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Gas chromatography and TCAP for WDS

Authors : Mr. Silvano TOSTI (ENEA)

TITANS - Contract Number: 101059408

Project officer: Angelgiorgio Iorizzo

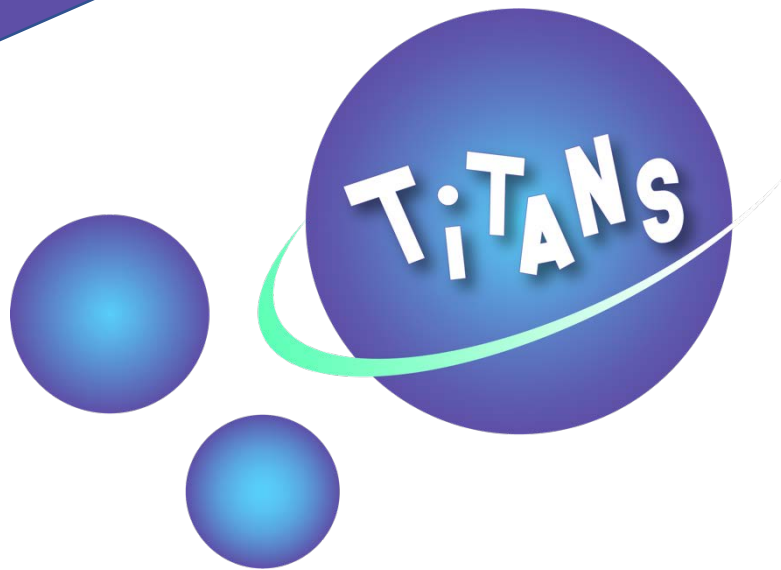
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Summary

This report analyzes the state-of-art of water detritiation processes with particular focus on the hydrogen isotope separation systems based on the displacement gas chromatography and the thermal cycling adsorption process improved with the use of an "inverse column". These processes have been evaluated critically in order to establish their application for the final purification of the DT stream recovered at the bottom of the cry-distillation column of a water detritiation unit designed for mobile applications. In principle, both solutions (GC and TCAP with inverse column) exhibit safe and feasible operation, have achieved a good technological level and are capable to meet the main design specifications required by the Water Detritiation Mobile Unit (WDMU), namely raffinate and product streams of purity > 99% and feed flow rate of 5 L/h ($\pm 50\%$). However, the use of GC has to be preferred since this system can operate with modest temperature cycling and exhibits a purity of the produced streams (close to 100%) higher than the TCAP system (approx. 99%).

Approval

Date	By
2024-05-07 12:44:02	Dr. Ion CRISTESCU (KIT)
2024-05-07 16:13:44	Mrs. Elodie BERNARD (CEA)



TITANS

Tritium Impact and Transfer in Advanced Nuclear ReactorS

Gas chromatographic and TCAP for water detritionation

WPI

06.05.2024

Silvano Tosti (ENEA)



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Abbreviation and Acronyms

Acronym	Description
AGHS	Active Gas Handling System at JET
CD	Cryogenic Distillation
CEA	Commissariat a l'Energie Atomique et aux Energies Alternatives
CECE	Combined Electrolysis and Catalytic Exchange
CFFTP	Canadian Fusion Fuel Technology Project
FC	Frontal chromatography
FDC	Frontal displacement chromatography
DC	Displacement Chromatography
GC	Gas Chromatography
ICSI	Institute for Cryogenic and Isotopic Technologies at Rm. Valcea, Romania
JET	Joint European Torus, Culham, UK
k	Kieselguhr, a diatomite chiefly composed of amorphous silica



LPCE	Liquid Phase Catalytic Exchange
MS	Molecular Sieves
MS4A	Type 4A Molecular Sieves
PFR	Plug Flow Reverser
SRNL	Savannah River National Laboratory, USA
STP	Standard Temperature and Pressure conditions (273.15 K and 100 kPa)
TCAP	Thermal Cycling Absorption Process
TLK	Tritium Laboratory of Karlsruhe, DE
TRL	Technological Readiness Level
VPCE	Vapour Phase Catalytic Exchange



