PLASMA EXHAUST GAS PROCESSING FOR FUSION REACTORS: DEVELOPMENTS AND PROBLEMS

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Recent progress at the Tritium Laboratory Karlsruhe is presented on the development of tritium technology for ITER in areas such as fuel clean-up of plasma exhaust gas, qualification of components by long-term testing under a relevant tritium environment, and tritium accountability based on calorimetry.

1. Introduction

One of the main functions of the plasma exhaust clean-up system for the International Thermonuclear Experimental Reactor (ITER) is to recover most of the unspent deuterium-tritium fuel from the plasma exhaust gas and to produce, at the same time, a waste gas stream of extremely low tritium content. Particularly in the field of plasma exhaust clean-up has the progress achieved in several laboratories been impressive [1]. The worldwide activities during the past few years have been greatly stimulated by the increasingly demanding requirements of the ITER Team.

All current plasma exhaust clean-up concepts for ITER comprise three largely independent process steps, i.e. a so called front-end permeator battery, a main impurity processing loop, and an ultimate detritiation step [2, 3]. With a separation of the overall process into several basically independent detritiation steps very high decontamination factors (DF = tritium flow rate at the inlet of the process over tritium flow rate at its outlet) can be achieved in a relatively short period of time.

In the following, ongoing research aimed at the development of an integral fuel clean-up process for the plasma exhaust gas of ITER and activities related to the development and testing of components essential for this fuel clean-up system carried out at the Tritium Laboratory Karlsruhe (TLK) will be presented. Another related subject addressed is tritium accountability.

2. Test & selection of plasma exhaust clean-up components and development of an integral plasma exhaust clean-up process for ITER

In view that the engineering design phase of ITER is nearing completion and the construction phase of this reactor is becoming imminent, it is of increasing importance to select a fuel clean-up process complying with all current ITER requirements and to identify components suitable for the routine operation of the ITER Tritium Plant.

2.1. Development and test of components

Much work is currently in progress at the TLK concerning the test of selected components with relevant concentrations of tritium over extended periods of time. With respect to type and concentration of the impurities, pressures, temperatures, and flow rates, the
experiments are performed under conditions closely simulating those anticipated for the ITER Tritium Plant.

2.1.1. Permeator

A crucial component of the fuel clean-up system will be a palladium/silver permeator, capable of separating hydrogen isotopes from other gases. The achievable DF's at the front-end permeator level will be determined by the feed flow rate, the effective palladium/silver permeation area, the permeate pressure, the tritium activity bonded to the impurities and the concentration of the non-permeating impurities. Relative isotope effects for the permeation of hydrogen, deuterium, and deuterium tride through commercial palladium/silver permeators of 0.12 - 0.36 m² permeation surface area at permeate pressures between 10 and 400 mbar were thus determined experimentally at the TLK [4, 5]. Fig. 1 shows some typical DT bleed break through curves obtained with a permeator of 0.12 m² effective permeation area as function of the feed gas flow rate. The relative isotope effects found are compiled in Table I together with data reported in the literature. They indicate, that the isotope effects at the permeator level are significant and will therefore have an impact on the design and sizing of this component as well as on the supporting pumping system.

![Graph showing break through curves for DT mixture through a permeator](image)

**Fig. 1** Break through curves of an equimolar deuterium/tritium mixture through a permeator operated at 360 °C. The permeate pressure was held constant at ≈ 150, α = 20, Δ = 300, and ≈ 400 mbar, respectively.

<table>
<thead>
<tr>
<th>gas ratio</th>
<th>this work</th>
<th>Konishi et al. [6]</th>
<th>Tanaka, Kiyose [7]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂/D₂</td>
<td>1.72 ± 0.03</td>
<td>1.76 ± 0.09</td>
<td>1.61</td>
</tr>
<tr>
<td>H₂/DT</td>
<td>2.06 ± 0.03</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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From the point of view of permeator design both in/out (feed gas into the permeation tubes and permeate gas pumping at the outside of the permeation tubes) as well as out/in operation modes are possible. In some designs the bleed gas is removed via a tube inserted into the palladium/silver fingers [8] and in others it is passed through a palladium/silver spiral [9]. While the in/out mode is favoured when very low permeate pressures are desired, the effect on the permeator throughput is much dependent upon the size of the selected palladium/silver tubes and - if available - that of the inserted tubes.

