┌─────────────────────────────────────┐
│   **DEMANDE D'AUTORISATION**   │
│   **DE COMMUNICATION OU DE PUBLICATION** │
└─────────────────────────────────────┘

PUBLICATION - Titre :

Auteur(s) : ░░░░░░░░░░░ ℛ∘39

Nature de la Publication :

Editeur(s) (CEA, AIEA, OCDE,...) :

COMMUNICATION - Titre : **Tritium permeation through helium-heated steam generators of ceramic breeder blankets for DEMO.**

Auteur(s) : **M. FUTTERER, X. RAEPSAET, E. PROUST**

Titre de la Conférence : **3rd INTERNATIONAL SYMPOSIUM OF FUSION NUCLEAR TECHNOLOGY (ISFNT-3)**

Lieu et Date : **LOS ANGELES (USA) - 27 Juin - 1er Juillet 94**

Organisateur(s) : UCLA

Date de remise des textes : 28/6/94
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Tritium permeation through helium-heated steam generators of ceramic breeder blankets for DEMO

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The potential sources of tritium contamination of the helium coolant of ceramic breeder blankets have previously been evaluated for the specific case of the European BIT DEMO blanket. This confirmed that the control of tritium losses to the steam circuit is a critical issue which demands development concerning 1) permeation barriers, 2) tritium recovery processes maintaining a very low tritium activity in the coolant, and 3) control of the coolant chemistry. The specifications of these developments required the evaluation of the tritium losses through the steam generators and includes the definition of its operating conditions by thermodynamic cycle calculations, and its thermal-hydraulic design. For both tasks specific computer tools were developed. The obtained geometry, surface area, and temperature profiles along the heat exchanger tubes were then used to estimate the daily tritium permeation into the steam cycle. Steam oxidised Incoloy 800 austenitic stainless steel was identified as the best suited existing material. Our results indicate that in nominal steady-state operation the tritium escape into the steam cycle could be restricted to less than 10 Ci/d. The conditions for this are specified but their feasibility demands in particular the resolution of certain gas chemistry problems, and their validation in the more stringent environment of an operating blanket. Tritium permeation during temperature and pressure transients in the steam generator (destruction and possible self-healing of the permeation barrier) was identified to bear a large tritium release potential. The problems associated with such transients are discussed and possible solutions are proposed.

1. Introduction

Within the European Test Blanket Program CEA and ENEA are jointly developing a helium-cooled ceramic Breeder Inside Tube (BIT) blanket for DEMO [1]. As in most realistic blanket concepts, tritium losses from the blanket into the steam cycle and eventually into the environment are of major concern.

For the BIT design, when no countermeasures are taken, the primary sources of tritium (T) contamination of the helium (He) coolant have been identified as the 1st wall (up to 100 g/d), the breeder rods containing the annular ceramic breeder pellets (~ 25 g/d) and T release from the beryllium (up to 4 g/d) [2]. In this work, T permeation through a typical He-heated SG is quantified. This was done by

1) defining the steam cycle architecture and the operating conditions for the SG using the specially developed computer code CYTHER [3];
2) designing a helical coil tube bundle SG according to commercially applied procedures with the newly developed computer tool HE2SG [7], and
3) determining the tritium permeation through the SG material applying literature data for clean and steam oxidised Incoloy 800 austenitic steel and taking into account the temperature profile of the SG tubing.

For a given permeation barrier efficiency the maximum allowable T activity in the He coolant was calculated.

2. Definition of the steam cycle

The computer tool CYTHER was written to assemble typical steam cycle components to form a Rankine cycle (example cf. Fig. 1, input data printed in bold). The code enables the calculation of pressure, temperature, enthalpy, steam quality, entropy, exchanged power and flow-rates for every component by solving a matrix of mass and energy balances.

The assumptions for the steam cycle definition (Table 1) are based on data usually employed for the design of fission reactors [4]. The relative pressure drop $\Delta p/p$ in the steam generator stems from iterations with the program HE2SG. The pinch point ΔT expresses the minimum temperature difference between heating and heated medium. This value is dictated primarily by economic considerations (capital cost per transfered heat).

generator efficiency	0.975
HP turbine efficiency	0.92
LP turbine efficiency	0.84
pump efficiency	0.75
feedwater pump turbine efficiency	0.75
steam generator $\Delta p/p$ for feedwater pressure 8.03 MPa	0.15
steam generator $\Delta p/p$ for feedwater pressure 16.5 MPa	0.026
HP turbine inlet $\Delta p/p$	0.10
LP turbine inlet $\Delta p/p$	0.025
extraction lines $\Delta p/p$	0.05
feedwater heater inlet $\Delta p/p$	0.02
feedwater heater $\Delta p/p$	0.02
SG minimum pinch point ΔT	35 K
feedwater heater steam pinch ΔT	4 K
feedwater heater purge pinch ΔT	8 K
condenser pressure temperature	8 kPa 41.5 °C

