Tritium Permeation Through Steam Generator Materials*

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MASTER

Abstract

Various subjects related to tritium permeation through steam generator
materials are discussed. Isotope effects based on protium and tritium
permeabilities of nickel range from 1.36 at 500°K to 1.63 at 1000°K. Tritium
permeation rates from a given quantity of T_2 molecules will be reduced by
the addition of protium and/or deuterium to a point that the tritium rates approach
an inverse 0.5 power dependence on the protium and/or deuterium pressures.
The permeability constants and the permeation activation energies essentially
are equal for several ferritic alloys, but these parameters are significantly
different from those for several austenitic type alloys. Oxide layers on
construction alloys can reduce permeation rates by 2 to 3 orders of magnitude
but information on this subject may not be applicable to operating steam generator
systems. Recent results indicate that tritium permeation rates through oxide
and glass materials are 0.5 rather than first power dependent on pressure.

Introduction

Tritium permeation in a fusion power plant from the coolant through the
steam generator material into the steam system can be an important limiting
factor to utility fusion power. Such tritium essentially will be lost to the

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environment, because recovery of very dilute tritium from the water in a power plant will be prohibitive. Acceptable operating conditions for a fusion power plant based on tritium release from fission power plants could permit a total tritium release rate of 1 to 10 Ci/day where the permeation rate into the steam system accounts for as much as 50% of the release rate. Considerations of such limits and of current designs for fusion power plants with steam generators made of conventional construction alloys indicate that tritium permeation rates through the steam generators must be reduced by two to three orders of magnitude less than the projected rates based on the permeability of bare materials.[1] This implies that tritium permeation barriers will be required in conjunction with the steam generator structural material. Materials with tritium permeabilities lower than those of construction alloys are known and are available, but problems with materials compatibilities and construction techniques do not permit the construction of steam generators from such materials. Current materials technology requires the use of iron or nickel base alloys, and the tritium permeabilities of these materials with the application of permeation barriers is an important subject.

Different types of permeation barriers have been discussed,[2,3] and there is a near consensus that the most effective and most economical barrier to tritium permeation through metals likely would be layers of oxides formed in situ on the metal by steam (or medium) oxidation at or near operating conditions. The oxidation chemistry of an alloy and the oxide composition will depend on the thermodynamics for oxidizing the components in the alloy, and this feature gives some control in forming selective oxides on a construction alloy. An example is the suggestion that unusual high concentrations of aluminum in an alloy can produce by water oxidation an oxide that is primarily aluminum

oxide with good barrier characteristics.[3] However, the real situation is that we know very little about the fundamental barrier characteristics of oxides formed by the water oxidation of conventional construction alloys.

An important aspect of tritium permeation rates is the isotopic purity of the tritium source. No functioning part of a fusion power plant will contain pure tritium, and this certainly includes the coolant in contact with the steam generator. Thus fusion technology is forced to consider the effects of the presence of protium on tritium release rates. The effects of protium on tritium permeation rates from a mixture of H_2 and T_2 molecules with no exchange interaction between the different molecules would be nil. However, such a system cannot exist, because chemical reactions form HT molecules, and the reaction rate is especially fast in the presence of hot metals. Therefore, most systems of protium and tritium in fusion power plants can be considered as equilibrium systems according to the reaction,

$$H_2 + T_2 \rightleftharpoons 2HT \; ; \tag{1}$$

and the equilibrium constants at various temperatures have been established.[4] The effects of diluting tritium with protium were recently mentioned,[5] but are further clarified herein along with isotope effects on permeation.