Permeator poisoning caused by radiation-induced reactions of hydrocarbons, carbon monoxide, or carbon dioxide with tritium is a matter of concern. At the TLK comparatively rapid poisoning of permeators was noticed, when the palladium/silver surface was exposed to polytritiated hydrocarbons at the permeator operating temperature, i.e. 350 °C. After sufficiently long exposure time, i.e. 150 hours, the permeation properties of the permeator changed to the point that the hydrogen isotope permeation was completely suppressed. Poisoning by hydrocarbons and carbon oxides was found to be reversible. To fully restore the permeation properties of a permeator, repeated treatment for several hours with laboratory air at elevated temperatures was found to be necessary. Periodic regenerations with laboratory air of permeators installed in the fuel clean-up system of the ITER Tritium Plant will hence have to be contemplated in the design.

A commercial palladium/silver permeator, installed in an insulation vacuum to keep permeation losses into the glove box at very low levels, has been exposed regularly in various kinds of experiments to deuterium tritide in the presence of carbon monoxide, carbon dioxide, polytritiated deuterio methane, and to some other not yet well identified higher tritiated deuterio hydrocarbons produced by radiation-induced reactions for a period of almost two years. During this period no permanent damage of the permeator was noticed. Whenever loss of permeability was observed, a treatment with laboratory air sufficed to completely regenerate the permeator. From the performed tests it can be concluded that permeators are sufficiently robust for their application in the ITER Tritium Plant.

2.1.2. Pumps

In another investigation a tritium compatible two-stage Siemens metal bellows pump was tested over prolonged time with several hydrogen isotopes. The experimental results indicate that the results of tests with similar conditions and their combinations are selected for specific process duties in the ITER Tritium Plant. The measured compression ratios were found to be in the range 7.9 at discharge pressures down to 100 mbar. Similar tests with an oil-free PV12 scroll pump (18 m³/h) backed by a two-stage Siemens metal bellows pump show that with this pump combination vacua as low as 0.2 mbar can be attained at a discharge pressure of 1000 mbar. The compression ratios measured for DT with this pump combination were found to be in the range 10⁴ - 10⁵, depending upon the discharge pressure. During the long-term operation with equimolar deuterium/tritium mixtures both pumps were found to be absolutely leak-tight. In Table II the pumping characteristics of the Siemens metal bellows pump at several exhaust pressures is compared with that of this pump combined with a Normetex scroll pump. Since the experiments were performed in closed loop operation, the various back pressures could easily be achieved by varying the total pressure in the loop. It is seen that the pumping
<table>
<thead>
<tr>
<th>Exhaust pressure [mbar]</th>
<th>attainable vacua at zero flow [mbar]</th>
<th>double stage bellows/Normetex 18 m³/h pump combination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂</td>
<td>D₂</td>
</tr>
<tr>
<td>1000</td>
<td>118.9</td>
<td>116.2</td>
</tr>
<tr>
<td>900</td>
<td>106.7</td>
<td>103.6</td>
</tr>
<tr>
<td>800</td>
<td>94.7</td>
<td>92.1</td>
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<tr>
<td>700</td>
<td>82.7</td>
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<tr>
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<td>24.5</td>
</tr>
<tr>
<td>100</td>
<td>13.3</td>
<td>13.4</td>
</tr>
</tbody>
</table>

The efficiency of the metal bellows pump does not depend upon the type of gas pumped and that, on the other hand, the scroll pump shows this dependancy particularly at low exhaust gas pressures. This type of data underlines the importance of a proper choice of pumps for an efficient design of the front-end permeator section as well as of the impurity detriration sections.