Summary

TITANS (Tritium Impact and Transfer in Advanced Nuclear reactors) is a 3 years multidisciplinary project aimed to contribute to Research and Innovation to “improve knowledge on tritium management in fission/fusion facilities” and provide “robust science to EU safety regulators, radiation protection authorities and decision makers”. TITANS will answer the main challenges of the call:

- Tritium permeation description and associated modeling,
 - tritium measurement,
 - mitigation of tritium release,
 - gain expertise on dismantling activities,
 - improve knowledge in radiotoxicity and radiobiology, both combined to dosimetry specific to each biological model studied.
- Specifically, TITANS will improve modeling tools to assess tritium inventory/migration in nuclear fission/fusion reactors in order to identify where the new barrier concept developed within TITANS are needed to limit the spread of tritium. The tritium release during dismantling of tritium-contaminated setup will be evaluated with the help of innovative tritium inventory measurement techniques developed within TITANS. Finally, to ensure tritium circular economy, a mobile device for tritiated water processing will be developed. At last, human and environmental toxicity impacts after an accidental release of tritiated particles will be assessed.

The present work is a part of the activities foreseen in the ambit of the Work Package 1 (WP1) – Proposals for enhancement of barriers against tritium permeation and tritiated waste management. In particular, it refers to the deliverable 1.1 – Gas chromatography and TCAP for WDS.




The scope of this report is to carry out a critical review of the state-of-the-art on Gas chromatography and TCAP (Thermal Cycling Absorption Process) systems for hydrogen isotopes separation and water detritiation and to assess the applicability of these processes in fusion-fission facilities for water detritiation.

1 Introduction

The water detritiation is required for the treatment of process and cooling water coming from fission and fusion plants. Depending on their flow rates and tritium levels, several strategies and processes for the treatment of tritiated water streams have been proposed. For low activity water, these treatments consist of the direct disposal (e.g., the release to rivers). In case of higher tritium levels, the tritiated water is processed with the aim to produce concentrated tritium streams to be grouted and disposed in burial sites or further processed to recover and valorize their tritium content.

Well-known processes for the treatment of the tritiated water use the water distillation and the water/gas catalytic exchange that, in turn, could be combined with the electrolysis [1-10]. Although these processes are characterized by large energy consumptions (heat and/or electricity), they rely on good technological levels (TRL = 6-7) and have been applied worldwide in several plants.

The different affinity of the materials with the hydrogen isotopes can be exploited for performing their separation. Several materials have been considered for taking advantage of such behaviour in the hydrogen isotopes separation processes. In



practice, all the metals and alloys exhibit a different selectivity in absorbing the hydrogen isotopes according to the so-called “isotopic effect”. When the equilibrium pressure of hydrogen isotopes in gas and solid phases is $p_{H_2} > p_{D_2} > p_{T_2}$ a “normal isotopic effect” occurs, meaning that the hydrogen is preferably absorbed into the metal lattice. Diversely, if $p_{T_2} > p_{D_2} > p_{H_2}$ an “inverse isotopic effect” takes place and the heavier isotopes are preferably absorbed in the metal [11, 12]. The kind and intensity of the isotopic effect depends on the occupancy of the hydrogen atoms into the metal, i.e. potential energy levels of the interaction of the hydrogen atoms with the lattice structure. For instance, the Pd-alloy with Ag 25 wt.% at low temperature and high pressure (high hydrogen/metal ratios) exhibits a normal isotopic effect that inverts by increasing the temperature or reducing the pressure. Same behavior is characteristic of the V-H and Ti-H systems [13].

Due to its best performances, the Pd is largely adopted in units where a gaseous phase containing the hydrogen isotopes is put in contact with the metal. The lighter hydrogen isotope is preferably absorbed by the Pd: as a result, this isotope will be enriched in the solid phase of the Pd, while the heavier isotope will be enriched in the gas phase [14-16].