A research program on high temperature materials chemistry at the Oak Ridge National Laboratory is investigating tritium permeation through metals, construction alloys, and barrier materials, and has considered the effects of mixed hydrogen isotopes on tritium permeation rates. Results of these studies include: (1) hydrogen isotope effects with nickel, (2) the similarities in the permeabilities of ferritic alloys, (3) similarities of permeabilities of austenitic and high nickel base alloys, (4) the in situ steam oxidation of Incoloy 800 at 500 to 700°C

to reduce tritium permeation rates by factors of 200 to 500, (5) the chemical analysis of oxides formed on Incoloy 800 by steam oxidation at 500 to 700°C, (6) the dependence of oxidation and the formation of oxide barriers on time, temperature, oxidation potential, alloy composition, and the surface and bulk pretreatment of the alloy, and (7) strong indications that tritium permeation rates through oxide layers and through fused quartz are 0.5 rather than unity power dependent on the driving pressure. These results are discussed and summarized in this paper.

Experimental

The experimental techniques for measuring tritium permeation rates at high temperatures through clean metals and through metals into oxidizing atmospheres of 0-1 atm H_2O have been described.[5,6] The overall procedure includes a pre-equilibrated source of parts per million tritium in protium flowing continuously around a tube sample. Measurements with clean metals have ∼1 atm protium flowing inside the sample and carrying the tritium to a tritium monitor ionization chamber. Measurements with metals while the downstream side is oxidized by steam have an argon carrier gas passing through a boiler and condenser and then carrying up to 0.95 atm water to the inside of the sample. Tritium that permeates through the sample is 99.9% exchanged with protium in the water and is condensed for analysis by liquid scintillation counting.

Discussion

Mixed Isotopes

The presence of protium in a given amount of tritium will decrease the tritium permeation rate. The greatest effect will be when equilibrium is

established, Equation 1, because the maximum number of T_2 molecules have reacted.
For equilibrium at 600°K the tritium partial pressure, P_{T_2}, will be

$$P_{T_2} = \frac{(P_{HT})^2}{3.45 \, P_{H_2}} \quad , \tag{2}$$

where P is the pressure of the indicated molecules and the equilibrium constant,
K, is 3.45.[4] Fundamental thermodynamics requires that the equilibrium partial
pressure of T_2 always defines the tritium activity, whether the gas is pure T_2
molecules or also contains H_2 and HT molecules. The tritium permeation rate,
J, through clean metals into vacuum always will be 0.5 power dependent on the
T_2 pressure or the T_2 partial pressure,

$$J = DKP_{T_2}^{1/2} \tag{3}$$

or

$$J = DK \, \frac{P_{HT}}{K^{1/2} \, P_{H_2}^{1/2}} \tag{4}$$

where DK is the permeability at a given temperature. The temperature dependence
for DK is the typical Arrhenius relation

$$DK = (DK)_o \, e^{-\Delta E/RT} \quad . \tag{5}$$

Equation 4 clearly shows that the tritium permeation rate will directly depend
on the ratio of the HT partial pressure to the square root of H_2 partial pressure.
Furthermore, the limiting partial pressure of HT will be twice the initial T_2
pressure, or twice the T_2 pressure if all the tritium existed as the T_2 molecules.

Therefore, as the partial pressure of HT approaches the limiting pressure, the tritium permeation rate will approach an inverse dependency on the square root of H_2 partial pressure. A major barrier to one's acceptance of the above discussion has been a tendency to consider the hypothetical case of pure HT and the tritium permeation rate from such a source. The cursory assumption that a tritium permeation rate from hypothetical pure HT is first power dependent on the HT pressure is incorrect. That rate also would be 0.5 power dependent on the HT pressure because HT must dissociate before entering the metal, and the rate controlling step is the diffusion of the non-distinguishable atoms.

