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Material compatibility issues in EU fusion fuel cycle R&D and design

D.K. Murdoch [a,*], I. Cristescu [b], C. Day [b], M. Glugla [b], R. Lässer [a], A. Mack [b]

[a] *EFDA Close Support Unit, MPI für Plasmaphysik, D-85748 Garching, Germany*
[b] *Forschungszentrum Karlsruhe, P.O. Box 3640, D-76021 Karlsruhe, Germany*

Abstract

Many material selections for fusion Fuel Cycle systems are determined by the properties of tritium, including its behaviour as a hydrogen isotope, and its decay product, ^{3}He. Within the EU R&D program, the following issues related to tritium service have been addressed. The mechanical integrity and longevity of the sorbent/bonding agent/substrate system used for cryosorption pumping have been extensively tested under tritium exposure. Extended testing of palladium/silver membranes used for separation of elemental hydrogens from impurities has been carried out to confirm longevity in tritium service. For all high temperature (~150 °C) components, tritium permeation through primary containments must be confined by outer (low temperature) jackets, and designs have been developed to achieve this. For wetproof catalysts and solid polymer electrolysers used for water detritiation, tests are in progress to determine the operating life. Testing of the ITER reference tritium storage getter material is under way.

1. Introduction

Many material selections for fusion Fuel Cycle systems are determined by the properties of tritium, and its decay product, ^{3}He. Within the EU Fuel Cycle R&D program issues have been addressed. This paper presents an overview of some of these.

2. Cryosorbent development

The cryopanels of all major ITER cryopumping systems (Torus, Neutral Beam and Cryostat) pump by cryosorption at ~5 K on activated charcoal. As all of these pumping systems will be exposed to (varying amounts of) tritium, the tritium-compatible substrate/bonding agent/sorbent system specified in Table 1 is proposed for all of these applications.

Tests to determine the residual tritium inventory in cryopanel coupons have been carried out [1]. The results of these tests are strongly influenced by the impurity gas species to which the panels are exposed and the (pressure and temperature) conditions under which the panels were regenerated.

In laboratory scale tests carried out by the ITER Russian Federation Home Team, small (~12 cm^2) coupons fabricated to the above specification, were exposed to ITER-relevant tritium doses (~2×10^8 Pa s) and then regenerated at ambient temperature and a vacuum of 10^{-2} Pa. Residual

* Corresponding author. Tel.: +49 89 3299 4235; fax: +49 89 3299 4198.
E-mail address: david.murdoch@tech.efda.org (D.K. Murdoch).

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Table 1
Data for cryopanel materials (torus exhaust, neutral beam and cryostat pumps)

Component	Material
Substrate	Stainless steel, SS 316 L (~1.5–2.0 mm thick)
Bonding agent	Two component inorganic cement
Sorbent	Granular coconut shell activated charcoal, Size 12–30 US-mesh, (1.2 mm), BET surface 1100–1200 m^2/g, microporous (maximum at 1.0–1.2 nm pore width)

tritium inventories up to 3 mCi (10 MBq) were measured. Scale-up to the aggregate panel area of the ITER Torus Exhaust Cryopanels (a factor of $\sim 10^5$) would suggest a total tritium inventory of 300 Ci (10 TBq). This is an acceptable level of tritium recovery for cryopump operation, but would mandate end of life recovery prior to consigning the panels to the Hot cell waste storage facility.

In order to replicate more closely the ITER gas compositions and regeneration conditions, a near full scale panel was used to pump the torus exhaust of JET, and will be regenerated at ITER impurity regeneration temperature (475 K) and then destructively analysed to determine the residual tritium loading.

The mechanical integrity of the coupons was investigated with pull tests and no deterioration of the bonding strength of the sorbent to the substrate detected. Analogous tests of the JET panel will be carried out.

3. Roots pumps

The standardized design of the ITER rough pumping trains for tritiated streams includes two stages of roots pumps. Commercially available roots pumps have a number of features which compromise their tritium compatibility, namely porous casing material with O-ring seals, a mechanically sealed drive shaft and contact between the process gas and the oil used for lubricating the timing gears. Contact between the gas and the oil risks oil migration into the process gas, which could deposit on downstream piping walls and also poison permeators and catalysts in the tritium plant. Tritium pick-up by the oil could degrade its performance and would create a troublesome waste stream. A tritium-compatible design with a metallic sealed stainless steel casing and magnetic drive coupling to reduce the external leak rate to acceptable levels, and ferrofluidic shaft seals to separate the tritiated pumped gas from the oil (and its cover gas) is being developed at the FZK (Karlsruhe Research Centre) in Germany [2].