Thanks to its easy and reliable realization, the displacement chromatography is the technique adopted for the hydrogen isotope separation exploiting the isotope effect of Pd-based materials [17, 18]. Further progress of hydrogen separation techniques has been made by the Thermal Cycling Adsorption Process, a concept invented at Savannah River Laboratory in 1980. It is a semi-continuous process in which the separation



effect typical of the displacement chromatography is enhanced by acting on the temperature since the isotopic effect increases as the temperature decreases [19, 20].

This report contains a critical review of the Gas chromatographic and Thermal Cycle Adsorption Processes as potential back end technologies for tritium recovery through a Water Detritiation Mobile Unit (WDMU).

First, the materials used by the displacement chromatography systems will be discussed with focus on their interaction with the hydrogen and the effect on the separation properties on the main operating parameters.

Then, the process configurations proposed for both the displacement chromatography and TCAP systems presently adopted in the main laboratories will be presented with the discussion of the results validated in experimental test campaigns.

Finally, this report will analyze the feasibility of GC and TCAP units for the final separation of the DT stream that is extracted from the bottom of a cryo-distillation column of a WDMU.

2 Gas Chromatography

Chromatography is a technique adopted for separating the components of a mixture. It was originally developed for extracting the pigments of chlorophyll by passing petroleum ether extracts of plant material through a column packed with

powdered chalk: from this first application, this technique derived its name coming from the greek words χρώμα chroma, which means "color", and γράφειν graphein, which means "to write".

Chromatography has been developed both for separation and analytical purposes of mixtures in gas (vapor) and liquid phases. The working principle relies on the different affinity of the components of a gas mixtures with a stationary phase: as a consequence, when the gas stream passes through the stationary phase a distribution of mixture components between mobile and stationary phases occurs. In the applications for the hydrogen isotope separation, the gas-adsorption chromatography techniques adopt the stationary phase consisting of a bed solid adsorbent usually located inside a tube ("column chromatography").

2.1 Gas Chromatography configurations

There are several operative modes of gas chromatography separation. In the basic mode (elution mode), usually preferred in analytical chromatography, the mixture gas is fed into the column often together with a carrier gas. Due to the different affinities of the mixture's compounds with the bed material, they are retained by the column for different times, causing them to separate. The curve representing the composition of the outlet stream (elution curve) will exhibit a series of peaks that, in principle, correspond to every component of the feed mixture. In the displacement chromatography (DC) all the components of the feed mixture are absorbed into the column bed. Then a substance, the displacer, that has a very strong affinity with the




bed material (much stronger than that of the mixture's components) is fed into the column and move away the previously adsorbed components by realizing their separation. This method has been developed for the hydrogen isotopic separation where protium is used to force the gas mixture through the column [18, 21, 22].

The frontal chromatography (FC) uses columns fed with a continuous gas input and filled in with materials that favor the absorption of all the components but one: such a component is extracted at high purity level at the column exit. Displacement and frontal chromatography can be combined in the frontal displacement chromatography (FDC) where the feed gas, continuously flowing, acts as the displacement gas as well: the component having the highest affinity displaces the other ones earlier adsorbed that are enriched at the outlet of the column.

3 Materials

The characteristic of some materials of absorbing the hydrogen can be used to develop hydrogen separation processes. In particular, a different affinity of the hydrogen isotopes with the absorbent material makes the separation system more efficient.

In principle, all metals and metal alloys exhibit the capability of absorbing hydrogen and then can be used to separate mixtures of its isotopes. For these applications, the preferred material is the palladium since its hydrogen absorption shows a large isotopic effect: in particular, the equilibrium pressures of the hydrogen isotopes in the order of protium < deuterium < tritium, i.e. protium is more preferentially uploaded in the metal lattice



than deuterium and tritium. Such a behavior is called “normal isotopic effect” [14, 15, 20]. Among the other materials, uranium has been also studied because it absorbs larger amount of hydrogen than other metals do [21]; however, the realization of isotopic separation systems is limited by its modest separation performances. The absorption of the hydrogen isotopes has been studied also in intermetallic compounds: Yawny et al. measured the equilibrium pressure difference between deuterium and hydrogen of LaNi_5 and Ti_2Ni and demonstrated the second one to be more promising as isotope-separation material [22]. Among the other alloys of interest, the Pd-Pt exhibits a heat of hydrogen solution lower than Pd and therefore can operate at room temperature with low tritium inventory and without using any replacement gas for the desorption [23-25].