The effect of H_2 dilution on tritium permeation is diagramed in Figure 1, where the tritium permeation rate is plotted against the equilibrium partial pressures of T_2, HT and H_2. Two initial T_2 pressures are considered, 1 torr and 10^{-2} torr, and H_2 is added from 10^{-4} to 10^{2} torr. The permeation rate decreases as the partial pressures of H_2 and HT increase and as the partial pressure of T_2 decreases. The validity of these considerations is supported strongly by the success of determining tritium permeability of nickel with a tritium source of ppm quantities of tritium in protium,[5] and by the excellent analogies with deuterium and protium permeabilities.[5]

A real D-T fusion system probably will have all three hydrogen isotopes equilibrated in various sections of the plant. The tritium permeation rate from this source still will be 0.5 power dependent on the T_2 partial pressure which will be defined by all possible species of the three isotopes. There are six possible reactions in a mixture of the three isotopes. The equilibrium constants for each of the six reactions,

$$H_2 + D_2 = 2HD \tag{6a}$$

$$H_2 + T_2 = 2HT \tag{6b}$$

$$D_2 + T_2 = 2DT \tag{6c}$$

$$H_2 + DT = HT + HD \tag{6d}$$

$$D_2 + HT = DT + HD \tag{6e}$$

$$T_2 + HD = HT + DT \tag{6f}$$

have been determined over a wide temperature range by Jones.[4] The sum of the six reactions is

$$H_2 + D_2 + T_2 = HD + HT + DT \tag{6}$$

which also is the sum of 1/2 of Equations 6a, 6b, and 6c. Then the equilibrium constants for Equation 6 at 600 and 1000°K are 7.14 and 7.70, respectively. The partial pressure of T_2 in a three isotope system at 600°K that compares to Equation 2 is then

$$P_{T_2} = \frac{(P_{HT})(P_{HD})(P_{DT})}{7.14(P_{H_2})(P_{D_2})} \ . \tag{7}$$

Isotope Effects

Differences in protium, deuterium and tritium permeabilities of nickel have been presented,[5] and isotope effects for hydrogen permeation were compared to those for hydrogen solubilities and diffusivities in nickel. These isotope effects for permeation through nickel should be applicable to most construction metals and the ratio of protium to the other isotope permeabilities can be expressed as a function of temperature as,

$$\frac{(DK)_{H}}{(DK)_{D}} = 1.48 \exp (-240/RT) \ , \qquad (8)$$

and

$$\frac{(DK)_{H}}{(DK)_{T}} = 1.96 \exp (-360/RT) \ . \qquad (9)$$

Permeabilities of Clean Metals

Hydrogen permeation measurements through clean construction alloys at high temperatures are difficult because the alloys contain metals that are extremely susceptible to oxidation. The free energies of formation for oxides is an excellent way to determine the conditions under which a particular alloy will oxidize. Such thermodynamic values for oxides most likely to form on structural alloys were tabulated recently,[6] and trends in the formation of various oxides on Incoloy 800 agreed with the relative free energies. The oxidation potential for a given H_2O-H_2 system can be expressed by the H_2O/H_2 ratio.[8] Such considerations have indicated that chromium will form Cr_2O_3 at temperatures up to about 600°C in an atmosphere with a H_2O/H_2 ratio of 10^{-6}, and permeation measurements have shown that Incoloy 800 (23% chromium) will oxidize to affect permeation rates at temperatures to 575°C in 1 atm H_2 that contains 0.7 ppm H_2O; i.e., the H_2O/H_2 ratio was $\approx 10^{-6}$.[9] These observations and the difficulty in maintaining H_2O/H_2 ratios $<10^{-6}$ essentially forces one to protect the alloy surface with a non-oxidizing metal.

It is experimentally convenient to avoid the oxidation of nickel, and electroplating construction alloys with nickel requires only common techniques. We have measured tritium permeabilities of seven clean construction alloys by first electroplating both sides of the tube samples with 7.6 μm nickel.

The permeability of these materials is determined by bulk diffusion of tritium atoms and one would not expect the dissociation or the recombination of hydrogen molecules at the nickel surfaces to significantly affect the measured permeabilities. Also, diffusion through the thin layers of nickel is not significant. The tritium permeabilities of seven construction alloys, a tungsten alloy and nickel are shown in Figure 2 for the 550 to 1000°K range. Hydrogen permeabilities of several alloys are in the literature, but this may be the only data set from a single laboratory with the same apparatus that includes measurements with nine metals. The accuracy of these data based on comparison with the best data for hydrogen permeability of nickel[10] will be seldom matched and the precision in comparing the permeabilities of these materials with each other cannot be approached elsewhere.