The main challenge is the incorporation of ferrofluidic seals to meet the tight dimensional tolerances consistent with reasonable pumping performance. Recent tests with a 250 m^3/h pump equipped with four cartridge-type ferrofluidic seals (one at each side of the pumping chamber on each shaft) have demonstrated adequate leak tightness ($\sim 10^{-7}$ Pa m^3/s) over several months of operation. Tritium exposure tests to investigate the tritium uptake in the very small quantities (a few nanolitres) of ferrofluid are in progress. The design of larger, ITER-relevant pumps has been initiated; scale-up of designs using ferrofluidic seals is expected to be relatively straightforward.

4. Pd/Ag Membranes and containment permeation

Hydrogen isotope permeation through palladium and the Pd/Ag alloy (23% silver) employed in technical applications is highly selective. Practically no gases other than hydrogens penetrate Pd/Ag membranes (typical thickness up to 100 μm) at operation temperatures of about 400 °C (670 K). Alloying silver to palladium hardly affects the permeabilities for hydrogen isotopes, but does substantially reduce the region of hydride stability. Hence embrittlement of the permeation membrane at elevated hydrogen pressures, particularly at lower temperatures, is avoided.

Under the ITER operating conditions, some tritium is constantly dissolved in the Pd/Ag tubes, raising concerns about mechanical deterioration of the membrane by ^{3}He production from tritium decay, trapping in the lattice matrix and bubble agglomeration. Studies [3] have shown only a slight change in the mechanical properties of palladium samples saturated with tritium for extended periods of time. At the CAPER (prototype Catalysis-Permeation-based Tokamak Exhaust Processing) technical facility of the Tritium Laboratory Karlsruhe (TLK) a 1/5 ITER size front-end permeator has been in tritium service for more than 10 years without showing any malfunction attributable to ^{3}He.

At an operation temperature of 400 °C (673 K), hydrogen isotopes do not only permeate through the Pd/Ag membrane tubes, but also through the stainless steel body of the permeator. For non-nuclear industrial applications, the hydrogen losses are insignificant, but, for tritium applications, the atmosphere of the secondary containment of all

processing systems involving heated components would become contaminated. Therefore, all permeators (and other tritium processing components heated to temperatures above about 150 °C 423 K) are operated in an evacuated outer containment maintained at ambient temperature. The vacuum interspace provides thermal insulation, reducing the heat load to the secondary containment, and allows recovery of the permeated tritium by periodic evacuation. For a 1 m^2 ITER front-end permeator, about 0.05 cm^3 (STP) equivalent to about 6 GBq (0.15 Ci) per day will permeate through the primary stainless steel structure of the permeator into the outer containment. With a volume of about 0.05 m^3 the interspace needs to be evacuated weekly. Experience at TLK has shown that a significant fraction of the permeated tritium is converted into tritiated methane, thought to be due to segregation of carbon from the stainless steel bulk to the surface and the time available for interaction.

5. Water detritiation system components

The Water Detritiation System for ITER is based on the Combined electrolysis catalytic exchange (CECE) process, which depends on the tritium compatibility of Nafion™ membranes of the solid polymer electrolyser (SPE) and a Teflon™ based wetproof catalyst for the liquid phase catalytic exchange (LPCE) column, respectively. Recent investigations in Europe have been carried out at the TLK in Germany, SCK-CEN (Nuclear Research Centre) in Belgium and ICIT (National Institute for Cryogenic and Isotopic Technology) in Romania. These tests complement the long operating experience which has been built up at other centres, including the Mound facility in the USA.

5.1. Solid polymer electrolyser

Experiments at TLK have investigated:

1. The performance of a small SPE cell over a long period functioning with tritiated water, with an activity of 1.2 Ci kg^{-1} 40 GBq kg^{-1}.
2. The mechanical properties (tensile strength and elongation) of a Nafion™ solid polymer membrane before and after exposure to tritiated and demineralised water.

