 (22 wt % Na - 78 wt % K), exhibits similar behavior. Although the term "NaK hydride" is often applied to the compound, it is likely that the hydrogen reacts preferentially with one of the alloy components (probably K). Efforts to identify the hydride compound have thus far been unsuccessful.

Hydrogen is absorbed in the NaK by the process of the hydrogen atom (or proton) occupying interstitial sites within the liquid metal lattice. When all available sites become occupied, the solubility limit is reached, and further addition of hydrogen causes the hydride compound to form and precipitate out of solution as minute crystals. From this point on, any further addition of hydrogen will produce additional solid hydride crystals. In all of these examples, the temperature of the NaK is assumed to be constant. As shown in Figure 5, the solubility limit is strongly dependent on temperature. This curve was established by independent plugging indicator studies and hydrogen dissociation pressure measurements. Any combination of temperature and hydrogen

Figure 5. Solubility Curve for Hydrogen in NaK
(Figure Unclassified)

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Figure 6. Hydrogen Dissociation Pressure Isotherms of Hydrogen in NaK
(Figure Unclassified)

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concentration which lies above the curve will cause precipitation of some solid hydride. The solid crystals which precipitate represent only a very small volume fraction of the NaK, and by no means implies that the NaK freezes solid. These hydride crystals might, however, cause fouling or plugging of the narrow coolant channels and orifices. As will become apparent in later discussions, under normal operating conditions of the SNAP reactors, precipitation of hydrides in the primary NaK loops is very unlikely.

It is common practice to refer to the driving force for hydrogen migration in NaK in terms of hydrogen partial pressure or dissociation pressure. Since dissociation pressure is a phenomenon related to free surfaces, such pressures per se cannot exist in a closed void-free NaK system. Actually, the terms "activity" or "fugacity" are more appropriate; but, if it is assumed that hydrogen behaves as an ideal gas (this is not a bad assumption for the conditions), then the terms partial pressure, activity, and fugacity are identical. Since pressure is a more tangible experimental quantity, it will be used throughout this report to denote the driving force for hydrogen diffusion.

NaK, with hydrogen absorbed in solid solution, possesses a finite hydrogen dissociation pressure. Like all gas-metal systems, this dissociation pressure is a function of hydrogen concentration and temperature. Dissociation pressure isotherms of NaK-H₂ compositions were established for several temperatures, as shown in Figure 6. This work, performed at AI, was undertaken primarily to determine solubility data for Figure 5, but it also gives an indication of the magnitude of the hydrogen dissociation pressures in the NaK-H₂ system. The sloping portions of the curves represent pressures at compositions where hydrogen is in solid solution in the NaK. The plateaus denote the magnitude of pressure when solid hydride is being formed. The knees of the curves reveal the concentration at which, for a particular temperature, the lattice can hold no more hydrogen in solution (solubility limit).

It is of interest to note that the solid hydride exhibits high dissociation pressures, and would be very unstable at reactor temperatures. For example, the solid hydride, even at 1000°F, has a dissociation pressure of about 20 atm. Since the fuel element hydrogen pressure is far below this figure, the NaK hydride would never form. The pressure (fugacity) in the NaK would build up until it equaled the fuel element pressure, and then all loss from the element would

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cease. Hydrogen loss through the NaK piping would make it even more remote that solid hydrides could exist at these temperatures. It is apparent that "NaK hydride" plugging is of concern only at temperatures considerably lower than those of normal reactor operation. As will be brought out in later discussions, predicted hydrogen concentration in the NaK is so small that the plugging problem is nonexistent, except in very cool side-stream loops. Potential plugging problems in advanced reactor systems, which will possess shutdown and restart features, are now under investigation.

From the curves in Figure 6, it is exceedingly difficult, if not impossible, to obtain anything but a gross indication of the dissociation pressure at the low NaK-H₂ compositions which are expected in the SNAP systems. For this reason, detailed studies are now underway, at both AI and Oak Ridge. Preliminary results, obtained at Oak Ridge,⁽¹⁴⁾ are presented in Figure 7. In these studies, calibrated amounts of hydrogen were added to a quartz envelope in which there was an Armco iron capsule containing about 10 g of NaK at test temperature. After each addition, the pressure on both sides of the iron capsule was allowed to equilibrate. This pressure represented the equilibrium dissociation pressure of the NaK-hydrogen solution. Data obtained, both on addition and removal of hydrogen, were further verified by postexperiment chemical analysis, giving a high confidence level for the experimental results. It is of interest to note that the data plotted in Figure 7 provide an ideal illustration of Sievert's law, where the concentration of hydrogen is directly proportional to the square root of pressure.

An experiment is underway at AI to provide additional information on hydrogen partial pressures in NaK. Elaborate capsules have been designed and built, to correlate these partial pressures with observed hydrogen permeation rates through stainless steel walls. No experimental information is available at this time. Further details on this experiment are found in Section VII.

As previously mentioned, the hydrogen dissolved in the NaK seeks release if a suitable "sink" is available. A "sink," in this case, is a region which has a lower hydrogen partial pressure than that of the hydrogen-NaK system. The ultimate sink for hydrogen in a SNAP reactor system is, of course, the vacuum of space, or in the case of ground test, the atmosphere surrounding the reactor system. Within the confines of the system, other intermediate or temporary

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Figure 7. Solubility of Hydrogen in NaK as a Function of the Square Root of the Hydrogen Pressure (Reference 14) (Figure Unclassified)

sinks exist. As the NaK is circulated through the primary loop, the dissolved hydrogen is brought in direct contact with the metallic walls of the system. Since the hydrogen sees a lower partial pressure on the other side of these walls, it will tend to leave the NaK, diffuse through the walls, and either be lost to space or enter other parts of the reactor system. It is this latter alternative which is of concern, and will be discussed in detail in later sections of this report.

Returning to the previous analogy of hydrogen flow to the flow of heat and to the flow of electricity, hydrogen sinks can be compared to units of extremely high specific heat and to units of extremely high capacitance, respectively. In

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all cases, there is a transient in the measured property until a saturation limit is approached, at which time the rates of input and output become equal.

The analogy to capacitance is especially appropriate to illustrate a hydrogen "getter." A "getter" is defined as a material which will absorb a large quantity of hydrogen under certain conditions of temperature and pressure.

The mechanism of hydrogen getter absorption can be illustrated by the idealized dissociation pressure isotherms in Figure 8. As initial hydrogen is absorbed at a constant temperature, T_1 , the hydrogen dissociation pressure of the getter increases with hydrogen composition along line AC. In this region, the hydrogen dissolves in the metal lattice of the getter to form an interstitial solid solution. When point "C" is reached, all available interstitial sites in the lattice have been filled (solubility limit) and the dissociation pressure and hydrogen composition are at P_1 and "X" wt %, respectively. When composition "X" is exceeded, a second condensed phase begins to form. The system is now univariant (two condensed and one vapor phase); and Gibbs Phase Rule dictates that, at temperature T_1 , the pressure must remain constant at P_1 as the hydrogen composition

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Figure 8. Idealized Metal-Hydrogen Dissociation Pressure Isotherms for a "Typical" Hydrogen Getter Material
(Figure Unclassified)

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increases from "X" to "Y" wt %. Therefore, with a system hydrogen pressure of P_1 , the getter can absorb up to "Y" wt % hydrogen. Exceeding this composition produces a single-phase hydride, and the dissociation pressure again increases rapidly with composition.

If the system pressure is lower (e.g., P_0), then, at temperature T_1 , point B on the isotherm cannot be exceeded. The absorptive ability of the getter is limited to a hydrogen composition of "W" wt %. Conversely, if the system pressure is of magnitude P_2 , then, at temperature T_1 , the getter will be able to absorb "Z" wt % hydrogen.

From these examples, it is apparent that the selection of a suitable hydrogen getter must be based on the pressure-composition-temperature relationships of the getter material, as well as on those of the system in which it will be used. Lack of sufficient information and/or uncertainties in reported data will require basic and engineering tests, to fully evaluate the efficiency of the selected getter material. A very slight change in system temperature or pressure will dictate whether the getter is in the "plateau" region, where it will be effective.

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Figure 9. Solubility of Hydrogen at 1 atm in Metals of Group A —
After Dushman⁽³⁾
(Figure Unclassified)

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Figure 10. Solubility of Hydrogen at 1 atm
in Metals of Group B — After
Dushman⁽³⁾
(Figure Unclassified)

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IV. HYDROGEN EFFECTS ON MATERIALS

A. MECHANICAL STRENGTH

The structural materials used in SNAP systems are required to withstand the deleterious effects of elevated temperature, irradiation, hard vacuum, and liquid metals. An additional environmental effect is that of hydrogen, which is produced during reactor operation. It is the intent of this section to consider the influence of hydrogen on the structural properties of metals, particularly those which are akin to the alloys used in SNAP systems.

Dushman⁽³⁾ has classified the interaction between hydrogen and the metals of interest in structural applications as:

Group A — Hydrogen forms true solutions with a number of metals, such as Cu, Ag, Cr, Mo, W, Fe, Co, Ni, and Al. These solutions have been verified by: (1) the observation that the solubility varies as $P^{1/2}$, and (2) the increase in solubility with an increase in temperature.

Group B — These metals of Groups III-A, IV-A, and V-A of the periodic chart have high solubility for hydrogen at low temperatures, with ultimate compound formation (Dushman points out that hydrogen is not absorbed by Au, Zn, Cd, In, or Tl).

Hydrogen solubility curves for these two groups are presented in Figures 9 and 10. It should be noted that the solubility of hydrogen in metals of Group B is 10^3 to 10^4 times that of the solubility in metals of Group A. The metals in Group B should be given careful consideration before selection for structural applications when hydrogen is present, because the hydride compounds formed are generally very brittle.

1. Low Temperature Properties

In considering Dushman's Group A metals (low solubility of hydrogen at low temperatures and no hydride phase present), it is found that iron and nickel (as well as Fe + Ni and Fe + Ni + Cr alloys) suffer embrittling effects.⁽¹⁵⁻¹⁹⁾ Even though hydrogen may be introduced during melting, solidification, heat treatment, and welding, most of the studies on these metals and alloys dealt with cathodically introduced hydrogen. This process introduces far greater quantities of hydrogen than would be absorbed by normal fabrication processes or by exposure to hydrogen gas at elevated temperatures.

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The embrittling effect of hydrogen in these metals is generally believed to arise from the hydrogen interacting with the deformation processes going on in the metal. The most common causes of hydrogen embrittlement in steels are electroplating and pickling. This embrittling effect is generally found only in low-alloy steels, the effect being virtually nonexistent for austenitic stainless steels. The hydrogen introduced from these operations (and that introduced cathodically, in most of the experiments) can be removed almost entirely by an adequate baking treatment. Even at room temperature, hydrogen diffuses in steel more rapidly than does carbon at heat-treating temperatures.⁽¹⁵⁾

A possible area of concern with hydrogen embrittlement would be the pickup of hydrogen by titanium braze alloys. Considerable caution should be used in brazing and subsequent heat treatment; further, the brazement should be qualified for service by simulated or real system tests.