It is noteworthy that the permeabilities of the seven structural alloys at 1000°K are all within a factor of 2.3, while at 500°K there would be a factor of 30 between the highest and lowest permeabilities. These data certainly do not include even the majority of structural alloys, but the trends in and the ranges of permeabilities may well represent all nickel and iron based alloys.

Equations for permeabilities of clean metals are given in Table 1. The data are grouped according to trends in permeability constants and permeation activation energies, and the same grouping is apparent in Figure 2. The construction alloys separate into two groups that coincide with a separation of the ferritic steel alloys from the austenitic and nickel base alloys. This somewhat indicates that the crystal structure of the alloys is an important parameter to permeation, but a more likely reason for the above grouping is the thermodynamics of the metal-hydrogen interactions. Perhaps this can be resolved as more data are obtained.

Table 1. Arrhenius equations for tritium permeabilities, DK,
of clean metals over the 500 to 1000°K range[a]

$$DK = (DK)_o \exp(-\Delta E/RT) \text{ cm}^3 [T_2(STP) \cdot mm/(cm^2 \cdot min \cdot torr^{1/2})]$$

$$R = 1.98 \text{ cal}/(deg \cdot g:atom)$$

Metal	Permeability $cm^3 T_2(STP) \cdot mm/(cm^2 \cdot min \cdot torr^{1/2})$	Type
Nickel	0.262 exp (-12680/RT)	Pure
Croloy, 2 1/4 Cr, 1 Mo	0.0862 exp (-11210/RT)	Ferritic
E-Brite	0.166 exp (-12500/RT)	Ferritic
406 SS	0.104 exp (-12200/RT)	Ferritic
Hasteloy N (Inor 8)	0.579 exp (-15800/RT)	Nickel base
Saniero 31	0.367 exp (-15610/RT)	Austinitic
Incoloy 800	0.566 exp (-16120/RT)	Austinitic
316 SS	0.535 exp (-16260/RT)	Austinitic
Tungsten Alloy (1.5% Fe, 3.5% Ni)	0.00788 exp (-14950/RT)	Refractory

[a]All of these equations were determined in the same laboratory with
the same equipment, techniques, and procedures.

Permeabilities of Metals with Oxide Coatings

There are only a few reports of hydrogen permeation rates through alloys that were measured while the alloy oxidized.[2,8,9,11-14] These works represent a variety of experiments and materials that have demonstrated that the in-situ surface oxidation of construction alloys can produce oxide barriers that may reduce tritium permeation rates by significant factors, Table 2. However, to date, there are no tritium permeation measurements that can be extrapolated to fusion reactor conditions and one must consider current conclusions only as indications of what could happen in a fusion reactor steam generator.

The effects of 0.3, 0.7, and 0.94 atm H_2O to oxidize Incoloy 800 at 520, 660, and 725°C, to form oxide layers, and to reduce tritium permeation rates were described recently.[9] The largest effect was observed with 0.94 atm H_2O at 660°C; lower H_2O pressures gave smaller effects. Similar studies indicated that the oxidation at 520°C was much slower than that at 600°C and the barrier effects were significantly lower. However, the material could be oxidized at a higher temperature, 650°C, and the temperature then reduced to 520°C and a barrier effect was observed at 520°C that was equivalent to that at 600°C. Even though the oxidation was faster at 725°C the permeation barrier effect was lower than that at 660°C. These results are summarized in Table 2, and the differences in barrier effects at different temperatures is believed to be the results of different oxidation reactions and rates.

An exhaustive chemical analysis of the oxides on Incoloy 800 produced by 0.94 atm H_2O oxidation at 520, 660, and 725 was reported recently.[11] Depth profile metal compositions throughout the oxide were determined by ion microprobe analysis as functions of oxidation time and temperature and of the pretreatment

Table 2. The effects of oxidation to form oxide layers and to reduce hydrogen permeation rates. The permeation impedance factor is that by which permeation rates are reduced.