As above-introduced, due to its best performances Pd is preferably adopted in most of the isotopic separation systems. Its separation performances are strongly affected by the parameters influencing the interaction between the hydrogen isotopes and the absorption material, specifically the gas-Pd contact area. In this view, Pd is prepared in form of powders or deposited over small particles of a support materials that are packed into separation columns. In several applications, porous kieselguhr (k), a diatomite chiefly composed of amorphous silica, is used as the support material of palladium (Pd on kieselguhr or Pd-k) [20]. Differently, the columns of the displacement chromatography systems, adopted by JET and discussed in the details in the followings, were filled in with 18 to 20 weight% palladium deposited on porous $\alpha\text{-Al}_2\text{O}_3$ [26]. The realization of Pd- Al_2O_3 pellets for hydrogen isotopic separation has also been reported by Deng et al. [15].

Other important parameters that control the separation kinetics and efficiency of these materials are the particle size, the specific surface area and the porosity. The packing of the absorption beds into the separation columns, i.e. its density and uniformity, is also important in order to control the pore diffusion resistance and then guaranteeing the best separation factors [15, 20, 27, 28].

3.1 Materials for GC

The Isotopic Separation System of TLK (Tritium Laboratory of Karlsruhe) operated since 1995 consisted of two consecutive Pd-based absorption columns manufactured by CFFTP (Canadian Fusion Fuel Technology Project). The columns, cooled by liquid nitrogen, were capable to separate the hydrogen isotopes (HT-DT mixtures) during several hundred hours of operation [29, 30]. A displacement gas chromatographic system has been installed at the JET Active Gas Handling System (AGHS): the GC system consisted of columns filled with palladium deposited on porous α - Al_2O_3 and exhibited the capability to produce deuterium and tritium purity well-above the technical specification of 98% [26].

3.2 Materials for TCAP

Shmayda et al. report the use of Pd or Pd-k in combination with molecular sieves (MS): the Pd-based materials acts for sorting the hydrogen species in form of atoms while cold MS separate the molecular hydrogen isotopologues [31].

4 Thermal Cycle Adsorption Process

When treating an isotopic mixture of hydrogen via GC, both T_2 and H_2 products elute from the same end of the separation columns by posing, in principle, a limit to the maximum purity of the tritium gas produced [32].

To overcome these drawbacks, a new process (Thermal Cycling Adsorption Process, TCAP) has been firstly studied at Savannah River Laboratories in the early '80s [33, 34].

TCAP operates on the principle similar to a gas chromatography using a palladium column, but in a semi-continuous manner. The isotope separation is achieved in columns filled with palladium on kieselguhr that exhibit large isotope effect when operated under temperature cycling. As above discussed, protium is more preferentially adsorbed in the metal lattice than deuterium and tritium and the differences in equilibrium pressures of the hydrogen isotopes are also temperature dependent since they decrease as temperature increases.


A TCAP unit mainly consists of: i) a Pd/k column divided into two sections (product and raffinate) with the feed point located in between, and a ii) a Plug Flow Reverser (PFR) packed with kieselguhr. Due to the isotopic effect, the lighter isotope is preferably adsorbed into the Pd-based solid phase and through the thermal cycles the hydrogen gas is transferred from the column to the PFR (heating) or from the PFR to the Pd-column (cooling). In this way, the heavier isotope is enriched at the dead (product) end of the column while it is depleted at the column end (raffinate) facing the PFR. Long experimental campaigns allowed to study and verify the material compatibility, namely aluminum alloy and stainless steel [35]. A pre-conceptual study



has considered different process designs (Improved TCAP and Rabbit TCAP) with the aim to optimize operating parameters, the heating and cooling technology and reduce the permeation [33].