2.1.3. Catalyst bed

A new type of tritium compatible catalyst reactor designed with a recuperative heat exchanger and a vacuum insulation has been demonstrated successfully in long-term operation with high levels of tritium. Several catalyst reactors of this type installed in the Catalytic Purification Experiment (CAPRICE) facility at the TLK have remained at their respective operation temperatures for most the past two years without contingencies. No tritium releases into the glove box were detected and no failures were registered during the whole test period. Tritium permeated into the insulation interspace was periodically recovered by evacuation into a tritium reprocessing system. The experience gained with these catalyst vessels demonstrates that they qualify for the ITER Tritium Plant.

2.1.4. Storage bed

A tritium storage bed containing ZrCo as getter material has been in frequent use since about two years in the "Permeations Experiment Radiochemie" (PERA) facility of the Tritium Laboratory Karlsruhe. The bed is used to deliver deuterium tritide when needed for an experiment as well as for the interim storage of this gas. After completion of each experiment deuterium tritide is gotten from the gas phase with ZrCo. For this purpose, the permeate is pumped from the secondary side of the permeator with the getter bed. By this procedure deuterium tri-
tide is recovered from the loop in a highly pure form. To recover deuterium and tritium bonded to impurities, in particular hydrocarbons, the gases exiting the permeator are passed through a small nickel catalyst bed on which surface they are decomposed into molecular hydrogen and carbon. The gas stream containing the molecular hydrogens liberated catalytically is then recirculated once more through the permeator and the permeating hydrogens immobilized on the ZrCo getter. The method described possesses a high degree of recovery of bonded and non-bonded hydrogen isotopes. During the whole period of usage of the ZrCo bed no signs of hydrogen disproportionation were noticed. Disproportionation was avoided at the PETRA storage vessel by pumping all hydrogen isotopes liberated immediately when the getter was heated. In this way conditions known to cause rapid disproportionation of ZrCo, i.e. temperatures over 306 °C in the presence of high partial pressures of hydrogen, were circumvented [11].

2.1.5. Analysis of tritiated species

In radiocelulogical experiments with an equimolar deuterium-tritium mixture in the presence of either carbon monoxide, carbon dioxide, or polytritiated methane, infrared spectroscopy was used to follow changes in the partial pressure of these gases over a period of up to weeks. The instruments employed, i.e. MEGOS and SPECTRAN spectrometers from Perkin Elmer, are equipped with interference filters placed on a rotating disk. One of the filters is transparent to a radiation absorbed by the sample and the other is used as a reference filter. Internal calibrations are carried out with cells small containing one bar of the corresponding gas. The signal obtained, given by

\[ \text{Ext.} = - \log \left( \frac{I_{\text{sample}}}{I_{\text{ref}}} \right) \]

was found to be independent of optical changes, i.e. transmission of the cell, intensity variations of the radiation source, etc. and is therefore appropriate for long-term kinetic measurements. Conceivably, these instruments could be used for process control purposes in a tritium installation.

2.2. Plasma exhaust clean-up process

The technical facility CAPRICE has been erected at the Tritium Laboratory Karlsruhe to demonstrate plasma exhaust clean-up technology for ITER with relevant concentrations of tritium and throughputs. The facility, which is now being upgraded to constitute the CAPRICE + PERMCAT, the latter stands for combined Permeator-Catalyst facility (see Fig. 2), comprises three essentially independent zones, i.e. recovery of unspent fuel, impurity processing, and final detritiation.

2.2.1. Recovery of unspent fuel

In the first zone plasma exhaust gas simulant is prepared by mixing deuterium, tritium, deuterated methane, carbon monoxide, carbon dioxide, deuterated water and helium in appropriate concentrations. Tritiated species, i.e. C(D,T), and (D,T)2O, are produced by catalytic isotope scrambling on a hot nickel catalyst. Then the plasma exhaust simulant is pumped into a permeator of 0.22 m² permeation area. In this component ultra pure hydrogen isotopes are removed from the impurities. This component represents the front-end permeator battery proposed for the ITER Tritium Plant. At the CAPRICE facility the permeate is pumped down to a few millibars with a large 150 m³/h scroll pump installed in a separate glove box. The pumped permeate gas is send back to the front-end buffer vessel containing the simulant gas.
Fig. 2 Simplified block diagram showing the various zones and the essential components of the CAPER facility.