Alloy	Temp. °C	Oxidant	Time	Permeation impedance factor	Ref.
Incoloy 800	660	0.32 atm H_2O	150 days	167	9
Incoloy 800	660	0.70 atm H_2O	150 days	178	9
Incoloy 800	660	0.94 atm H_2O	150 days	419	9
Incoloy 800	660	0.94 atm H_2O	150 days	519	9
Incoloy 800	520	0.94 atm H_2O	150 days	41	9
Incoloy 800	725	0.94 atm H_2O	150 days	148	9
Vanadium	350-700	10^{-5} torr[a]	62 days	>100 to <1000	15
446 SS	1058	air	[b]	1000	11
Fe-Cr-Al	1095	air	1 day	1000	11
Incoloy 800	800	[c]	85 days	100-1000	14,15
21-6-9 SS	50-400	HNO_3	[d]	100-1000	16

[a] Residual H_2O and O_2.

[b] Preoxidized for non-disclosed time.

[c] A process gas of 43.5% H_2, 35% H_2O, 8.9% CH_4, 6.9% CO, and 5.7% CO_2

[d] Samples apparently pickled in HNO_3 bath for few minutes.

of the material surface. These results indicated that the _____ _____
of the oxide depended on all of these parameters as well as the _____ of
the alloy and the oxidation potential imposed on the alloy. Therefore, the
comparison of oxidation permeation barrier effects reported by different
experiments probably gives no meaningful results. In the future _____
should include the detailed characterization of the alloy, the _____ oxide,
and consideration of the most minor components. A _____ experiment study of
the oxides is mandatory for understanding the oxidation of alloys and hence the
permeation barrier characteristics.

Hydrogen permeation through metals involves the diffusion of at _____ thru
the bulk metal. This is a well established fact, whereas the permeation of
hydrogen through glasses, and ceramics generally has been assumed to involve
the diffusion of the diatomic molecules through the bulk material. However,
a recent paper[9] has discussed reasons to doubt that assumption and has suggested
that hydrogen permeation through glass and ceramic materials may be also 0.5
power dependent on pressure, i.e., this permeation also involves the diffusion
of hydrogen atoms rather than molecules.

That intriguing suggestion prompted measurements of tritium permeation
through glass materials in the clean metal apparatus. Some preliminary results
are given in Table 5. These data may be compared with those from Lee[17] for
hydrogen permeation through fused quartz, who reported permeabilities based on
a single driving pressure of 1 atm. The permeability equation given by Lee[17]
and the half power assumption converts to

$$DK = 4.30 \text{ E-5} \exp(-9020/RT) \; \frac{cm^3 (H_2 \cdot STP) \cdot mm}{cm^2 \cdot min \cdot torr^{1/2}}$$

Pressure, torr			Permeation rate	Permeability
$P^{1/2}$	III	$P^{1/2}$	$cm^3 H_2, STP/mm$	$cm^3/cm \cdot s \cdot cm^2 \cdot torr^{1/2}$
27.7	2.35 E-2	1.77 E-3	1.77 E-8	1.32 E-7
27.7	1.12 E-2	2.11 E-3	7.05 E-9	1.24 E-7
27.7	1.67 E-5	3.12 E-3	1.98 E-9	1.27 E-7
			Average	1.28 E-7

which gives a permeability value of $\sim 1 \cdot 7$ at $150°C$. This . . . .
with the values in Table 5. These data certainly indicate that tritium . . . . . .
rates through fused quartz are 0.5 power dependent on pressure and therefore
suggest that such hydrogen permeation involves the diffusion of bulk . . . . . .
rather than molecules.

Conclusions

Differences in protium and tritium permeabilities represent the greatest
isotope effect on hydrogen permeation. For nickel at 500 and 100°C the ratios
of protium to tritium permeabilities are 1.56 and 1.65, respectively. Such
values also should be applicable to construction alloys.