At CEA Valduc, Pd coated on alumina was packed in columns adopting an original design allowing short thermal cycles and high efficiency: in this way, it has been demonstrated that high purity tritium can be recoverable from a 'poor' mixture [32].

New TCAP processes using columns with different filling materials have been studied by several authors [20, 34, 36]: in these approaches, the PFR has been replaced by an "active" or "inverse" column. In fact, the main function of PFR is that to provide a volume for regenerating the Pd/k column while it does not provide any separation of the isotopes: for this reason, the conventional TCAP can easily produce high purity heavy isotope (product) but it cannot easily produce high purity light isotope (raffinate). In order to improve its performances, in the new TCAP concept the PFR is replaced by an active column (called "inverse column") that can work both as the PFR and provide an opposite isotopic effect of the palladium column. According to this new concept, at Savannah River Laboratories the use of a pair of separation columns packed with Pd/k and type 4A molecular sieves (MS4A) has been realized [20]. These two materials are characterized by opposite isotopic effect, positive for Pd and negative for the molecular sieves (MS). These last materials, in fact, exhibit the equilibrium pressures of the hydrogen isotopes in the order of protium>deuterium>tritium. Through both numerical studies and experiments, it has been demonstrated that this configuration can double the throughput and produce a quality raffinate better than that of a traditional system based



on a Pd/k column and a plug flow reverser (PFR) packed with kieselguhr. In such a way, the thermal efficiency of the separation process was improved too: the extensive heating and cooling equipments of the traditional TCAP was replaced in the new concept system by small electric heaters and liquid nitrogen cooling tubes thus reducing the foot print of the process equipment by a factor of 10 [20]. An improved TCAP process adopting an oil bath heating and cooling system has been recently designed and tested with H₂-D₂ mixtures.[37]. Pd/Al₂O₃ has been selected as filling material of the separation columns since it exhibits better thermal conductivity and greater Pd mass per unit volume than Pd-k.

5 Potential application of GC and TCAP in a Water Detritiation Mobile Unit

Water Detritiation Mobile Unit (WDMU) is developed for the treatment of tritiated water of activity of around 1 Ci/kg and flow rate up to 25 kg/h. It is represented schematically in fig. 1: in particular, the bottom stream of the cryogenic distillation column is finally treated via GDC or TCAP. Based on the above-described literature, a critical review of these two technologies is reported in the following. This analysis will consider the intrinsic feasibility aspects of these two technologies in order to establish their appropriateness for the proposed application.

A general specification for the final treatment of the stream leaving the bottom of the cryo-distillation column consists in the achievement of detritiation factor of at least 99%. The other main characteristics of this process unit are:

- feed flow rate 5 L/h ($\pm 50\%$),
- D inlet conc.: 50-99%,
- T outlet conc.: $> 98\%$.