The permeate pressures recommended for ITER should be higher than those used in the CAPRI facility on one hand to minimize cracking of hydrocarbons and on the other to avoid the condensation of water (such as will be released during each total regeneration of the torus cryopumps). Another advantage of higher permeate pressures is that the use of smaller pumps becomes possible. If high permeate pressures are selected decontamination factors of the order of 10-30 are expected in the front-end permeator zone, also on account of the tritium inventory existing in bonded form.

2.2.2. Impurity processing

The impurities separated in the front-end permeator are continuously fed into another down stream buffer vessel. As soon as a given pressure is reached in this vessel, the accumulated gas is transferred into the so called impurity processing loop. Here the impurities are processed at a recirculation rate of 40 mol/h with the aim of converting all bonded hydrogen isotopes existing in the impurities into molecular hydrogens and other non-tritiated products.

In the impurity processing loop the tritiated impurities are catalytically processed according to the following reactions

\[
\begin{align*}
\text{CH}_4 (g) &= \text{C (g)} + 2 \text{H}_2(g) \\
\text{CH}_4 (g) + \text{H}_2O (g) &= \text{CO (g)} + 3 \text{H}_2(g) \\
\text{CO (g)} + \text{H}_2O (g) &= \text{CO}_2 (g) + \text{H}_2(g)
\end{align*}
\]
CO₂(g) + C(s) = 2 CO(g). \hspace{1cm} (4)

While in the past two catalyst vessels, one containing a nickel catalyst at 480 °C (hydrocarbon cracking) and another containing a zinc stabilized copper chromite catalyst at 200 °C (water gas shift reaction) were used to process the impurities, in the upgraded CAPER version, both catalysts have been integrated into a single unit operated at the temperatures indicated above. Hydrogens liberated in reactions (1) - (3) are removed selectively and continuously from the impurity processing loop with a second permeator and sent back into the afore mentioned upstream reception tank. The experience accumulated at the TLK so far indicates that a decontamination factor of more than 1000 can be achieved in the impurity processing loop in less than one half hour of recirculation. This decontamination factor has been verified with ionization chambers (total DF’s), and by gas chromatographic analysis of tritiated methane and of tritiated hydrogens (partial DF’s).

2.2.3. Final detritiation

The fourth and final zone of CAPER comprises a PERMCAT unit and another permeator as main components. The PERMCAT is a counter current swamping device. Tritized impurities are passed once-through along a palladium/silver tube submerged in a catalyst bed and protium is passed, also once-through but in counter current manner, through the inside of the palladium/silver tube. Because only hydrogen isotopes can permeate back and forth through palladium/silver, tritium is depleted from the impurities by catalytic exchange and permeation, the protium stream becoming progressively tritium-enriched as the gas flows through the PERMCAT unit. The performance of the PERMCAT unit has been successfully demonstrated with deuterium and tritium both in experiments performed in Chalk River, Canada, as well as at the TLK, Karlsruhe. The laboratory results have been validated with two different mathematical models [11]. With the PERMCAT device DF’s of 40 000 have been routinely achieved employing all non-tritiated and tritiated impurities expected in the exhaust stream of the impurity processing loop.

Based on the experience gained with a single tube PERMCAT reactor and relying on the modelling calculations, a technical scale PERMCAT unit having ITER throughput has now been designed and constructed at the TLK. The unit is presently being installed in a separate glove box adjacent to the CAPRICE glove boxes. The upgraded PERMCAT design allows manifolding of up to 21 palladium/silver tubes. The manifolded tubes are housed in a stainless steel containment whose evacuated interspace provides the required thermal insulation.

To avoid excessive burden to the molecular sieve beds of the waste gas treatment system by the water produced from the oxidation of hydrogens exiting the PERMCAT, it is proposed to pass the tritium-depleted bleed steam from this unit through another permeator to recover excessive hydrogens and feed them into the Isotope Separation System of the Tritium Plant. The tritium-enriched permeate fractions from the PERMCAT unit are also sent to the Isotope Separation System for the recovery of tritium and deuterium [12]. Proton is given to waste.