During six months of continuous operation, the voltage drop applied to two electrolysis cells working with tritiated and untritiated demineralised water was maintained constant, and the current through the cells continuously recorded. In Fig. 1, the behaviour of the cell current of the two electrolyser cells over six months operation period is shown. The current in both electrolysis cells showed similar behaviour patterns, the instabilities being due to the relative movement of the electrodes when pressure fluctuations occurred.

The chemical composition of tritiated water processed in the experimental rig was measured after two and six months operation, see Table 2. The concentration of cations in the tritiated water decreased very slightly after three months operation, probably due to their fixation within the solid polymer membrane.

The mechanical properties, including tensile strength and elongation, of the membranes used at TLK during the tests with the two small electrolysis cells were measured. The average values for tensile strength and elongation for the SPM after operation in the two electrolysis cells, in service with tritiated and demineralised water respectively, differed only very slightly from each other and from the virgin SPM cells. The small differences in mechanical properties between the two SPM do not appear to be caused by β radiation of tritium.

Experiments reported in [4], in which a sample of these compounds was irradiated by gamma rays up to 850 kGy (corresponding to exposure to tritiated water with 250 Ci/kg (~10 TBq/kg) for approximately three years) indicated no serious deterioration in the strength or ion exchange capacity of the (Nafion) membrane.

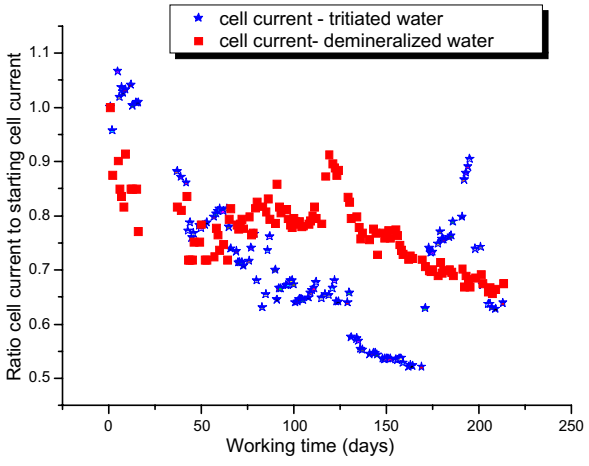

Fig. 1. SPE Cell current variation with time (days).

Table 2
Composition of tritiated water after exposure (all concentrations in mg l^{-1})

Ion	Feed water	After two months	After six months
Al	<0.2	6.1	5.0
Ca	0.11	4.9	3.3
Fe	<0.05	2.6	0.87
P	<0.5	6.0	4.1
S	<0.5	4.3	4.7
Si	0.68	7.8	8.9
Ti	<0.5	4.2	0.4
Chloride	0.09	6.99	3.2
Fluoride	0.45	37.6	22.7
Phosphate	0.15	7.8	8.4
Sulfate	0.26	9.1	10.9
pH	5.5	3.0	3.8

5.2. LPCE catalyst

Tests on candidate catalyst/packing mixtures were carried out. These catalysts typically contain ~1% (w/w) platinum, 19% (w/w) activated carbon and 80% (w/w) PTFE (polytetrafluorethylene). Typically catalyst particles of ~2 mm diameter and 2 mm height are used in a 1:2 volumetric ratio with the packing. The catalyst and packing may be combined in a homogeneous mixture, or in alternating discrete layers. As the tritium content of the water in the column increases by a factor of up to 10^8 (for ITER) from the top to the bottom of the column, tritium tolerance of the catalyst in the lower sections of the column where the tritium concentration will be up to ~25 Ci/kg (~1 TBq/kg) needs to be confirmed.

At ICIT, endurance testing of an SCK-CEN catalyst–packing mixture (Type MO 1254) was carried out. The catalyst/packing mixture was exposed to β-tritium radiation, in dynamic and static modes, to get comprehensive data on the influence of β-tritium radiation and impurities on catalyst activity and stability.

After each three months of continuous exposure, physico-structural parameters of the Pt-catalyst, separation performances and water quality were measured and compared to initial values. The test results, summarized in Table 3, indicate no significant long term evolution of key catalyst properties.