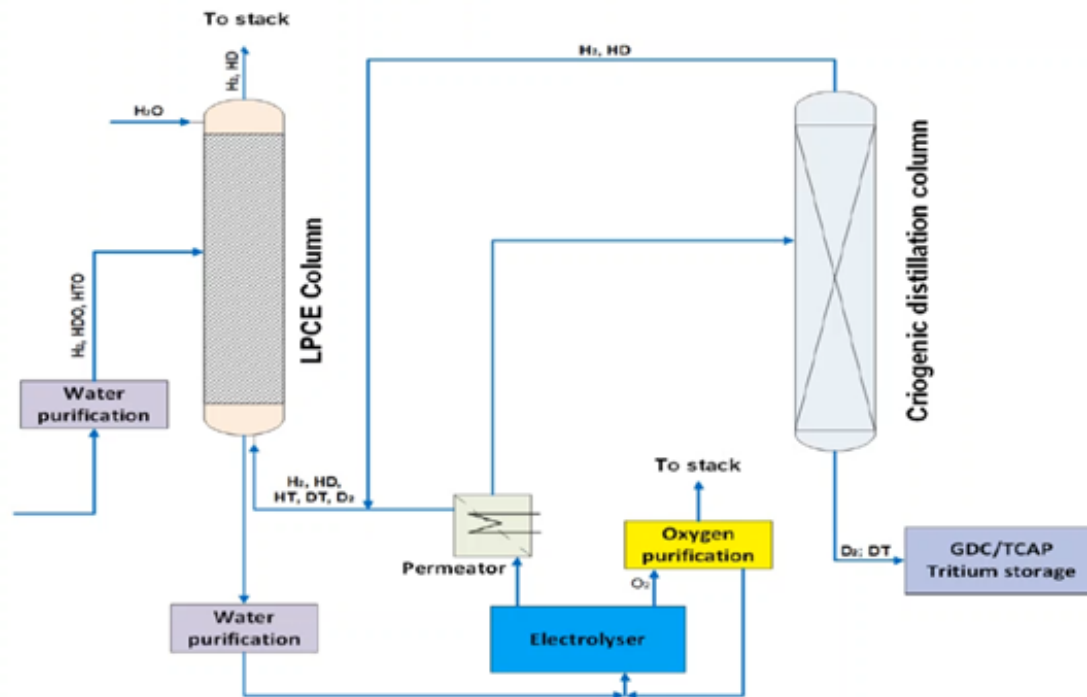


Figure 1: Process scheme of the mobile detritiation unit [cristescu, presentation at TITANS meeting Apr 2023].

5.1 Gas Chromatography

Extensive experience of gas displacement chromatography has been done at Tritium Laboratory of Karlsruhe. Neffe et al. report the treatment of about 2000 L of hydrogen isotopes with an activity of 2.21014 Bq tritium [29]. It was possible to reduce the protium content in the gas mixture to very low levels, with minimum tritium losses: the non-tritiated fractions (H_2 and HD) contained less than 10^{10} Bq m^{-3} of tritium while deuterium/tritium fractions containing less than 0.1% of protium.

In the Active Gas-Handling System (AGHS) of the JET, the hydrogen isotopes extracted from the torus are treated for producing streams of tritium (T_2) and deuterium (D_2) through two separation systems, the cryogenic distillation (CD) and the displacement gas chromatography (GC) [26]. These two systems can work in parallel or interact by complementing each other: e.g., the CD system can be used to pre-enrich in tritium the isotopic mixture before sending it to the GC system.