2. Elevated Temperature Properties

The previous section discussed the embrittlement of metal by hydrogen which occurred only at intermediate temperatures, generally near room temperature. Since SNAP systems will be operational only at elevated temperatures, the mechanical behavior of metals in a hydrogen environment at elevated temperatures becomes of prime importance.

The literature concerning the mechanical behavior of metals in hydrogen at elevated temperatures is very limited. It has not been until the last four or five years that anyone has been concerned with this subject, and the research in this field is only beginning.

Douglas⁽²⁰⁾ reported that the creep rate of columbium at 1800 to 1850°F is greatly accelerated in any environment where hydrogen is present, whether as pure hydrogen or as water vapor. However, hydrogen did not seem to reduce the elevated temperature ductility of the material.

Garofalo⁽²¹⁾ concluded that the creep and creep-rupture properties of several ferritic and austenitic stainless steels at 1000 to 1200°F were not affected by an atmosphere of helium plus 2% hydrogen.

Klima⁽²²⁾ investigated the elevated temperature fatigue and stress-rupture properties of three high-temperature alloys in hydrogen. The test temperature for A-286 was 1200°F, while Inconel 700 and S-816 were tested at 1500°F. The

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fatigue properties of all alloys were unaffected by hydrogen. It was found that the stress-rupture life of the S-816 alloy at 19,000 psi was less in hydrogen than in air, and that the properties of the other two alloys were equivalent in both environments (57,000 psi for A-286 and 40,000 psi for Inconel 700).

The latest and most complete study has been performed by H. E. McCoy⁽²³⁾ The materials studied included two heats of Inconel, Nickel 200, Nickel 270, and electron-beam zone-refined melt of nickel, high purity copper, Armco iron, electrolytic iron, and Type 304 stainless steel. All of the nickel-base materials and copper exhibited inferior creep resistance in hydrogen, and the iron-base materials were not influenced by environment. Some of McCoy's conclusions on nickel-base alloys are:

- 1) At the same stress and temperature, the minimum creep rate is about 20% greater in a hydrogen environment than in argon.
- 2) The rupture life is 25% less in hydrogen than in argon at an equivalent stress and temperature.
- 3) The rupture ductility is not influenced by hydrogen.
- 4) Prestraining seemed to reduce the influence of hydrogen.
- 5) Hydrogen exerted a larger influence with decreasing strain rate and increasing temperature.

The chromized Hastelloy N cladding on SNAP fuel elements performs a multipurpose role. It protects the fuel from the NaK coolant, and serves as a base on which the ceramic hydrogen barrier is applied. In addition, the cladding must have good high-temperature strength, to withstand the internal hydrogen pressures produced by dissociation of the zirconium-uranium hydride fuel rods. Because this moderate, but constant, pressure is exerted on the cladding for thousands of hours, the creep properties of the cladding have been of prime concern.

Since hydrogen diffuses through the cladding during reactor operation, one of the parameters in the creep testing program at Atomics International was the effect of hydrogen diffusion on the creep behavior of the cladding. The tests were for 1000 hr duration at 1400°F. Test specimens were SNAP 8 cladding tubes which were internally pressurized to produce biaxial (hoop) stresses of 4000, 5000, 8000, and 12,000 psi. Duplicate tests were conducted with both

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hydrogen and argon as the pressurizing gas. The external environment on the tubes was vacuum ($\sim 10^{-3}$ torr.) Hydrogen permeated continuously through the specimens which were hydrogen pressurized.

Comparison of pre- and postdiametral measurements on the tubular specimens yielded the total strain experienced during testing. The creep rates obtained from this information are plotted in Figure 11. While a slight increase in creep rate during the hydrogen tests is indicated at the high stress level (12,000 psi), this effect is reversed at the low stress (4,000 psi). A more detailed analysis showed that all data fall within a normal scatter band, to be expected for such tests. It is therefore concluded that hydrogen, diffusing through the chromized Hastelloy N cladding, does not appreciably alter the creep characteristics of the material, under the temperature and stress conditions imposed. It should be noted that the stress levels in these tests were significantly higher than would be experienced by SNAP fuel elements. The high stresses were intentionally selected to provide a measurable strain in 1000 hr. Similar tests, designed for 5000 hr duration at a lower stress (1250 psi), are currently in progress to evaluate long-term effects.

It does not appear that the hydrogen in the SNAP systems will reduce the elevated-temperature strength of the current metals and alloys used in these systems. In those tests in which detrimental effects were observed, the test conditions

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Figure 11. Effect of Hydrogen on Creep Rate of SNAP Fuel Element Cladding (Reference 30)(Figure Unclassified)

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were more severe than those likely to be encountered in SNAP systems. Klima used cylinders for specimens with an internal hydrogen pressure of 500 psi, and McCoy used a flow rate of $0.5 \text{ ft}^3(\text{STP})/\text{hr}$. SNAP systems will not see pressures or flow rates of these magnitudes.

B. CORROSION

1. NaK

The effects of hydrogen on corrosion in NaK systems are being investigated by Aerojet General and Oak Ridge, as well as at Atomics International. To date, there has been no information generated which shows a significant effect of hydrogen on corrosion or mass transfer.

Most of the investigations have been with NaK-78 in loops at 1300°F , or at 1400°F maximum, conditions comparable to those in the SNAP 8 primary cooling loop. This NaK system operates at higher temperatures than SNAP 10A, and corrosion should be more severe than in the cooler systems.

Under the SNAP program at Atomics International, several thermal convection loops were designed to circulate NaK-78 at 1300°F , or at 1400°F maximum, with a ΔT around the loop of 200 to 250°F . Two of these SNAP NaK loops (SNAK III and SNAK IV) have been operating almost continuously for over a year with hydrogen in the NaK. Both were built of Type 316 stainless steel, filled with NaK, the oxygen level reduced with zirconium getters, and placed in service in December 1963. SNAP III has been operated empty (no fuel element or specimen inside), and has not been opened since the zirconium getters were removed 15 months ago; it is believed to contain very clean NaK. On the other hand, SNAK IV has been opened four times to change the fuel element in it. It has not been opened since May 1964. Initially, these loops were operated at 1300°F outlet for about 2-1/2 months. Then the outlet temperature was increased to 1390°F and maintained at this temperature to the present time. One loop (SNAK III), containing hydrogen added to the cover gas, has operated for 8450 hr at 1390°F (this includes 1450 hr operation without hydrogen). The second loop (SNAK IV) has been at temperature continuously for 6500 hr with hydrogen being supplied from a full size SNAP 8 fuel element in the hot leg of the loop.

Loop performance was monitored by observing changes in the ΔT , and also the power needed to maintain constant outlet temperature.* Results from these

*Previous experiments with comparable loops (SNAK I and SNAK II) had shown that these data are extremely sensitive indicators of mass transfer in thermal convection loops having an orifice just below the heater leg.

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Figure 12. Diagram of ORNL SNAP 8 Corrosion Loop
(Figure Unclassified)

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Figure 13. Diagram of ORNL SNAP 8 Hot Spot Loop
(Figure Unclassified)

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two loops show no discernible effect on mass transfer (evidenced by an increase in ΔT around the loop) caused by hydrogen additions. SNAK I and SNAK II exhibited pronounced plugging of the orifice holes by mass transfer deposits in a few hundred hours; the NaK in these loops had higher oxygen content. Reducing the oxygen content in one of these loops reduced its plugging rate, but no effect of hydrogen on the plugging rate was noted.

At Oak Ridge, an extensive evaluation of certain variables in the SNAP 8 primary NaK loop is nearing completion.^(14, 24-27, 41) Variables include oxygen, hydrogen, $T_{\max}$, and the velocity of the coolant. A total of 11 pumped NaK loops have been tested or are currently under test. The basic design of these loops is shown in Figure 12. Materials for loop construction were selected to include all alloys in the SNAP 8 primary system, and the relative surface areas exposed to NaK closely approximate the full-scale system. Two loops were modified slightly, as in Figure 13, to provide a hot, low-flow region to simulate a hot spot condition between two or more fuel elements. Some of the loops received a continuous hydrogen injection of 0.6 cc(STP)/hr throughout the test interval. The test conditions and variables for the ORNL loops are given in Table 1.

Results of the evaluations made to date are briefly summarized in Table 2. These results show essentially no detrimental effects of hydrogen on corrosion or mass transfer. In fact, there are indications that hydrogen may be advantageous in inhibiting carbon transfer from the Croloy 9M boiler material.⁽²⁸⁾ Hydrogen in the NaK may also reduce the oxide content somewhat, by formation of oxide complexes. The rather drastic effect of oxide content on corrosion and mass transfer supports similar observations at GE/San Jose⁽²⁹⁾ and at AI.

In summary, there is no significant effect on mass transfer or plugging which is related to hydrogen in NaK systems at typical SNAP operating conditions. Nor has any corrosion problem been recognized which can be related to the presence of hydrogen or to a hydrogen level. This is in sharp contrast to oxygen, which is known to create serious mass transfer problems.

2. Mercury

Mercury and hydrogen are essentially inert to each other. Hydrogen is reported⁽⁴²⁾ to be insoluble in liquid mercury. Therefore, there are no property changes in mercury attributable to the presence of hydrogen. There are,

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TABLE 1
PROGRAM OF ORNL LOOP STUDIES IN SUPPORT
OF SNAP 8

Loop	Time (hr)	Maximum [§] Temperature (°F)	O ₂ (ppm)	H ₂
1	700	1425 [†]	<30	0
1a	2003	1425	<30	0
2	2004	1425	~80	0
3	2000		Deferred	
4	2033	1425	>30	SNAP 8*
5	5133	1425	<30	SNAP 8*
6			Deferred	
7	2021	1300	>80	SNAP 8*
8	2053	1300	<30	SNAP 8*
9	2000	1300	>80	0
10	2000	1300	<30	0
11				Deferred
12				Deferred
13	2000	1300/1450**	<30	SNAP 8*
14	~700	1300/1450	<30	SNAP 8*

*SNAP 8 signifies hydrogen in the NaK to the extent expected in the full-scale SNAP 8 system.

[†]Maximum fuel cladding surface temperature in SNAP 8.

[§]1425°F is a wall temperature. 1300°F is a liquid outlet temperature, in which case the maximum wall temperature will be about 1320°F.

**1450°F is the temperature of the hot spot loop, while 1300°F is the main loop temperature.

however, two "side effects" worthy of consideration and comment. These are the effects of hydrogen on: (1) mercury corrosion, and (2) wetting.