6. Getters

Based on bench-scale experiments the intermetallic compound zirconium–cobalt (ZrCo) has been selected as reference getter material for the storage of deuterium and tritium in the storage and delivery system (SDS) of the ITER tritium plant, considering only scientific criteria. Despite its good hydrogen gettering properties (comparable to those of uranium), under certain conditions typical for routine delivery of gases (simultaneous high partial pressure of H_2 and temperatures in the 350–400 °C 620–670 K range), ZrCo progressively loses its activity during repeated absorption–desorption cycles [5]. The hydrided getter material $ZrCoH_x$ tends to disproportionate into ZrH_2 and $ZrCo_2$. As the ZrH_2 needs a much higher temperature (~650 °C 920 K) for hydrogen release, a semi-permanent trapped inventory of hydrogens results. This trapped inventory increases the quantity of tritium in the SDS, which is undesirable from safety and tritium economy perspectives, while reducing the available effective storage capacity of the beds. Although the getter can be reproportionated to ZrCo, its original performance cannot be completely restored. The high temperature and high vacuum required undermine the practicality of carrying out this procedure on a routine basis, compromise the endurance of the beds and give rise to concerns over safety.

A second undesirable feature of ZrCO is its significant apparent isotopic effect upon fast deloading. During tests of an ITER-scale prototype storage bed initially filled with an equimolar hydrogen/deuterium mixture, an inverse isotope effect was

Table 3
Physico-structural parameters of MO 1254 catalyst before testing and after three and six months exposure to β-tritium radiation

Property	Value		
	Before test	After three months	After six months
Platinum content, (wt%)	0.916	0.914	0.920
Macropore volume (cm^3/g)	0.1467	0.1397	0.1495
Micropore volume, (cm^3/g)	0.1005	0.0413	0.090
Pore average radius (Å)	42.15	57.76	48.50
Specific area (m^2/g)	117.3	98.677	102
Adsorbed H_2 vol. (cm^3/g cat)	0.58	0.47	0.51
H/Pt dispersion (atom ratio)	1.06	0.89	0.94
Pt active surface (m^2/g)	290	274	281
Platinum particle size Pt (Å)	8.1	9.6	9.0

observed. The deuterium was found to be released preferably. During the deloading, the H/D ratio in the gas delivered by the bed was significantly (up to 20%) different from the H/D ratio in the gas initially absorbed in the bed. While these tests should in due course be repeated with an ITER-scale bed using deuterium and tritium, this effect will complicate the supply of gases with tightly specified isotopic composition to the ITER Fuelling System, which must be achieved within short time scales and with limited involvement of gas analytical systems.

A review of the merits and concerns of potential alternatives to ZrCo could now be undertaken in a more focussed manner, following the confirmation of the ITER site selection.

7. Conclusions

A number of issues relating to the interaction of tritium with structural and process-specific materials are being systematically investigated. While no insurmountable problems have been identified, several instances where material selections and related design details can exert a strong influence on maintenance requirements are subject to ongoing development work

The sorbent–bond system adopted for ITER cryopumps has been extensively tested to ensure its mechanical integrity and longevity under tritium exposure. Conditions have been established for cryopanel regeneration, to release quantitatively the diverse tritiated gas species originating predominantly from plasma wall interaction.

Processing of highly tritiated gases includes separation of the hydrogens from impurities by palladium/silver (Pd/Ag) membranes. Extended testing has been carried out to confirm that adequate lifetimes can be achieved despite decay helium bubble formation within the membrane lattice.

Water detritiation, by the CECE (Combined Electrolysis Catalytic Exchange) process, relies on wetproof catalysts with a teflon matrix, and tests are in progress to determine the operating life as a function of tritium concentration in the water. Similar tests on the nafion membranes in solid polymer electrolysers are under way; initial results are positive.

Tritium storage systems, for both stationary and transport applications, use metal getters, which must release tritium at a reasonable rate and quantitatively under moderate conditions. Testing of the ITER reference zirconium–cobalt (ZrCo) getter material for stationary applications has shown that significant disproportionation, resulting in semi-permanent trapping of tritium and other shortcomings, occurs under normal ITER operating conditions. This behaviour is of concern.

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