Table 1: Assumptions for the thermal cycle definition in CYTHER

Renner and Raue [21] measured T permeation through clean and oxidised (0.2 MPa steam at 482°C during 28 days) Croloy T22 ferritic SG steel with the composition Fe, 2.01 wt% Cr, 0.96 wt% Mo, 0.08 wt% C, 0.04 wt% Mn, 0.013 wt% P, 0.014 wt% S, 0.14 wt% Si, 0.12 wt% Ni, 0.02 wt% V and 0.01 wt% Ti. The T permeated from contaminated sodium into a small steam circuit which was of a representative chemical composition. The water was deionised, the pH was adjusted to 9.0 - 9.5 with ammonia, and hydrazine was added as an oxygen scavenger. The activation energy for clean Croloy T22 was determined (39.14 kJ/mol) but not for the oxidised steel. In all experiments and even at T partial pressures in the sodium as low as 5×10^{-2} - 7×10^{-12} Pa (!) the permeation remained 0.5 power dependent hinting at atomic diffusion as the rate determining step. Steam oxidation reduced the T permeation rate by factors up to 150 which they attributed to the formation of black Fe_3O_4 (uniform thickness approximately 5 μm with numerous cracks) which also contained unquantified amounts of Cr, Mo and Mn. Self-healing of the oxide barrier could be confirmed after accidental temperature step induced crack formation. The measured permeation rate increased by a factor 5 approximately and returned to its original low value after about one day of steam exposure at 482°C).

Between 1976 and 1980 Bell et al. published a number of articles [11-15] which were focused on the development of suitable oxidation conditions for Incoloy 800. He found that the kinetics of oxidation were governed by the diffusivity of the more easily oxidised metals in the alloy and the oxide, i.e. by temperature. He succeeded to form an efficient self-healing oxide barrier (formed in 94 kPa steam at 660°C) on preannealed Incoloy 800 which was characterised by Bittner [16] and which resulted in permeation reduction factors of 210 after 15 days up to almost 700 after 150 days (extrapolated) for T activities down to 10^{-6} Pa. Oxidation at the lower temperature 520°C in 94 kPa steam was much less efficient (permeation reduction factors between 30 and 40) but preoxidation at high temperature with consecutive slow temperature decrease led to the same permeation reduction factors as at high temperature. A temperature step from 660°C to 550°C in a few minutes with immediate return to 660°C fractured the oxide film and the measured permeation rate increased as if no barrier existed [13]. The complete self-healing of the film at 660°C took approximately 5 days.

In order to determine the activation energy for the permeability, Bell varied the test temperatures only by approximately ± 50°C in order to preserve the chemical composition of the surface oxide. He found an identical activation energy for clean and oxidised Incoloy 800 of the order of 67.5 kJ/mol. This indicates that the created oxide barrier was partly defective and works by blocking the adsorption sites

on the surface rather than by the oxide's own low permeability. This could also explain why the pressure dependence for Incoloy 800 oxides remained 0.5 power dependent even at very low tritium partial pressures (<< 1 Pa) whereas other authors found 1.0 power dependence for ideal oxides with no defects. The T permeabilities were measured in $He/H_2/T_2/HT$ mixtures and related to the square root of the residual molecular T_2 pressure which was calculated from thermodynamic equilibrium data. From [12] we can determine the tritium permeabilities for clean Incoloy 800 to

$$\Phi_{clean} = 4.3324 \cdot 10^{17} \exp\left\{-\frac{67491}{RT}\right\}\left[\frac{at}{m \cdot s \cdot \sqrt{Pa}}\right]$$

and for preoxidised Incoloy 800 with defects (barrier factor 400) to $\Phi_{ox} = \Phi_{clean}/400$.

The 0.5 power dependence of the permeability leads to conservative results in tritium permeation calculations, but corresponds more realistically to SG operating conditions (defects) and is therefore applied in this work.

We conclude that Incoloy 800 is a well established SG material with the potential to form efficient self-healing tritium permeation barriers by preoxidation. Therefore, we adopted Incoloy 800 as a reference SG material for this study.

5. Results and discussion

The required high pumping power for the He coolant makes maximising of the reactor's thermal efficiency the predominant task. In order to define the Rankine cycle operating conditions, two different SGs were designed for the feedwater pressures 8.0 and 16.5 MPa. Pressures higher than the 6.0 MPa in the He coolant circuit are required to prevent the tritium contaminated He penetrating into the steam circuit in case of tube leakage. Very high steam pressures are, however, also to be avoided (pressure resistance of the blanket structure in case of SG tube failure) but were considered here as well to evaluate their influence on thermal efficiency and SG design. The He inlet and outlet temperatures in the SG are dictated by material requirements of the martensitic blanket structure. The feedwater inlet temperature and the steam exit temperature on the other hand were chosen with the objective to limit the SG size, exchange surface area and capital costs. The total reactor power of 3000 MWth (blanket + divertors) was assumed to be transfered by 4 identical SGs of 750 MWth each. The main characteristics of the resulting design versions are presented in Table 2, the corresponding Rankine cycle architecture and operating conditions for the feedwater pressure 8.0 MPa are given in Fig. 1. It should be noted that the HP version benefits from considerably larger heat transfer coefficients and therefore needs 6% less water throughput accompanied by a much higher subcooling than the LP version in order to respect a minimum pinch point temperature difference. These