It is difficult to postulate, on any theoretical basis, an effect of hydrogen on the corrosion of materials by mercury. As a result, this has never been a subject of systematic investigation. In studies conducted on Haynes-25 for the Mercury Rankine Program, corrosion in mercury systems seems to be a diffusion-controlled process, and not a surface-recession phenomena. The rate-limiting step is the diffusion of soluble elements to the surface of the Haynes-25 and their subsequent solution into the mercury.

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TABLE 2
EFFECT OF TEMPERATURE, TIME, OXYGEN, AND HYDROGEN ON CORROSION OF MATERIALS
IN SNAP 8 FORCED FLOW NaK CORROSION LOOPS*
[Corrosion (mg/cm²)[†] adjusted for carbon migration]

Material	Effect of Temperature (2000 hr in Low-O ₂ NaK)		Effect of Time (at 1400°F in Low-O ₂ NaK)		Effect of O ₂ (2000 hr at 1400°F)		Effect of H ₂			
							2000 hr, 1300°F, Low-O ₂ NaK		2000 hr, 1300°F, High-O ₂ NaK	
	1300°F	1400°F	2000 hr	5100 hr	<30 ppm	~80 ppm	No H ₂	0.6 cc/hr	No H ₂	0.6 cc/hr
Chromized Hastelloy N	-3	-8	-8	-20	-8	-8	-3.1	-2.5	- 7.6	-6.0
Type 347 Stainless Steel	-1	-1	-1	- 2	-1	-3	-0.8	-0.9	-35.1	-6.3
Croloy 9M	+0.1	+0.3	+0.3	- 0.3	+0.3	-1.5	+0.1	-0.03	Not reported	

*Information supplied by Oak Ridge National Laboratory

[†]23 mg/cm² $\approx$ 1 mil of uniform corrosion

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It is not anticipated that the presence of hydrogen will either increase the diffusion rates of the Haynes 25 elements that are soluble in mercury or significantly alter the corrosion process to change the rate controlling phenomena. Therefore, the boiler corrosion characteristics should not be adversely affected by the relatively small amount of hydrogen that may be present on the mercury-exposed surface.

The picture regarding the effect of hydrogen on mercury boiler wetting and heat transfer is far from clear. This is, in large part, due to the fact that the understanding of mercury wetting, even in the absence of hydrogen, is not well understood. Theoretically, boiler wetting may be improved by the presence of hydrogen. This would be accomplished by the hydrogen role in increasing the solid surface tension or surface energy by reduction of oxide surface films, and possibly by the reduction of the liquid surface tension.

The following effects of hydrogen have been verified:

- 1) Hydrogen annealing of Haynes 25 boilers at 2250°F does recondition boilers.
- 2) An extremely pure hydrogen atmosphere will be required to reduce the surface oxides of Haynes 25 at 1200°F.

In summary, hydrogen permeation from the NaK system into the mercury system should not adversely affect corrosion or boiler conditioning; and, indeed, it may improve the boiler performance.

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V. REACTOR EXPERIENCE

Four nuclear tests of SNAP reactors have been conducted successfully at Atomics International. Time-at-temperature data are summarized in Table 3. In the two reactors that have been disassembled, there was no evidence of any effect of hydrogen. Neither showed any evidence of mass transfer.

After S2DR shutdown, examination of core components showed some interaction between two fuel elements and adjacent beryllium internal reflectors. At the contact area, some beryllium had diffused into the Hastelloy N cladding. However, the small amount of diffusion did not affect performance of these elements. Future occurrence of such contact has been prevented by a design change, incorporated in the S2DRM-1 reactor.

In S8ER, currently on test, with more than 9,000 hr at 1300°F reactor outlet temperature, there has been no degradation of hydraulic performance, which would be indicative of a flow blockage by corrosion and mass transfer. Sampling of the cover gas above the surge tanks of the primary NaK loop and a secondary NaK loop (a heat rejection loop used for ground test in the absence of the power conversion system) has been performed.⁽³³⁾ Hydrogen was found in gas samples from both loops. Over a three-week period, a buildup of hydrogen was observed in the primary and secondary loops. The quantitative significance of these measurements has not yet been determined, but it does provide experimental verification of the ability of hydrogen to migrate to a secondary system.

During early power operation of S8ER, a NaK leak occurred in the discharge-header end cap of the pump being used to circulate NaK through the core. This pump was designed for ground testing only; it is not a flight component. Tests with a water-plastic model, assembled to study flow patterns in the header, revealed that a high-speed vortex was present. This confirmed the hypothesis of erosive action, which was suspected from the observed thinning and surface condition of the cap.⁽⁴³⁾ There was no evidence that the presence of hydrogen contributed to this problem.

The SNAP 10A Flight System-3 (FS-3) reactor is the first SNAP reactor to be coupled to a power conversion system. The FS-3 is a SNAP 10A reactor with thermoelectric power conversion, and is an exact duplicate of the first flight systems. It has been operating successfully for about two months. It is

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TABLE 3
SNAP REACTOR TEST CONDITIONS

Test	Power (kwt)	Time (hr)	Reactor Outlet Temperature (°F)	Test Completed
SNAP 2 Experimental Reactor (SER) ⁽³¹⁾	50	1875	1200	Nov. 19, 1960
		2290	1000 to 1200	
	<50	1860	1000	
SNAP 2 Developmental Reactor (S2DR) ⁽³²⁾	30, 55	2850	1200	Dec. 21, 1962
		1290	1100	
		1340	1000	
SNAP 8 Experimental Reactor (S8ER) ⁽³³⁾	450, 600	9040	1300	In progress *
		380	1000	
SNAP 10A Flight System-3 (FS-3) ⁽³⁴⁾	40	1080	1000	In progress

*Data as of March 16, 1965

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premature, at this time, to attempt to evaluate hydrogen effects on this system, but no problems have been observed or are anticipated. It is planned to monitor the hydrogen content in the vacuum chamber surrounding the reactor system and, hopefully, gain a better understanding of hydrogen losses from actual working systems.

In summary, over 20,000 hr of nuclear operation of SNAP reactors, at temperatures between 1000 and 1300°F, have been logged. In no instance has hydrogen been observed to degrade performance of primary loop components or inhibit NaK coolant flow. However, it should be noted that, except for FS-3, the nuclear systems tested to date have not contained prototype power conversion systems and their associated components. The potential effect on these systems and their components will be considered next.

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a. SNAP 10A System

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b. SNAP 10B System

Figure 14. Electrical Analogy to Hydrogen Flow
(Figures Unclassified)

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VI. EFFECTS OF HYDROGEN ON SYSTEMS AND COMPONENTS

A. SYSTEM CONSIDERATIONS

The distribution of hydrogen throughout a reactor system is an extremely complicated process, and all of the mechanisms of migration and flow are not completely known and understood at this time. An attempt has been made to illustrate the hydrogen flow through each reactor system by the diagrams in Figure 14. In these diagrams, the electrical analog to hydrogen diffusion is used to pictorially describe the flow patterns of each system. No attempt has been made to assign quantitative values to the electrical components. As pointed out in a previous section of this report, diffusion of hydrogen through a solid is met with a certain amount of resistance, while solubility and absorption represent a capacitance to the hydrogen flow. The following discussions present a qualitative view of hydrogen distribution for each SNAP system. The potential effect of hydrogen on each major component is considered; and, wherever possible, specific problem areas are discussed quantitatively.

1. SNAP 10A

The acceptance specification for SNAP 10A fuel elements results in a reactor core hydrogen loss rate of less than 1.66 cc/hr at full power conditions. A calculation which is extremely conservative may be based on the assumption that all of the hydrogen released by the fuel elements is contained by the NaK. With a 28.7 lb inventory of NaK, the upper limit of hydrogen concentration in NaK after 10,000 hr is only 0.004 wt %, or 40 ppm. As shown in Figure 5, this corresponds to a NaK hydride formation temperature of 460°F. This temperature is several hundred degrees lower than the coldest (750°F) portion of the NaK loop. Actually, some percentage (which will increase as the hydrogen concentration in the NaK increases) will diffuse through the core vessel, piping walls, and converter tubes (carrying the thermoelectric elements); and will be lost to space, as illustrated in Figure 14a. The hydrogen flow in SNAP 10A is a direct process, with no subsystems to divert or inhibit diffusion to space. Equilibrium hydrogen concentrations in the NaK are predicted to be low, and no hydride precipitation is anticipated.

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c. Mercury Rankine Program

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d. SNAP 8 System

Figure 14. Electrical Analogy to Hydrogen Flow (Continued)
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2. SNAP 10B

The SNAP 10B reactor system design calls for a small, lightweight reactor, operating at NaK outlet temperatures of 1300 to 1350°F during its operating lifetime. The reactor is to operate at a power level of at least 100 kw for periods of 1 to 5 years, and will depend on builtin static reactivity control devices. One approach to obtain these objectives is to substantially eliminate hydrogen loss from the reactor core during its operational lifetime. It appears, on the basis of currently available yttrium hydride dissociation pressure information,⁽⁴⁷⁾ that hydrogen losses from a SNAP 10B reactor could be reduced by the use of an yttrium getter in the core. This hydrogen loss could probably be reduced to 5% of that obtainable without the getter in the reactor.

Hydrogen escaping from the fuel elements enters the NaK coolant, and eventually is lost to space or other non-nuclear areas. Presently, this loss of hydrogen is not excessive; but it calls for some control capabilities, in order to account for the loss in moderation. The proposed method for eliminating the need for this control is to locate yttrium metal sleeves around the fuel elements in the NaK channels. The yttrium would then be expected to hydride, if the equilibrium hydrogen partial pressure in the NaK at 1300°F were above about 0.02 mm Hg, as shown in Figure 15. Since the dissociation pressure of yttrium hydride reaches a plateau of about 0.02 mm Hg at 1300°F, and maintains this pressure over a large composition range, the yttrium could absorb most of the hydrogen escaping from the fuel elements before it was absorbed and distributed by the NaK (see Figure 14b). This would result in a low hydrogen loss from the core proper. The main problem lies in the area of predicting the partial pressure of hydrogen in the NaK, under SNAP 10B operating conditions. If the pressure is <0.02 mm Hg, the hydrogen concentration in the yttrium will not reach the plateau of the partial pressure vs concentration curve, and the yttrium will not retain much hydrogen. However, if the pressure is >0.02 mm, the yttrium will hydride and be very beneficial in extending reactor lifetime.