2.2.4. System reliability

For safety reasons CAPRICE is provided with numerous interlocks. Basically, the safety related measuring points are redundant, with
one measuring circuit connected to the associated process control system and the other to a hard wired safety system. Selected measuring points are connected to a hard wired safety system that will shut down the experiment in case of pressure or temperature excursions. All heated components of the CAPRICE facility are provided with an insulation vacuum to strictly avoid permeation losses into the glove box [13, 14].

The technical facility CAPRICE (and since recently a preliminary version of CAPER) has now been routinely in operation with up to 90 % tritium in deuterium and a total tritium inventory in the facility of up to 7 g for nearly two years, using all relevant ITER impurities at realistic concentrations and relevant throughputs. During this period the facility was successfully operated within a wide range of experimental parameters by scientists, engineers and technicians under constant availability of all safety devices and interlocks without contingencies [11]. On the basis of the numerous CAPRICE and CAPER type experiments performed, it can be concluded that the original process concept developed in Karlsruhe has now been experimentally validated. The process was shown to be robust, insensitive to changes in feed gas composition and to deliver DF's that meet the requirements of ITER. The experience gained with the CAPRICE facility has stimulated many research developments elsewhere and has provided a valuable basis of information for the design of the ITER Tritium Plant.

3. Accountancy at the TLK

Accountancy is of considerable importance in tritium technology. The most common techniques currently employed to account for tritium are volumetric assay in combination with a chemical analysis and calorimetry.

For tritium accountancy by volumetric means first the total amount of gas is determined by a pVT procedure. The tritium inventory is then obtained from a chemical analysis of the gaseous mixture. The most common analytical techniques employed are gas chromatography, mass spectrometry, and laser Raman spectroscopy. As a rule more than one analytical technique is required for an accurate analysis of isotopically substituted gases. In the case of gas chromatography the use of a thermal conductivity detector together with an ionization chamber have proved to be adequate. Main drawbacks of the PV'T method are the need of tritium analytics and the production of radioactive waste, particularly when gas chromatography is used.

A calorimetric determination of tritium requires no chemical analysis. To perform a measurement, tritium is normally gottentered in a transportable uranium storage bed that fits into the particular calorimeter being employed. While in principle all tritium-containing species can be measured calorimetrically regardless of their chemical form, in practice, tritium needs to be available as molecular hydrogen, because other gases are not gottentered quasitatively by uranium - at least at room temperature. Calorimetry is a relatively fast (hours) and very accurate technique.

3.1. Accountancy strategy

A basic control strategy for tritium is to limit the inventory in a laboratory or technical facility to a reasonable minimum. Tritium inventories can be minimized by appropriate design measures. It is good practice to replace protium and/or deuterium by tritium.
only when strictly necessary and to limit the absolute number of experiments by careful planning. In general, the access to laboratories in which large inventories of tritium are handled should be subjected to some kind of access control. All materials & equipment entering/leaving the laboratory should be controlled by an independent radiation protection service or by laboratory personnel. When these conditions are fulfilled a tritium laboratory can be treated as a single material balance area (MBA) (see Fig. 3).

Fig. 3 Basic flow diagram showing the fate of tritium in a material balance area

Larger amounts of tritium are shipped either in the form of uranium tritide in small transport vessels or as gas in large containers placed in a safe overpack. Eventual shipper/receiver differences should be identified before the tritium is accepted and distributed within a facility. Experience at the TLK from a comparison between three calorimeters of different manufacturer and different measuring principle with one and the same tritium containing uranium storage yielded a very good accuracy (839.5 ± 1.2 Ci). After verification of the contents of the received transport bed, the bed can either be placed in a safe, be delivered to the experiments or into some storage facility. Shipper/receiver ratios measured respectively by a volumetric and a calorimetric technique in the range 0.996 - 0.999 are currently obtained at the TLK for gram amounts of tritium.

In the laboratory tritium can be secured from unauthorized persons. When tritium is in a primary system in a glove box or immobilized in an installed getter bed in a glove box, it is practically no accessible to persons not acquainted with the laboratory. Safety measures currently used in modern tritium facilities, e.g. programmable logical controllers, that convey an experiment into a safe state when non-professional handling of the equipment takes place, constitute another significant safety barrier.