The addition of protium and/or deuterium to a given quantity of tritium
will reduce the tritium permeation rate, because the partial pressure of T_2
is reduced. However, the tritium permeation rate will always be directly
proportional to the square root of the T_2 partial pressure. When the T_2 partial
pressure is reduced by a factor near 100 the tritium permeation rate approaches
an inverse 0.5 power dependence on the H_2 and/or D_2 pressures.

Tritium permeabilities of clean construction alloys may be grouped according
to permeability constants and activation energies and such grouping appears to
separate the ferritic alloys from the austenitic and high nickel alloys.

Surface oxidation of construction alloys can produce oxide films that act
as effective tritium permeation barriers. The chemistry of the oxide films
and the barrier characteristics depend on the oxidation time and temperature,
the oxidation potential of the medium, the composition of the alloy, and on
the annealing and surface pretreatment. There are no permeation data that can
be assumed to apply to steam generator operating conditions.

Tritium permeation rates through oxide coated alloys with permeation barrier factors greater than 100 have been observed to be 0.5 power dependent on pressure. Preliminary data indicate that tritium permeation rates through fused quartz are 0.5 power dependent on pressure.
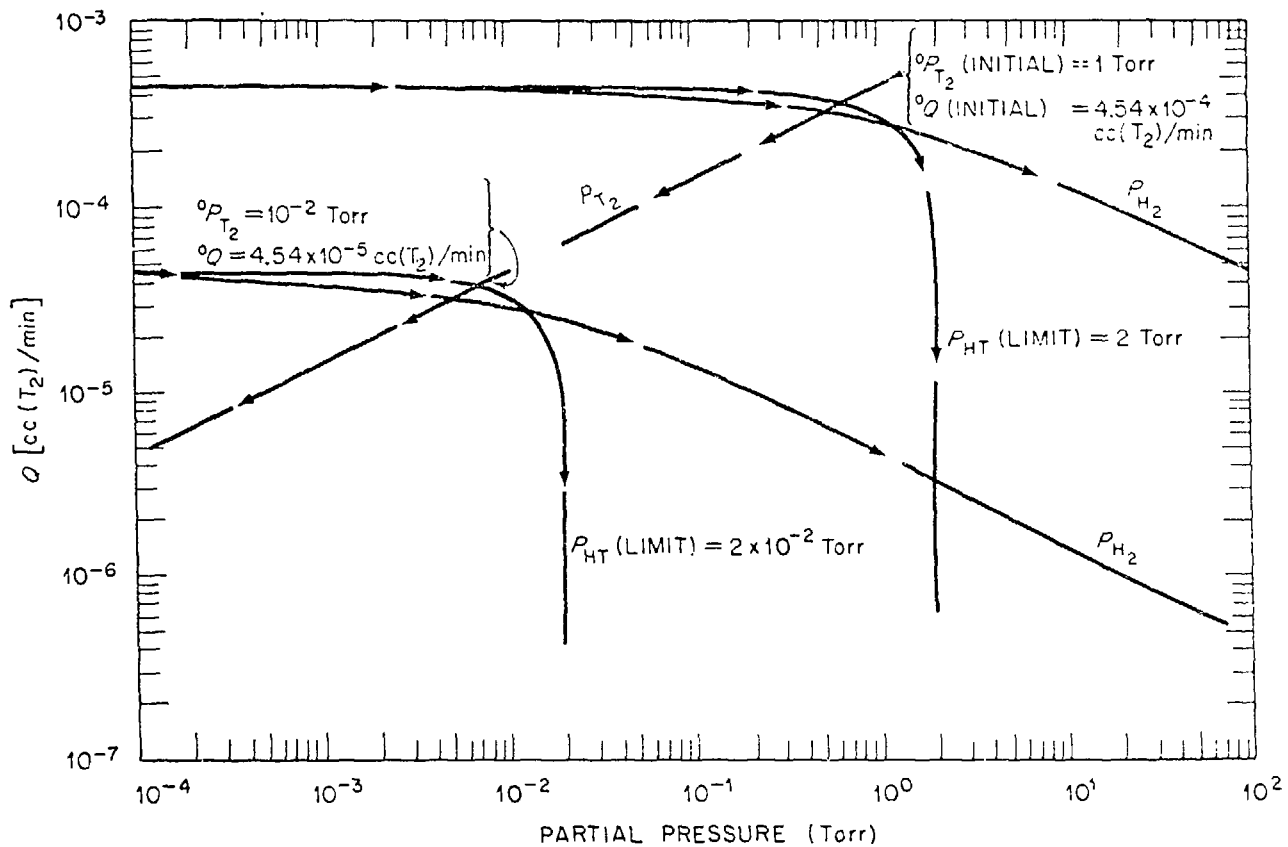
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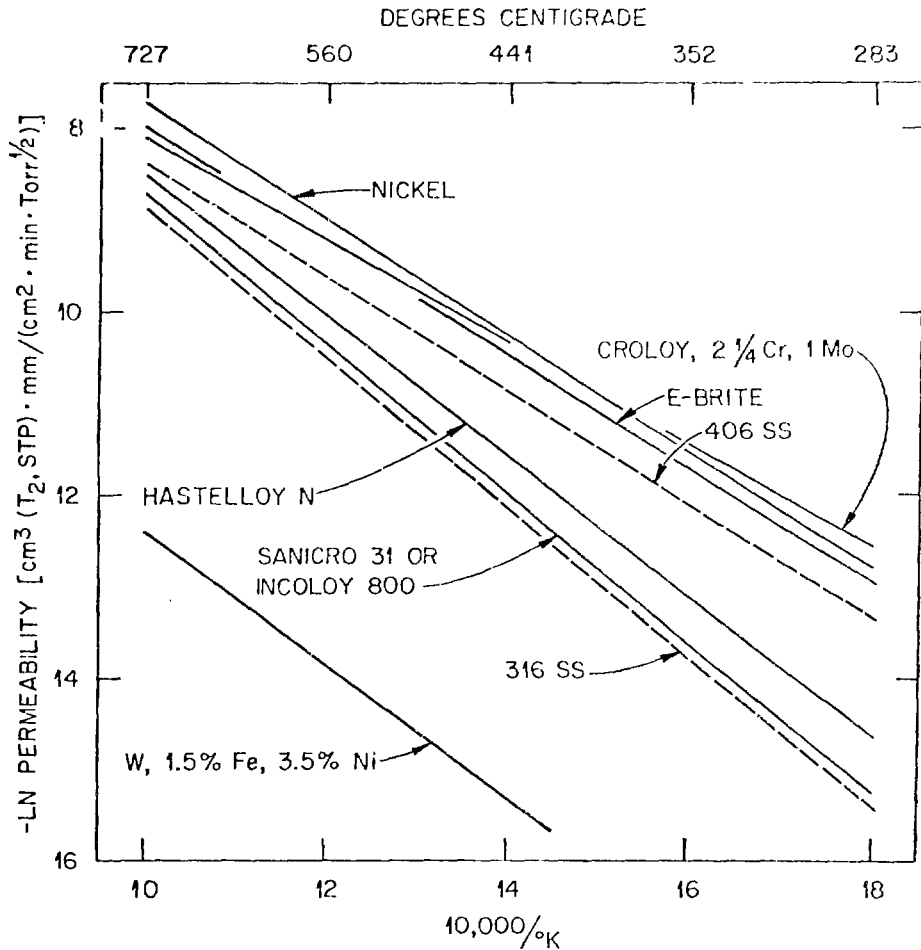
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The Tritium Permeation Rate (Q) Decreases From an Initial Rate (^{0}Q) as Hydrogen is Added. (Nickel at 10^{3}°K, 1-cm^2 Area, 1-mm Thick)

The Tritium Permeabilities of Clean Metals and Alloys