The determination of partial pressures of hydrogen in NaK at extremely low concentrations has had little or no previous experimental attention. A test is in progress to both demonstrate the validity of the yttrium concept and measure the partial pressure of hydrogen in the NaK. This test will also provide information

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Figure 15. Dissociation Pressure Isotherms for the Yttrium-Hydrogen System (Reference 47)
(Figure Unclassified)

on hydrogen permeation rates through various metals, both at extremely low hydrogen partial pressures, and when the hydrogen is supplied to the metal in the atomic state. These data will, in turn, allow calculation of the SNAP 10B system partial pressure, and will determine whether or not the yttrium concept will work in a full-size system. The details of the experiment are found in Section VII.

In addition to retention of hydrogen in the core for nuclear advantages, the SNAP 10B concept will greatly reduce the hydrogen content in the primary NaK. This, in turn, will reduce the hydrogen diffusion to other subsystems and components.

3. Mercury Rankine Program

Most of the hydrogen entering the NaK is subsequently lost to space, either by diffusing directly through the primary system pipe walls or by first entering the coupled Mercury Rankine power conversion system (by diffusing through the boiler tubing) and then diffusing to space through the secondary system pipe walls. This process is depicted by the electrical analog in Figure 14c.

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Since the presence of hydrogen in the mercury system suggests possible undesirable effects, an analytical model⁽³⁵⁾ has been established to describe potential problem areas. In this simplified model, all the hydrogen entering the Power Conversion System (PCS) is forced to diffuse to space between the boiler outlet and the Radiator-Condenser (R/C) liquid interface. Also, the hydrogen moves through the system at the same velocity as the mercury vapor. Consistent with this model, the pressure of the hydrogen in the mercury vapor between the boiler and the R/C liquid interface is not great enough to permit the hydrogen entering from the boiler to diffuse to space before reaching the R/C liquid interface. Consequently, a volume of relatively high-pressure hydrogen gas builds up immediately above the liquid interface, until the combination of hydrogen pressure and R/C tubing area is sufficient to establish a steady-state condition. The length of R/C tubing containing this relatively high-pressure hydrogen is referred to as the "hydrogen length" in the R/C. More recent experimental observations of condensing mercury in glass tubes in the presence of noncondensable gases strongly suggest that the restriction of the noncondensable gases to the vapor region may be unrealistic. Hydrogen entrainment by liquid mercury is quite likely; thus, recycling of hydrogen to the boiler is expected. The hydrogen interaction with the R/C liquid-vapor interface has a large effect on the power conversion system. These effects are covered in more detail in the following discussions.

a. No Hydrogen Entrainment at the R/C Liquid-Vapor Interface

(1) Steady State

Using the NaK system and boiler parameters shown in Figure 16 and Table 4, together with the expected hydrogen leak rate from the reactor [15 cc(STP)/hr], the steady-state hydrogen weight concentration in the NaK system is found to be 1.1 ppm. With the postulated model, 79% of the hydrogen [11.9 cc(STP)/hr] diffuses directly to space from the NaK, and 21% [3.15 cc(STP)/hr] enters the mercury system through the boiler. The hydrogen pressure in the NaK at the boiler inlet (1195°F) is 2.7×10^{-5} atm. The hydrogen concentration in the mercury vapor at the boiler exit is 0.46 ppb, corresponding to a partial pressure of 3.8×10^{-7} atm. It is seen that the hydrogen pressure in the NaK is a factor of 71 greater than that in the mercury at the corresponding point. By

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Figure 16. Mercury Rankine System Simplified Flow Schematic (3 or 5 kwe system)
(Figure Unclassified)

TABLE 4
MERCURY RANKINE PROGRAM SYSTEM GEOMETRY

Region	Material	Average Temperature (°F)	S $\left[\frac{\text{cc(STP)}-\text{mm}}{\text{hr}-\text{cm}^2-\text{atm}^{1/2}}\right]$	A/d (cm ² /mm)	$\sum \frac{SA}{d}$ $\left[\frac{\text{cc(STP)}-\text{mm}}{\text{hr}-\text{cm}^2-\text{atm}^{1/2}}\right]$
NaK to Space					
1 - 2	Type 316 Stainless Steel	1202	0.20	4,470	2333
2 - 3*		1190	0.18	3,025	
3 - 4*		1102	0.104	3,025	
4 - 5		1020	0.059	3,910	
5 - 6		1115	0.11	3,159	
NaK to Hg*					
2 - 3	Haynes-25	1190	0.067	6,100	616
3 - 4		1102	0.034	6,100	
Hg Vapor to Space (excluding R/C)					
6 - 7	Haynes-25	1180	0.065	843	-
7 - 8		625	0.0008	9,990	
8 - 9	Variable	600	Variable	42,000	

*Model 7 Boiler with inner can vented to space

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summing the pressure drops due to diffusion, the CRU turbine, and the various pipe configuration changes, the hydrogen pressure at the inlet to an R/C tube is found to be about 3×10^{-8} atm.

The steady-state accumulation of hydrogen in the R/C is determined by the permeability of the R/C tubing. The effect of R/C tube material on the amount of hydrogen expected to collect at steady state has been examined, and some values are presented in Table 5. The calculations assume a basic Mercury Rankine Program R/C with 40 round tubes. The tubing ID in the interface region is 0.21 in. A tube wall thickness of 15 mils and a loss of 60° of the tube circumference to diffusion (as a result of the braze to the fin) were assumed.

TABLE 5
EFFECT OF R/C TUBE MATERIAL ON HYDROGEN ACCUMULATION
(No Entrainment Model)

Tube Material	Hydrogen Permeability at 600°F [cc(STP)-mm/hr-cm ² -atm ^{1/2}]	Hydrogen			
		Length (in.)	Pressure (psia)	ΔT (°F)	Volume/Tube [cc(STP)]
PH 15-7 Mo	3.1×10^{-4}	(in excess of length available in R/C)			
Haynes-25	8.1×10^{-4}	>50	6.2	>300	>6.5
Type 316 Stainless	3.3×10^{-3}	6.1	4.6	108	0.53
Type 410 Stainless	1.2×10^{-2}	2.3	1.2	23	0.051
Low-Carbon Steel					
Type 430 Stainless	2.6×10^{-2}	1.9	0.23	8	0.008
Croloy 9M					

From Table 5, it is immediately apparent that neither PH 15-7 Mo nor Haynes-25 is desirable as an R/C tube material, since neither material is sufficiently permeable to prevent excessive hydrogen accumulation. The compounding feature of sizeable hydrogen lengths generating sizeable temperature drops leads to lower average temperatures in the hydrogen region, with associated lower permeabilities. Tubing with a hydrogen permeability equal to that for Type 316 stainless steel offers an order of magnitude reduction in the hydrogen length and volume over Haynes-25. It is apparent why early analysis, (35) employing a Type 316 stainless steel permeability in lieu of actual data on

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proposed PH 15-7 Mo and Haynes-25 tubed R/C designs, gave overly optimistic results. Hydrogen lengths of 6 in. and volumes of 0.5 cc(STP) per tube are not so large as to preclude satisfactory PCS performance. Published permeability data for Type 410 stainless steel and low-carbon steel at R/C temperatures indicate that another order of magnitude reduction in hydrogen volume is possible. Permeabilities extrapolated from higher temperature measurements on Type 430 stainless steel and Croloy 9M also indicate very little hydrogen accumulation would be expected with these materials.

It is apparent that, if long hydrogen lengths are expected, the R/C must be made sufficiently long to contain the hydrogen and provide the required condensing and subcooling lengths, to avoid spilling large volumes of gas from the R/C exit. The weight penalty would be severe for long hydrogen lengths, both from the standpoint of a larger R/C and increased mercury startup inventory. However, as already mentioned, the accumulation of long lengths of hydrogen is considered unlikely, due to the strong possibility of entrainment.

(2) Time Behavior

Consistent with the system model detailed in Reference 35, the time required for the hydrogen in the NaK system to reach 95% of the steady-state concentration is approximately 40 hr. This value is substantially lower than earlier estimates, due to the lower steady-state NaK concentration estimated from recent hydrogen solubility data.⁽¹⁴⁾ The mercury system time behavior is a function of the R/C tubing material. Earlier estimates, based on R/C tubes with Type 316 stainless steel permeability, yielded a time of about 8 hr to approach 95% of the steady-state hydrogen level. With Haynes-25 R/C tubing, the approach to equilibrium in the mercury system should take longer than in the NaK system.

(3) Parametric Variations

Parametric studies of the hydrogen in the Mercury Rankine system have been confined primarily to evaluating the effect of reactor leak rate on system performance, the effect of R/C tube material on hydrogen accumulation, and the effect of multiple PCS operation with the SNAP 2 and 8 reactors.

The amount of hydrogen input to the PCS is directly proportional to the reactor leak rate. The buildup of hydrogen in the R/C is not directly proportional

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to the input, due to the interacting effects of hydrogen length and average tube temperature in the high-pressure hydrogen region. This effect causes the correspondence between hydrogen length and input rate to be greater than 1:1. The effect of R/C tube material on hydrogen accumulation has been examined in Section VI-A-3-a-1.

The hydrogen accumulation in higher-power systems composed of multiple power conversion systems is shown, in Figure 17, relative to the basic SNAP 2 type Mercury Rankine system. Information on SNAP 8 reactor hydrogen leak rates at current MRP conditions (1200°F) and as a function of thermal power level were obtained from References 36 and 37. The effect of distributing the hydrogen to multiple PCS's more than overrides the increase in hydrogen leak rate with increasing power level. Application of the SNAP 8 reactor at the less severe SNAP 2 conditions provides a marked reduction in the hydrogen accumulation in the PCS. For example, a three-PCS (15 kwe system), using the SNAP 8 reactor, would accumulate only 10% of the hydrogen volume that the basic SNAP 2 PCS would accumulate.

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Figure 17. Relative Hydrogen Volume per 5 kwe PCS
at Steady State
(Figure Unclassified)

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b. With R/C Entrainment of Gas

Condensation of mercury in tubes whose diameters are below the critical Taylor wave length given by

$$\lambda_{cr} = 2\pi \sqrt{\frac{\sigma}{g(\rho_L - \rho_V)}} \quad \dots(12)$$

where

σ = surface tension (g-cm/sec)

g = acceleration of gravity (cm/sec²)

ρ_L = density of liquid (g/cc)

ρ_V = density of vapor (g/cc)

leads to the slugwise entrainment of noncondensable gases above the liquid interface. In the near-zero "g" environments of likely space application of the MRP system, the critical diameter is at least one or two orders of magnitude greater than present MRP condenser tubing diameters. Mercury condensation in glass tubes, of diameters both above and below the critical value, in the presence of noncondensable gases has been studied at AI.⁽⁴⁵⁾

The phenomenon of noncondensable entrainment in a below-critical diameter tube appears experimentally to be independent of orientation in the gravitational field, to the extent of the tests performed.