Tritiated gaseous effluents are normally released through stack via tritium retention systems in very low concentrations from the
material balance area. Tritium emitted from laboratories is normally monitored 24 h per day for HT and HTO by an administratively independent radiation protection service. When authorized levels are exceeded the operation of the laboratory must cease until the cause has been identified and eliminated.

Tritium in wastes is determined by procedures that depend upon the type of waste. Specimens from structural materials can be analyzed for tritium by oxidation with a humid gas (either oxygen or oxygen diluted in an inert diluent). The produced HTO is collected in a bubbler and tritium is measured by liquid scintillation counting. Tritium in adsorbers and catalyst beds is obtained either by an isotopic dilution technique or by administrative procedures (integration over the gas flowing through the bed).

3.2. Accountancy procedures

Tritium can be accounted for within a material balance area by different strategies. One such strategy is shown schematically in Fig. 4. Tritium imported into the MBA is received from a transportable tritium storage getter bed (or gas cylinder) in a so-called Transfer Station, in which the tritium is assayed by a PVT-c measurement. If the impurity degree of the hydrogen isotopes exceeds acceptable levels the gas is subjected to a purification. This can for instance be accomplished with uranium beds heated to sufficiently high temperatures, e.g. 500 - 900°C. Under these conditions oxygen, nitrogen and carbon are gettered and the bonded hydrogen isotopes liberated. The so obtained hydrogen isotopes can then be separated into their constituents, for example by a cryogenic or a gas chromatographic isotope separation technique. Of these only the tritium fractions are recovered and returned to the transfer station, where another tritium accountancy is performed. Subsequently the gas can either be used in experiments or be stored in an appropriate Storage System.

The amount of tritium introduced into an experimental facility can be obtained from the difference between the calorimetrically measured original amount of tritium in the transport vessel and that remaining in the vessel after the supply has been completed (see Fig. 5). Alternatively, it is also possible to rely on a PVT-c measurement carried out in an installed tritium Transfer Station equipped for tritium assay. The amount of tritium introduced into the experiment can.

Fig. 4 Fate of tritium in a material balance area
eventually be confirmed by another pVT-c measurement within the experiment itself.

After completion of a series of experiments, tritium can be recovered into a tritium transport vessel previously assayed for tritium by calorimetry or into an installed tritium Transfer System by pumping via double walled tubing from one glove box to another. An additional calorimetric measurement of the transport vessel will give the "available" tritium in the experiment. The tritium remaining in the experiment after the transfer is the so called "non-available tritium". It is immobilized in getters and/or dissolved in structural materials, and other components. It may also have been incorporated into adsorbers and/or catalysts by exchange reactions.

Gram amounts of tritium are recoverable to more than 99 % from a metallic primary system that does not contain adsorbers or catalysts using a docked-on uranium or zirconium/cobalt getter bed, provided the impurity levels, e.g. helium, hydrocarbons, etc. are low. When this is not the case, it is necessary to flow the gas through the bed to circumvent the blanketing effect. To improve the recovery of tritium from getters and catalysts the component containing the material is heated to the highest permissible temperature while evacuating the primary system. The degree of recovery can be significantly improved by sweeping with protium or deuterium.

4. Conclusions
An integral process for the recovery of unspent fuel from the plasma exhaust gas of a fusion reactor has been developed and demonstrated successfully with tritium at the Tritium Laboratory Karlsruhe employing the industrially manufactured, technical experimental facility CAPRICE complemented by the isotopic swapping component PERMCAT. With the process subsystems an overall decontamination factor of more than $10^4$ has been demonstrated with relevant concentrations of tritium. All major compo-
nents of the facility, i.e. pumps, permeator, catalyst vessels, instrumentation, etc. have been subjected to long-term testing in a tritium environment and in the presence of all relevant ITER impurities at their respective concentrations. Other components suitable for use in the ITER Tritium Plant such as a ZrCo tritium storage bed and infrared gas analyzers have also been tested and demonstrated with tritium under analogous conditions.

A tritium accountability strategy basically relying on pVT-c and calorimetry is discussed.

References