the overall water vapor concentration and thus facilitate the extraction of HTO (by molecular sieves or cold traps). Two problems which are difficult to quantify must be mentioned in this context: (1) the strong dilution of the HTO with H_2O causes a waste water problem because the T concentration in the water traps of the coolant purification units will be prohibitively low for an economical T recovery; (2) at the high temperatures in the superheater T will be desorbed as HT (no chemisorption of water on hot surfaces, free hydrogen from radiolysis and dissociation of water in the blanket) and the desired conversion to HTO in the gas phase will probably be too slow (coolant residence time in the blanket of the order of one second), even at elevated water vapor concentrations. The oxidation of HT to HTO, e.g. by a copper oxide bed, is in principle feasible but, in return, would cause an unacceptable coolant pressure drop.

Water vapor provokes the growth of passive oxides on the steel surfaces which not only act as permeation barriers but also impede the catalytic reduction of tritiated water to permeable HT. The combination of the various phenomena (water vapor addition, HTO trapping, and oxide formation) suggests, however, that an assumed T activity of the order of 10^{-3} Pa is not overly optimistic.
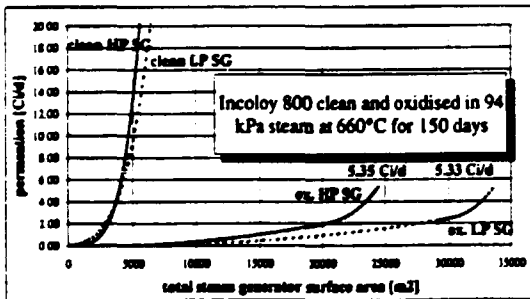
Fig. 3: Expected permeation through clean and preoxidised steam generator tubes vs. steam generator surface area

For the evaluation of the total tritium losses we also have to take into account tritium escape due to He leakage from seals and material imperfections in the coolant circuit. Here, the assumption was, that only HT and T_2 (the components that are responsible for the "equivalent T partial pressure") can escape through He leaks, while the single leaks are too small for significant HTO leakage. When we consider a realistic He leak rate of 0.025% of the coolant per day [21] and an estimated 8.8×10^3 kg coolant inventory (same as for a 3000 MWth General Atomic HTGR [22]) we obtain a total tritium loss rate which is plotted in Fig. 4 as a function of the equivalent T partial pressure in the He coolant for either of the two SG designs. The contribution of leakage to the total losses is negligible.

The total admissible reactor site T release rate will be of the order of 100 Ci/d per GWe which must be shared among different systems such as the plasma fuelling and exhaust, the T recovery circuit,

the thermal cycle and so forth. Because it is very difficult to allot a specific T loss-rate to each of these systems, we fixed an arbitrary 10 Ci/d release limit for the thermal cycle while keeping in mind the general rule to reduce T losses as much as practically feasible. Our results for steady-state operation suggest that a probably acceptable 10 Ci/d release limit can be respected as long as the T activity in the He coolant remains below a value of approximately 3×10^{-3} Pa.
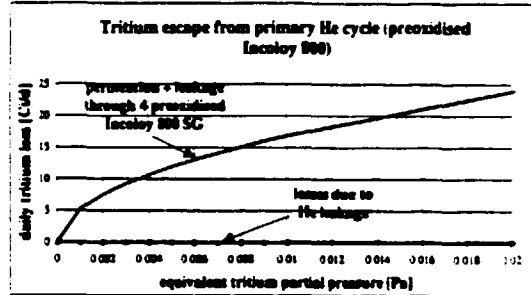
Fig. 4: Tritium permeation and leakage from primary He cycle (8.8×10^3 kg He inventory, leak rate 0.025% per day)

The precise chemical composition of the He coolant should, however, be the object of a more detailed analysis, because any hydrogen addition will certainly lower the oxidation potential of the coolant while water addition might adversely affect the corrosion behavior of other blanket components. The addition of other gases such as CO or CO_2 to the coolant could also be worth further studies, because these gases are known to block desorption sites.

Even though T permeation in steady-state does not seem to raise severe problems, temperature and pressure transients can exert a detrimental effect on the oxide barrier. Bell [13] reported that a quick temperature step can fully destroy the oxide's barrier effect, but that the normal operating conditions (660°C, 94 kPa steam) could completely restore the barrier effect within 5 days. This self-healing period, albeit short, is worth particular attention. We found that the additional T losses correspond to about 190 days of steady-state operation with an intact barrier. In other words, during only two transients with complete destruction of the barrier, the additional T permeation amounts to more than one year of operation with an efficient barrier.

This guess, though quite rough, underlines the necessity of future work on T release during temperature/pressure transients. In our SG design the temperatures are even lower than in Bell's experiment, so that we must suppose that self-healing will require more than the reported 5 days. On the other hand, the role of potentially attenuating factors should be investigated which could smoothen strong permeation spikes. Such factors are in particular the water volume in the secondary loop, the temperature decrease in the SG, the reduction of the T activity in the He circuit with time by conversion into HTO, or the stop of the T source (during reactor shut-down).