The liquid-vapor interface is held in a stable position by surface tension effects. Noncondensibles accumulate in the vapor region immediately upstream of the interface. When the slug of noncondensibles becomes appreciable (the actual number here is unknown, but it appears to be of the order of 10 tube diameters), the droplets condensing upstream are slowed by viscous damping in the gas. Furthermore, no condensation takes place in the region of the condenser occupied by noncondensibles. Condensing on the walls upstream creates many liquid droplets, which therefore run (propelled by vapor shear and momentum transfer) into the slug of noncondensibles. Immediately upstream of the noncondensable layer, new droplets forming on the wall are not accelerated rapidly, and hence droplets generated further upstream impinge on these to form larger droplets. Such a large droplet was observed to be formed so

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quickly, in this manner, that the droplet bridged the tube before it passed completely thru the noncondensable layer. Hence, a slug of noncondensibles has been entrained in the liquid leg. Typically, the slugs observed to be entrained at inlet pressures of 10 to 12 psia and liquid flows of ~0.1 lb/min were of length equal to 1 or 2 tube diameters. The noncondensibles collect upstream of this new interface, and the process repeats with good regularity. Bear in mind that the condenser does not, at any one time, entrain all the noncondensibles that have built up at the interface; but it does trap approximately the same portion every time, provided flow conditions are not varied.

The influence of the pertinent flow parameters (mercury and noncondensable flow, pressure, and condensing length) are presently being investigated.

The principal result then is that noncondensibles will be entrained into the liquid leg in large bubbles in the condenser in zero "g," regardless of the tube diameter.

(1) Steady State Behavior

An effect of the recycle of hydrogen from the R/C to the boiler is to increase the hydrogen pressure within the boiler, thereby leading to a reduction in the ΔP_{H_2} across the boiler tubing wall, and hence a reduction in the rate of hydrogen entering the mercury. This reduction will cause a slightly higher equilibrium hydrogen concentration and pressure in the NaK. The hydrogen which collects in front of the liquid-vapor interface in the R/C will be entrained as gas bubbles. The parameters influencing the size and frequency of these entrained gas bubbles are:

- 1) Mercury vapor velocity
- 2) Hydrogen gas flow rate
- 3) Mercury vapor flow rate
- 4) Tube geometry
- 5) Condensing interface pressure.

The mechanism of the influence of these parameters is not analytically derivable in a straightforward manner. Consequently, these factors will be evaluated in mercury condensing experiments.

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An extreme case of entrainment is where the hydrogen is assumed to be uniformly distributed throughout the mercury system, with diffusion to space occurring only in the mercury vapor region. In this case, there is no buildup of a high-pressure hydrogen layer adjacent to the interface, and the steady-state rate of hydrogen flow into the PCS is calculated to be about 2 to 3% of the reactor hydrogen leak rate, compared with 21% for the nonentrainment case. This condition leads to a steady-state hydrogen concentration in the NaK of 1.3 ppm and a hydrogen pressure at the boiler inlet of 4.2×10^{-5} atm. The hydrogen concentration in the mercury vapor leaving the boiler is about 26 ppb, with a partial pressure of 2.1×10^{-5} atm. Table 6 is included to indicate the hydrogen input to the PCS and hydrogen concentrations and pressures in the Mercury Rankine System for various hydrogen lengths with Haynes-25 R/C tubing. It is not known, at this time, what the steady-state hydrogen length will be, but Table 6 serves to fill in some of the region between the two extremes of no entrainment and complete entrainment.

TABLE 6

EFFECT OF ENTRAINMENT ON HYDROGEN ACCUMULATION IN THE PCS

Hydrogen Length (in.)	Hydrogen Interface Pressure (psia)	Hydrogen ΔT ($^{\circ}F$)	Boiler NaK Inlet, Hg Outlets				
			H ₂ in NaK (ppm)	H ₂ Pressure in NaK (atm)($\times 10^5$)	H ₂ in Hg (ppb)	H ₂ Pressure in Hg (atm)($\times 10^5$)	H ₂ Flow, NaK to Hg [cc(STP)/hr]
0*	$\sim 10^{-4}$	0	1.31	4.2	26	2.1	0.25
0.5	0.4	5	1.31	4.2	26	2.1	0.28
1	0.6	10	1.30	4.1	25	2.0	0.30
2	1.3	17	1.29	4.1	24	1.9	0.37
5	4.1	96	1.28	4.0	22	1.7	0.54
10	4.9	132	1.26	3.9	17	1.3	0.84
20	5.6	181	1.23	3.7	12	1.0	1.19
$\sim 50^{\dagger}$	6.2	300	1.10	2.7	0.46	3.8	3.15

*Complete entrainment

$\dagger$ No entrainment

Under conditions of entrainment, there exists a finite probability that bubbles exiting from one tube into the liquid manifold will coalesce with a bubble from another tube which is passing into the liquid manifold. Probabilities of bubbles of given sizes (knowing the bubble size expected from one tube and the flow rates of the mercury and the gas) are predictable.

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A digital computer program has been written at AI for this purpose. Analysis and experiment in the area of noncondensable entrainment and its effects is just getting underway, and little in the way of quantitative results are yet available.

c. Uncertainties in the Analytical Model

The analysis employed in the determination of the hydrogen distribution contains many assumptions, a number of which may be questionable. In summary, the analysis showing a maximum of 21% of the reactor hydrogen entering the PCS is reasonable and conservative. The split of the hydrogen between diffusion directly to space and into the mercury is basically a function of relative area, wall thickness, and permeability, all relatively well defined. The largest uncertainty lies in the disposition of the hydrogen in the PCS, particularly in the R/C. These and other uncertainties are discussed in the following sections.

(1) Reactor Leak Rate

The hydrogen leak rate from the reactor is fundamental to the quantitative results presented. The value of 15 cc(STP)/hr is used in this report for the Mercury Rankine Program reactor (Interim 10A/2) at 100 kwt and 1300°F outlet temperature. It is based on fuel element hydrogen permeation measurements and actual reactor operation at the design conditions. It is not unreasonable to assume that this value could have a 50% tolerance. Damage to the fuel element hydrogen barrier would increase the hydrogen leak rate from the core.

(2) Hydrogen Diffusion and Permeability Data

The square root of pressure dependence of the rate of diffusion used in the analysis may not hold for regions in the system where very low hydrogen pressures are predicted. As discussed earlier (in Section III-A), some workers have shown a variable pressure dependency, ranging from the square root of pressure at ambient pressures to a linear pressure dependence at very low pressures. Related to this aspect is the application of permeability data obtained at 1 atm pressure to systems of 10^{-5} atm pressure, a substantial extrapolation. Furthermore, it is pointed out that agreement between laboratories on hydrogen permeation, within a factor of 2, is considered good agreement. However, none of the uncertainties mentioned would significantly alter the relative amount of hydrogen entering the PCS.

(3) Behavior in NaK

The effect of NaK on the diffusion of the hydrogen from the primary system is not well known. Some work has been proceeding at ORNL (see, for example, References 14, 24-27) in this regard. There is evidence that permeabilities obtained with a pure free gas are not strictly applicable where the gas is in solution in a liquid metal. The corrosive effect of the liquid metal on the walls may influence the effective permeability of the piping for hydrogen. Finally, the pressure-composition-temperature data for dilute hydrogen solutions in NaK may be subject to error. The uncertainties discussed in the preceding sections restrict any statement about the equilibrium concentration and pressure of hydrogen in the NaK to be only a gross estimate of the actual situation. Nevertheless, the relative flow of hydrogen into the PCS should still be valid, since the previous uncertainties are uniformly felt throughout the NaK system.

(4) Mercury PCS Uncertainties

As mentioned previously, the greatest uncertainty in the Mercury system analysis is the degree of entrainment to be expected in the R/C. This unknown has not been quantified, and should greatly influence the amount of hydrogen entering the PCS. In the mercury system, as in the NaK system, the hydrogen diffusion is assumed to be governed by relations characteristic of pure free gas and a clean metal membrane. Should mercury wetting occur in the R/C, the resultant additional diffusion resistance of a liquid mercury film would greatly affect the accumulation of hydrogen in the tubes. Furthermore, internal or external oxidation or contamination would also decrease the effective tubing permeability. Hydrogen permeability of metals is known to be greatly affected by surface oxidation.

4. SNAP 8

The SNAP 8 power conversion system is being developed by Aerojet General under NASA sponsorship. The system has three loops, (viz., a primary NaK loop, a secondary Mercury Rankine power conversion loop, and a tertiary NaK radiator loop). Expected hydrogen flow throughout the system is illustrated by Figure 14d.

a. NaK Loop

The core of the SNAP 8 reactor is expected to yield about 60cc H₂/hr to a NaK inventory of 80 lb. A calculation, similar to those performed for SNAP 10A

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and the Mercury Rankine Program, based on the assumption of total hydrogen containment in the primary system, yields a hydrogen concentration of 0.12 wt % H_2 in NaK after 10,000 hr. However, detailed analytical studies show that most of the hydrogen in NaK is expelled to space or into the secondary mercury loop. Analyses of the problem by Oak Ridge,⁽²⁴⁾ and confirmed by AI,⁽³⁷⁾ indicate that about 70% of the hydrogen from the core will diffuse into the secondary system. The hydrogen flow from the primary system is directly related to the heat transfer characteristics of the system.

An analytical model has been constructed to describe hydrogen buildup in the SNAP 8 primary system.⁽³⁷⁾ An equation, based on the following assumptions:

- 1) 1300°F isothermal NaK
- 2) 72.3 ft² of Croloy 9M boiler tubing
- 3) 15.7 ft² of 0.065 in. wall Type 316 stainless steel piping
- 4) 60 cc/hr (5%/yr) of H_2 entering 80 lb of NaK
- 5) The hydrogen supplied from the NaK is in the atomic state, so that the diffusion of hydrogen from the NaK is proportional to the first power of the pressure.

was established to describe the rate of hydrogen buildup in NaK. This equation:

$$t = -33.3 \ln (-3 \times 10^{-2} C + 60) + 136 \quad \dots(13)$$

where

t = time to reach equilibrium

C = cc H_2 in 80 lb NaK at time, t

yields the upper curve in Figure 18.

Practical equilibrium (95%) is reached in about 100 hr of reactor operation, although the equation reveals that 250 hr are required for complete steady-state conditions.

The concentration reaches a maximum value of 5 ppm H_2 in the NaK. At this time (~100 hr), the rate of hydrogen entering the NaK (60 cc/hr) equals that which is permeating through the piping and boiler walls, and equilibrium conditions are established. The estimated hydrogen dissociation pressure at this concentration (5 ppm) is 5×10^{-3} atm.

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Figure 18. Hydrogen Buildup in the SNAP 8 Primary System (NaK) During Reactor Operation (Figure Unclassified)

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Figure 19. Time History of Hydrogen Partial Pressure

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If the assumption is made that the diffusion rate of hydrogen out of the NaK is proportional to the square root of the hydrogen partial pressure, a similar analytical treatment yields the lower curve in Figure 18. Comparison of these two curves shows that the pressure dependence on diffusion can have a significant effect on equilibrium reactor conditions. Differences of 100 hr and 5 ppm vs 30 hr and 1 ppm illustrate the need for experimental work on the mechanism of hydrogen diffusion from NaK. Studies in progress at AI to obtain such information are outlined in Section VII.

b. Mercury Loop

An analysis comparable to that previously performed (and reported in Section VI-A-3) for the Mercury Rankine Program has been performed at Aerojet-General⁽³⁹⁾ for the SNAP 8 Power Conversion System.

The time history of the hydrogen partial pressure in all three loops is shown in Figure 19. The pressure (and therefore the hydrogen concentration) within the primary (NaK) and secondary (Hg) loops is predicted to approach steady state in about 300 hr. This is in fair agreement with the AI analysis of 250 hr for the primary loop. At this time, the pressure in the tertiary (NaK) loop is still increasing, and it is estimated that it will take ~10,000 hr to reach steady-state conditions.

5. Advanced SNAP Systems

The present SNAP reactors have been designed to provide continuous static and nonstatic operation for one year. Advanced concepts are considering several years operation, as well as manned rated missions. Such reactors must have shutdown and restart capabilities. During shutdown and restart, the system will be cooled somewhat after long-term, high-temperature operation. Potential hydrogen problems, due to NaK system plugging and materials embrittlement, are now under investigation. Corrosion and component performance under the rigorous conditions of extended lifetime and intermittent operation are also being studied.

The SNAP 10B concept, discussed in Section VI-A-2, offers excellent potential to fulfill the reactor requirements for the advanced SNAP missions. The retention of hydrogen in the core will greatly extend the reactor lifetime, as well as reduce the potential hydrogen problems in the rest of the system.

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a. Construction

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b. Module (Figure Unclassified)

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Figure 20. SNAP 10A Thermoelectric Converter

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B. COMPONENT PERFORMANCE

1. SNAP 10A

a. Thermoelectric Elements

The probability of diffusion of hydrogen to the Ge-Si thermoelectric pellets is very unlikely, because of the alumina and tungsten layers (both good hydrogen barriers) which separate the pellet from the NaK converter "D" tube (Figure 20). In addition, investigations have been conducted by the manufacturer (RCA) on an alternate fabrication process, which includes hydrogen brazing of the tungsten strap with the pellet in place. They have found no adverse effects of the hydrogen braze step on performance of the element.

The other materials used in the converter module (listed in Figure 20a) are all known to be stable to hydrogen.

b. Radiator

Hydrogen degradation of the emittance coatings on the radiator (tin oxide) is extremely improbable, especially on flight systems. The hydrogen path, in this case, is either through the thermoelectric "stack" or through the space-vacuum void which separates the radiator plates.

c. Temperature and Control Sensors

Resistance thermal detectors (RTD) are used for control purposes in SNAP 10A. These devices utilize the resistance temperature characteristics of a platinum strip. Their location, in wells in the primary loop, make them susceptible to hydrogen exposure. Very little experimental work has been performed to determine whether degradation results from hydrogen at temperatures of operation (1000°F). Although no problems are anticipated, the fact that platinum degrades in reducing atmospheres makes it mandatory that the problem be investigated under conditions of reactor operation. Such studies are now underway.

2. Mercury Rankine Program

The presence of hydrogen in the mercury power conversion system (PCS) poses several potential component and system operating problems. The PCS components which may experience adverse effects from the hydrogen are the combined rotating unit (CRU), including the mercury pump and the CRU bearings, and the radiator condenser. The entrainment of free hydrogen gas by

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liquid mercury leaving the R/C leads to the introduction of gas bubbles into the pump and bearings, with the attendant possibility of loss of circulation or cavitation. The accumulation of gas in the R/C impairs the thermal performance and presents material hydriding problems, due to diffusion of the hydrogen through the condenser walls. While many effects of hydrogen on system and component performance can be determined by ground experimentation, the complete definition of the hydrogen behavior in the system as a whole, and in the R/C in particular, can only be verified by a Mercury Rankine flight test. Non-condensable behavior in a zero-"g," high-vacuum environment cannot be completely simulated by ground test and experimentation.

a. Combined Rotating Unit (CRU)

(1) Pump

The gas-swallowing capabilities of the CRU V mercury pump are currently being evaluated on a subcomponent and component basis. As shown in Figure 21,

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Figure 21. Hot Mercury Pump Gas Capacities
(Figure Unclassified)

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a single test on the CRU V pump has demonstrated that a gas bubble up to 5cc(STP) can be injected without detrimental effects on the pump performance. Tests on a similar pump, in the Sunflower program, have demonstrated that bubbles up to 15 cc(STP) can be tolerated without loss of pump prime. In the latter case, the pump output pressure was considerably lower than the CRU V pressure (330 psia, as compared to 525 psia), and would be more susceptible to loss of prime than the CRU V pump with its high output pressure.

(2) Bearing

Parametric tests of the three pad bearings have demonstrated a large gas swallowing capability. The following data suggest that the gas swallowing capabilities of the bearings are equal to or greater than those of the on-shaft mercury pump.

Rotational Speed (rpm)	Shaft Load (lb/bearing)	Gas Bubble Size [cc(STP)]	Effect on Shaft Locus
0	9	35	none
36000	3	20	none
36000	30	35	none
40000	30	30	none

b. Radiator Condenser

Diffusion of the hydrogen through the R/C tube walls may lead to metallurgical effects, such as hydriding of certain R/C materials, with attendant loss of mechanical integrity. The current material of construction of the R/C are Haynes-25 tubing, Type 1100 aluminum fins, titanium plating on the tubes, and a high-emittance coating on the R/C surface. The two areas that most probably would experience hydrogen problems would be the titanium coating on the tubes and the SnO₂ layer of the high-emittance coating.

The titanium plating on the Haynes-25 tubes provides a mechanism that permits a ductile Hayes-25 - aluminum joint to be accomplished. One experiment, conducted to date, had indicated (after 600 hr of operation at 650°F with an internal hydrogen pressure of 6 psia) that the ductility of the titanium (as indicated by hardness evaluation) has not decreased. Tests continue to determine

TABLE 7

COMPONENTS AND MATERIALS CURRENTLY BEING USED IN THE MERCURY RANKINE PROGRAM

Component	Material	Environment			Potential Problems	Current Rational
		Maximum Temperature (°F)	Fluid	Approximate Hydrogen Pressure (psia)		
CRU	Alnico V	800	Vacuum	?	None	No major material effects are anticipated. Some minor changes in the stress-rupture and creep characteristics of the reference materials may occur, due to the H ₂ . However, these are considered to be second order problems.
	PH 15-7 Mo	750	Hg - Vapor	10 ⁻⁶ to 10 ⁻⁴	None	
	BG 42	600	Hg - Liquid	525	None	
	17-4 PH	860	Hg - Vapor	10 ⁻⁴ to 10 ⁻⁶	None	
	Nivco 10	950	Hg - Vapor	10 ⁻⁴ to 10 ⁻⁶	None	
	Bore Seal	750	Hg - Vapor	10 ⁻⁶	None	
	Haynes-25	1150	Hg - Vapor	10 ⁻⁶	None	
Radiator Condenser	Haynes-25	600	Hg	10 ⁻⁶ to 6	None	Effect on titanium being evaluated. Also, process change, to eliminate titanium, being investigated. SnO ₂ problem is expected to be very limited, and can be circumvented by a small weight penalty.
	Type 1100 Aluminum	600	Vacuum		None	
	Titanium Plating	600	Vacuum		Form titanium hydride	
	CR-CO-N Spinel	600	Vacuum		None	
	SnO ₂	600	Vacuum		SnO ₂ reduction	
Pressure Regulator	AM 350 SS or Haynes-25	550	Hg	6	None	No problems anticipated. System tests will verify.
Injection Tank	AM 350 SS or Haynes-25	550	Hg	550	None	
Hg Boiler	Haynes-25	1200	Hg	10 ⁻⁵ to 10 ⁻³	Corrosion and Conditioning	Boiler performance (i.e., conditioning) should not be adversely affected, and may be improved.
		1200	NaK	10 ⁻³		Hydrogen should not affect rate-limiting corrosion step, which is diffusion of soluble elements to surface of Haynes-25
TE Pump	Haynes-25	800	Hg	550	Degradation of performance, due to fissuring within TE elements	Hydrogen effects under evaluation at accelerated conditions, to verify adequacy of the design.
	Type 304 SS	1200	NaK	10 ⁻³		
	Chromel	1200	Vacuum	<550		
	Constantan	1200	Vacuum	<550		
	OFHC Copper	800	Vacuum	?		
	Alnico V	800	Vacuum	?		
Expansion Compensator	AM 350 or Type 300 series stainless steels	650	NaK	10 ⁻³	NaK hydride precipitation	NaK plugging temperature <300°F, problem will exist only during shutdown for long periods of time.

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the longer life effects. At the same time, the fabrication process is being examined, in an attempt to eliminate the requirement for the titanium interface barrier. This would eliminate any possible major metallurgical effects.

The effect of hydrogen on the SnO_2 high-emittance coating is not a major problem. The limited amount of hydrogen that finds its way to the emittance coating ($\sim 1/4$ of the total that diffused thru the Haynes-25 R/C tube) may locally reduce the emittance.

Table 7 presents a list of all the components and the materials that are currently being utilized in the MRP. The most critical environmental conditions are defined, and the most probable effect of the hydrogen is presented. As is noted, the potential effect on the R/C is currently thought to be the largest uncertainty; and this aspect is under investigation, both as to the effect and alternate methods of fabrication.

3. SNAP 8

a. NaK Pump

The temperature for precipitation of NaK hydride at 5 ppm hydrogen is estimated to be $<200^\circ\text{F}$ (see Figure 5). The SNAP 8 system has a small bypass circuit on the primary loop, to cool the bearings on the NaK primary pump motor assembly. This bypass loop is designed to operate in the 250 to 300°F range. Hydride precipitation in this loop is not anticipated; but, for additional assurance, either a cold trap or an increase in temperature on the loop are being considered.

Since the dissociation pressure of hydrogen in NaK is so low at equilibrium ($\sim 5 \times 10^{-3}$ atm), cavitation of the NaK pump due to release of free hydrogen is considered extremely improbable.

b. Temperature Sensors

Experiments to determine the stability of RTD "drift" due to the presence of hydrogen are planned. These detectors contain a platinum element which may be very sensitive to hydrogen. If significant drift is noted, a hydrogen barrier, such as tungsten, can easily be placed around the device. A NaK loop for testing these detectors is under construction. This loop will simulate actual environmental conditions to be encountered by the detectors. A hydrogen injection system for the loop is being considered. The backup for these detectors is a

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thermocouple element. "Drift" studies on endurance tests are being conducted; but, as yet, hydrogen contamination has not been studied.

c. Other Primary Components

The beryllium oxide used in the SNAP 8 internal reflectors (clad with Type 347 stainless steel) is known to be stable in hydrogen at the operating temperatures.

The brazing alloys specified for flight systems are known to be stable in the presence of hydrogen. In fact, many of the brazing processes employed utilize a high-purity hydrogen atmosphere.

Emittance control coatings on the primary loop are generally metallic materials which are insensitive to hydrogen.

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VII. PLANNED EXPERIMENTS AND STUDIES

From the foregoing discussions, it is obvious that technological gaps still exist to cloud the hydrogen picture of SNAP systems. A number of programs are currently funded which will reduce these gaps, and hopefully eliminate many of the uncertainties relevant to the hydrogen problem. These experiments and analytical studies are briefly outlined in the following sections.

A. OAK RIDGE WORK

The SNAP 8 Materials Corrosion Program at Oak Ridge is scheduled to phase out at the end of FY 65. This program, which is summarized in Section IV, has made a significant contribution to the SNAP System technology. In addition to primary system corrosion studies, it has provided timely information on hydrogen's effects and distribution in the reactor system. Toward this end, hydrogen release from the NaK corrosion loops, to which hydrogen has been injected into the NaK, is being monitored. Diffusion rates through the loop walls are measured at four jacketed stations, as shown in Figures 12 and 13. Results from these studies are inconclusive, at this time, but it is anticipated that valuable information on hydrogen diffusion from various parts of the primary system will be forthcoming.

Basic studies on hydrogen solubility in NaK and hydrogen permeation through a NaK-metal interface are also part of the ORNL program. Results obtained to date are discussed under Section IV.

B. AEROJET-GENERAL WORK

In the program for the SNAP 8 materials corrosion loops (shown in Figure 22) at Aerojet-General Nuclear (San Ramon), a hydrogen injection feature is planned on at least one three-loop system. Hydrogen injection will be into the primary (NaK) loop, and the effects on corrosion pattern and condenser performance of the secondary (Hg) loop can be studied. A prior injection, directly into the mercury loop, is being considered to show what effects to look for when the NaK hydrogen injection is made. It is not clear, at this time, just when these studies will take place.

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CORROSION LOOP LAYOUT - 1/15 SCALE SNAP 8

AEROJET-GENERAL NUCLEONICS, SAN RAMON, CALIF.

Figure 22. Corrosion Loop Layout — SNAP 8
(Figure Unclassified)

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C. ATOMICS INTERNATIONAL WORK

1. NaK-Hydrogen Partial Pressure Studies

An experiment, designed to measure hydrogen partial pressures in NaK and to study the hydrogen permeation kinetics of NaK-H₂ solutions, is in progress at AI. This information is essential for the selection of an efficient hydrogen getter in the NaK. Studies indicate that yttrium metal would be an excellent choice, if the partial pressure (fugacity) of hydrogen in NaK exceeds the plateau dissociation pressure of isotherms in the Y-H system. From the available information, it appears that, if the hydrogen partial pressure in the NaK is >0.02 mm Hg at 1300°F, the yttrium will absorb large quantities of hydrogen from the NaK. If this hydrogen can be retained within the core, it will greatly extend the lifetime capabilities of the reactor. In addition, this concept offers an attractive solution to potential hydrogen problems in the Mercury Rankine conversion system. If most of the hydrogen can be contained within the core, only a small fraction will be available to migrate to other parts of the reactor system.

The goals of the experiment are:

- 1) To measure the partial pressure of hydrogen above NaK for a variety of compositions and temperatures
- 2) To correlate the partial pressure measurements with observed hydrogen permeation rates through stainless steel, and establish a flow per unit area vs pressure curve at several temperatures
- 3) To establish a set of equations to predict partial pressures of hydrogen in NaK for any given temperature, hydrogen source, or permeation surface area
- 4) To correlate measured partial pressure values with calculated hydrogen concentration values, and establish an isochore chart for the low-pressure and low-composition region.

The NaK is contained within a stainless steel bellows capsule, shown in Figure 23. This bellows design is used to provide a large surface area for hydrogen permeation from the NaK. A line drawing of the capsule design is given in Figure 24. Within the NaK is a coated SNAP 8 cladding tube which can

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Figure 23. Experimental Capsule for H_2 -NaK Experiment
(Figure Unclassified)²

Figure 24. Schematic of H_2 -NaK Experiment
(Figure Unclassified)

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be pressurized internally with hydrogen. Flow of hydrogen through the cladding tube into the NaK can be controlled by adjusting the hydrogen pressure within the cladding tube. At a given temperature, the concentration of hydrogen in the NaK will build up to a level dictated by the resistance to hydrogen flow provided by the stainless steel bellows. The leak rate through the bellows is monitored by a mass spectrometer on a high-vacuum chamber surrounding the capsule.

At a point in time, the flow rate through the stainless steel must equal the flow rate into the NaK, and equilibrium will be established. A thin-walled nickel capsule (under static vacuum), located in the NaK, will also reach an equilibrium condition when the hydrogen gas pressure in the capsule (caused by hydrogen permeating from the NaK) is equal in fugacity to the hydrogen concentration in the NaK. A measurement of this pressure at the equilibrium flow rate gives one point on a pressure vs permeation rate plot. Integration of the rate of hydrogen input minus the rate permeating out with respect to time results in a calculated value for the hydrogen concentration in the NaK under the set of conditions. Therefore, each time the hydrogen input variable is changed, a value for pressure, flow, and concentration can be obtained. Individual capsules will be tested at 1100, 1200, 1300, and 1400°F.

This experiment should provide valuable information on hydrogen diffusion rates in NaK systems, and show the dependence of pressure on permeation through NaK-metal interfaces.

2. Radiator-Condenser Studies

Studies are being conducted on the effect of hydrogen on the integrity of the titanium metal plating on the R/C tubing for the Mercury Rankine Program. This titanium plate (0.002 in.) is added to the outside surfaces of the Haynes-25 R/C tubing, to facilitate braze bonding of aluminum radiator fins to the R/C.

Since it is predicted that hydrogen will be present inside the condenser tubing, there is concern that the integrity of the braze bond will be compromised by the reaction of hydrogen with titanium. Titanium is a good hydride former, and even small amounts induce brittle qualities in the metal.

Also, it has been shown that, during the brazing operation, the titanium interacts with the Haynes-25 R/C tubing to form an intermetallic layer. This

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raises the question of how this intermetallic layer affects hydrogen permeation velocities out of the R/C, and/or does it produce an unwieldy column of hydrogen gas accumulation in the R/C.

In the single experiment performed to date, the intermetallic layer produced by the brazing operation does not seem to affect the hydrogen loss from the R/C. It has been found, however, that the titanium plating acts as a "getter" for the hydrogen which permeates through the Haynes-25 tubing walls. This observation was made at 635°F and with 6 psia hydrogen pressure on the interior of the tubing. Impact tests and microhardness measurements failed to show any deterioration of bond strength. Additional tests are now being made, to study the hydrogen effects on the bond after longer periods of exposure.

An experiment is also planned, to study the influence of mercury on hydrogen permeation kinetics. A continuous film of mercury on the Haynes-25 tube walls might drastically alter the permeation characteristics of the tubing. Mercury has a very low solubility for hydrogen, and could severely reduce the rate of hydrogen migration out of the R/C system. Conversely, if the mercury cleans the surface of the Haynes-25 tubing, hydrogen losses could increase, and thereby improve R/C performance.

The experiment consists of a vertical mercury reflux capsule of Haynes-25, surrounded by a vacuum jacket which is connected to a hydrogen-sensitive mass spectrometer. A small pool of mercury would then be heated to above the boiling point (670°F), and the resultant Hg vapor would be condensed near the top of the capsule and return to the bottom by running down the tube walls. Hydrogen injection could be made through a properly baffled probe at the top of the capsule. By running the same capsule, both before and after adding mercury, an understanding of its effect on hydrogen permeation will be gained.

3. Low-Pressure Permeation Kinetics

In a program funded by SNAP 8, hydrogen permeation studies are being made, at low pressures, on metals and alloys of interest to the SNAP effort. From this work, a deviation from Sievert's law has been observed, as outlined in Section III. Further studies will extend to other metals — in particular, the SNAP 8 boiler tubing (Croloy 9M). It is anticipated that a better insight also will be

gained on the effect of thin surface films on hydrogen permeation. Such information is needed, to establish an accurate model for hydrogen distribution in SNAP systems.

4. Cladding Creep

Hydrogen effects on the creep characteristics of the fuel element cladding are under investigation, as detailed in Section IV. In the accelerated tests evaluated to date, no serious effects from hydrogen diffusion were noted. Tests are now in progress to study the low-stress, long-term creep behavior of the cladding.

5. Mercury Condensing Experiments

A series of single-tube mercury condensing experiments are being conducted under the Mercury Rankine Program, to determine the influence of hydrogen and other noncondensibles upon the condensing process. These experiments can be operated with either metal or glass condensing tubes, of different diameters, and placed in either the horizontal position or at small positive or negative inclinations (to impose either negative or positive accelerations). Fluoroscopic examination of condensing behavior is employed with metal tubes, while visual and photographic studies are accomplished with glass tubes. These tests will help define the influence of the important parameters upon the entrainment mechanism, both with and without mercury wetting.

6. Prototype System Mockups (PSM)

Several nonnuclear systems tests are planned, to demonstrate the performance capabilities and operating characteristics of the power conversion systems. Plans are being made to incorporate hydrogen injection features on the NaK primary loop of some of these tests. The systems will be tested in a high-vacuum chamber. By monitoring the vacuum exhaust for hydrogen, the hydrogen loss rate from the system can be measured. Since the amount of hydrogen injected into the NaK will be known, the difference will represent the hydrogen retention within the system. Effects of hydrogen on the PCS and the R/C will also be observed.

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VIII. REMEDIAL ACTION AND RECOMMENDED STUDIES

The effects of hydrogen on the overall system performance depend on its manner of migration and the amount which is accumulated in any individual subsystem. Of greatest concern is the influence of hydrogen on the performance of the power conversion systems. Solutions for the prevention of hydrogen buildup in the SNAP systems seem to resolve into three categories:

- 1) Containment within the primary loop by suitable "getters" or barriers
- 2) Getter containment in dormant regions of the mercury loop
- 3) Reduction in the resistance path to space, by the use of "windows" in the primary or secondary loops.

A. CORE CONTAINMENT

The ideal solution to the hydrogen problem would be to prevent all hydrogen loss from the fuel elements. While significant progress has been made in hydrogen barrier development at Atomics International, an "ideal" barrier material (if one exists) has not been discovered. Work is in progress to develop better barriers and improve closure techniques on the fuel elements. It is expected that the hydrogen loss can be reduced by at least an order of magnitude by this approach.

A most attractive concept for keeping the hydrogen in the reactor core seems to be the introduction of a hydrogen getter to the fuel element array. Extensive development work will be needed before this concept can be realized. Preliminary work has been started, as outlined in Section VII, and hardware fabrication and detailed development studies are proposed for FY 66.

The introduction of a soluble hydrogen getter into the NaK merits consideration. Oak Ridge ⁽¹⁴⁾ has suggested the use of lithium or yttrium. From cursory studies performed at AI, it appears that yttrium has a very limited solubility in NaK at 1300°F. Lithium, however, would be expected to have extensive solubility, and should be investigated. One concern, at this time, is that the lithium addition may adversely alter the corrosion behavior of the NaK, and/or that LiH precipitation may not be controlled to a well defined region.

A study at Atomics International ⁽³⁸⁾ has shown that the addition of a 10-mil thick diffusion barrier of tungsten to the boiler tubing will reduce hydrogen

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permeation from the NaK to the Hg loops by an order of magnitude. Recent development in coextrusion and chemical vapor plating techniques make such an approach highly feasible. Furthermore, it should be noted that there is no requirement for "continuity" of the tungsten diffusion barrier; the reduction of hydrogen migration is approximately proportional to the percentage of boiler area which is coated. Tungsten would be expected to have excellent compatibility with NaK. Another alternative is to apply a barrier to the mercury side of the boiler tubes.⁽⁴⁴⁾ The glass barrier currently used on the fuel elements may be adequate. Both of these concepts are feasible, and development work to determine their potential is recommended.

The introduction of a cold trap to the NaK loop would collect hydrogen at a specific location as a hydride precipitate. Oak Ridge⁽¹⁴⁾ has performed analytical studies on cold trap effectiveness in the SNAP 8 primary loop. They report a reduction of hydrogen diffusion into the secondary system of two orders of magnitude. However, they conclude that the adoption and maintenance of such cold traps, especially on flight systems, together with the loss in net power output of the system, is sufficient to exclude them from further consideration.

B. MERCURY LOOP GETTER

A hydrogen getter, such as yttrium, between the boiler and CRU could be considered as a potential method of trapping and retaining the hydrogen gas, prior to its entering the turbine and the subsequent system. A cursory examination has established this to be worthy of further study.

C. HYDROGEN "WINDOWS"

The possibility of eliminating the hydrogen introduced into the primary system by the use of hydrogen diffusion windows (Nb or Ni) has been investigated by both Oak Ridge⁽¹⁴⁾ and AI. It was concluded that excessive window area-to-thickness ratios would be required, to produce significant reductions in the hydrogen level.

The Mercury Rankine Program at AI is considering several new boiler concepts which would significantly reduce the hydrogen transfer to the mercury system. One of these, a radiation boiler, provides a vacuum between the NaK and hydrogen portions of the heat exchanger. Another concept separates the

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the mercury tubing from the NaK, in such a way that a hydrogen diffusion barrier could be introduced between the NaK and mercury loops. These concepts are currently being considered, to establish their advantages and limitations.

The amount of hydrogen gas that escapes to space from the mercury loop is highly dependent upon the R/C tubing material. If required, a highly permeable material (Type 400 stainless steel) can be substituted for the Haynes-25 condenser tubes, and thus increase by 10-fold the amount of hydrogen that will diffuse to space through the R/C. This technique will probably be considered, if the nonentrainment model (Section VI) is proven to be accurate.

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REFERENCES

1. F. J. Norton, "Permeation of Gases Through Solids," J. Appl. Phys., 28 (1) (1957) p 34-39
2. Adolf Fick, Pogg. Ann. 94, (1855)
3. S. Dushman, Scientific Foundations of Vacuum Technique Second Ed., (John Wiley and Sons, Inc., New York, 1962)
4. E. O. Braaten and G. F. Clarke, Proc. Roy. Soc. London A, 153, 504 (1935-36)
5. D. W. Rudd, D. W. Vose, and J. B. Vetrano, "The Permeation of Hydrogen Through Hastelloy B," NAA-SR-4898, Rev. (February 1, 1961)
6. L. S. Darken and R. W. Gurry, Physical Chemistry of Metals (McGraw-Hill, Inc., New York, 1953)
7. R. W. Webb, "Hydrogen Permeation Through Metals," NAA-SR-TDR-9844 (April 27, 1964)
8. F. M. Johnson and P. Larose, J. Am. Chem. Soc., 46 (1924) p 1377
9. G. Lewkonja and W. Baukloh, Z. Metallik., 25 (1933) p 309
10. P. S. Flint, "The Diffusion of Hydrogen Through Materials of Construction," KAPL-659 (December 14, 1951)
11. T. Smith, "Hydrogen Permeation of Oxide Films on Zirconium," NAA-SR-6267 (May 15, 1962)
12. C. J. Smithells and C. E. Ramsley, Proc. Roy. Soc. London, A, 150 (1935) p 172; 152 (1936) p 706
13. C. A. Edwards, Trans. A.I.M.E., 117 (1935) p 13
14. H. W. Savage et al., "SNAP-8 Corrosion Program Quarterly Progress Report for Period Ending August 31, 1964," ORNL-3730 (November 1964). Confidential
15. E. R. Slaughter, "The Effects of Hydrogen in Steel," J. Met. (April 1956), p 431
16. A. R. Troiano, "The Role of Hydrogen and Other Interstitials in the Mechanical Behavior of Metals," ASM Trans. 52 (1960) p 54-80
17. P. A. Blanchard et al., "Hydrogen Embrittlement in Steels, Titanium alloys, and Several Face-Centered Cubic Alloys," WADC-TR-59-172 (April 1959)

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~~CONFIDENTIAL~~

CONFIDENTIAL

~~CONFIDENTIAL~~

18. P. Cotterill, "The Hydrogen Embrittlement of Metals," Progress in Materials Science, Vol. 9, No. 4 (Pergamon Press, London 1961)
19. J. E. Srawley, "Hydrogen-Embrittlement Susceptibility of Some Steels and Non-Ferrous Alloys," NRL Report 5392 (October 19, 1959)
20. D. A. Douglas and H. E. McCoy, "Effect of Various Gaseous Contaminants on the Strength and Formability of Columbium," Metallurgical Society Conferences, AIME, Columbium Metallurgy (Interscience Publishers 1961) p 111-112
21. F. Garofalo, "Effect of Environment on Creep and Creep-Rupture Behavior of Several Steels at Temperatures of 1000 to 1200°F," Proceedings ASTM, 59 (1959) p 973-984
22. S. J. Klima et al., "Preliminary Investigation of Effect of Hydrogen on Stress-Rupture and Fatigue Properties of an Iron-, a Nickel-, and a Cobalt-Base Alloy," NASA-TN-D-1458 (December 1962)
23. H. E. McCoy, Jr., "Effects of Hydrogen on the High Temperature Flow and Fracture Characteristics of Metals," ORNL-3600 (June 1964)
24. H. W. Savage et al., "SNAP-8 Corrosion Program Quarterly Progress Report for Period Ending August 31, 1963," ORNL 3538 (January 6, 1964) CRD
25. H. W. Savage et al., "SNAP-8 Corrosion Program Quarterly Progress Report for Period Ending November 30, 1963," ORNL 3604 (March 1964) CRD
26. H. W. Savage et al., "SNAP-8 Corrosion Program Quarterly Progress Report for Period Ending February 29, 1964," ORNL 3618 (April 1964) CRD
27. H. W. Savage et al., "SNAP-8 Corrosion Program Quarterly Progress Report for Period Ending May 31, 1964," ORNL 3671 (July 1964) CRD
28. Bert Fleischer, ORNL, Personal Communication (March 3, 1965)
29. F. J. Hetzler and R. S. Young, "Sodium Mass Transfer, Screening Test Data and Analysis, Metallurgy," GEAP 3726 (June 1962)
30. R. W. Swindeman, "The Mechanical Properties of INOR-8," ORNL-2780 (January 27, 1961)
31. J. P. Beall and M. W. Hulin, Eds., "The Final Report on the SNAP 2 Experimental Reactor (SER) Operation and Test Program," NAA-SR-7088 (April 1962)
32. L. D. Felten et al., "Final Report for SNAP 2 Development Reactor Test Program," NAA-SR-8295 (April 1961)

NAA-SR-11164

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~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

33. V. L. Rooney, A.I., Personal Communication (March 2, 1965)
34. J. E. Brunings, A.I., Personal Communication (February 23, 1965)
35. R. T. Lancet et al., "SNAP 2 Performance Analysis," NAA-SR-9087 (February 15, 1965) Confidential
36. C. Q. Torrijos, "Hydrogen Leak Rate from S-8ER Core," NAA-SR-MEMO-8942 (September 16, 1963) Secret
37. L. M. Maki, "SNAP-8 Performance Limits," NAA-SR-MEMO-9347 (January 6, 1964) Secret
38. R. W. Webb, "Hydrogen Migration into the SNAP 8 Mercury Boiler Circuit," NAA-SR-MEMO-10138 (May 25, 1964)
39. L. G. Rico and J. W. Tindall, "Preliminary Analysis of Hydrogen Diffusion in the SNAP 8 System," Aerojet-General TM-340:64-1-248 (October 22, 1964)
40. E. A. Steigerwald, "The Permeation of Hydrogen Through Materials for the Sunflower System," TRW-ER-5623 (November 15, 1963)
41. H. W. Savage et al., "SNAP-8 Corrosion Program Quarterly Progress Report for Period Ending November 30, 1964," ORNL 3784 (March 1965)
42. C. J. Smithells, Metals Reference Book, 3rd ed. (Interscience Publishers, New York, 1962) p 570
43. R. S. Neymark, "Metallurgical Examination of the End Caps from the S8ER NaK Pumps," NAA-SR-TDR 9752 (April 9, 1964)
44. H. W. Carpenter and D. E. Johnson, "Ceramic Coatings for Mercury Boiler Linings," NAA-SR-TDR 11075 (March 3, 1965)
45. R. T. Lancet, P. Abramson, and R. P. Forslund, "The Fluid Mechanics of Condensing Mercury in a Low G Environment," Paper to be presented at the AFOSR/LMSC Symposium on Low G Fluid Mechanics, July 24 and 25, 1965
46. D. Randall and O. N. Salmon, "Diffusion Studies 1. The Permeability of Type 347 Stainless Steel to Hydrogen and Tritium," KAPL-904 (March 19, 1953)
47. Lymperios Yaunopoulos, The Thermodynamics of the Yttrium- Hydrogen System, Doctorate Thesis, Illinois Institute of Technology, Chicago, Ill (June 1963)

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