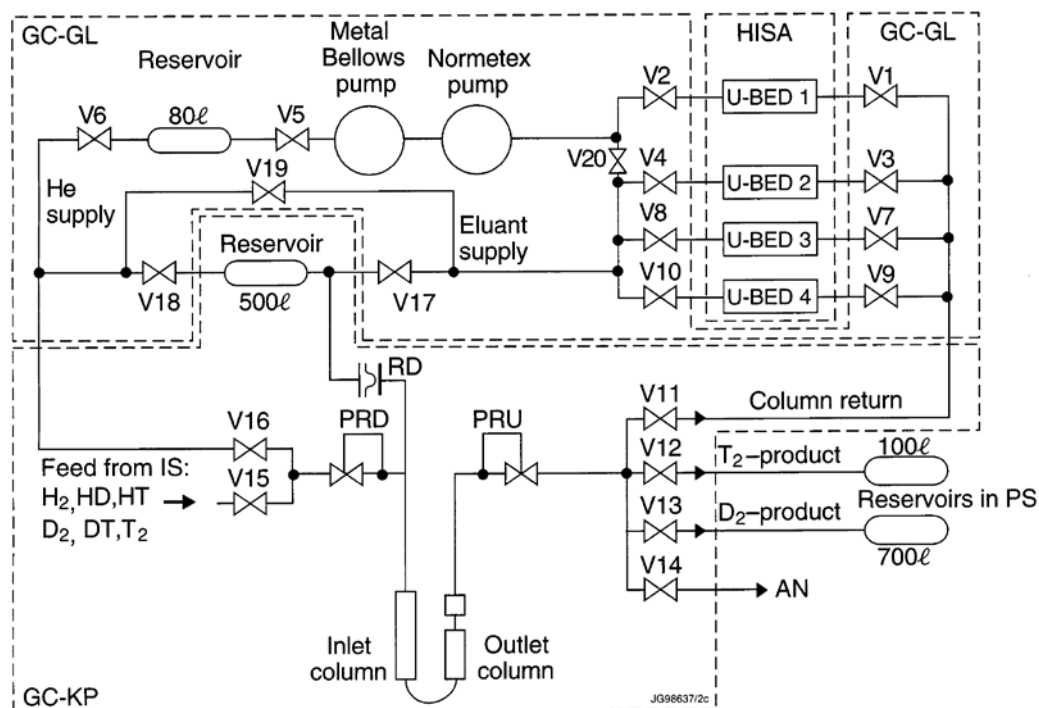


Figure 2: Schematic flow diagram of the gas chromatographic (GC)-system at JET.

The GC at JET is shown in Fig. 2 where: V1 to V20, are automatic valves; PRD (PRU), down (up) stream pressure regulators at the column inlet (outlet); RD, rupture disc; U-bed, uranium bed; IS, intermediate storage system; PS, product storage system; AN, analytical system. The GC system was operated between room temperature and 67 °C (340 K) and fed with flow rates in the range 1.2-10 NL/min of hydrogen isotope mixtures ($H_2+HD+HT+D_2+DT+T_2$) that had to be processed in order to



produce deuterium and tritium streams of purity larger than 98%. The main components of this GC system consist of a cylindrical vessel (1.2 m diameter and 5 m height) containing 4 Pd-columns and a box (0.83 x 1.3 x 2.9 m) housing pumps and a tank. In addition, a vessel (0.66 m diameter and 1 m length) is used to contain the U storage beds. Once fixed the Pd-columns' diameter and the feed flow rate, the capability of producing high purity streams (D_2 and T_2) depends on the overall amount of tritium treated: in particular, the smaller the columns' diameter the higher the purity achievable. As a consequence, the injection of a too small gas amounts with low tritium concentrations doesn't allow to enrich tritium close to 100%.

When mixtures of 1 g of tritium with various amounts of deuterium have been processed at JET AGHS, the following streams have been produced:

- deuterium-rich stream: H = 0.17%, D = 99.70%, T = 0.13%,
- tritium-rich stream: H = 0.03%, D = 0.01%, T = 99.96 %.

In summary, the JET experience on displacement chromatography demonstrated:

- the JET GC system was capable of separating hydrogen isotope mixtures of the six molecules into tritium, deuterium and protium,
- the best tritium and deuterium qualities achieved were in the range of 99.9 and 99.7%, respectively,
- the size of the JET system, designed for a feed flow rate of up to 600 NL/h (10 NL/min), when down-scaled to the feed flow rate of

the present application (5 NL/h) could be compatible for the use in a mobile detritiation unit,

- the operation at temperatures close to the ambient one makes the GC almost immediately ready for separation (differently from the CD system that needs some days for its cooling down to 19 K),
- the good safety operation (no tritium leaks were observed in the various secondary containments of the GC system with a final global test requirement of no leak indication in the 10^{-10} Pa m^3/s range).

5.2 Thermal Cycle Adsorption Process

In a preliminary work, a TCAP unit has been studied in the frame of the hydrogen isotopic separation process under development at ICSI Rm. Valcea with the aim of recovering tritium from tritiated water [38]. This process uses a system based on catalytic isotopic exchange between tritiated water and hydrogen/deuterium followed by a cryogenic distillation (CD) cascade consisting of four distillation columns [38]. In this work, the TCAP unit complements the CD cascade in order to reduce its tritium holdup. This TCAP unit adopts the basic (conventional) configuration where a palladium deposited on kieselguhr (Pd/k) packed column is coupled with a PFR (plug flow reverser). Such a solution produces a raffinate stream with a purity level of the light isotope lower than the TCAP advanced configuration that uses an active “inverse column”: for this reason, in the process studied at ICSI the raffinate stream can be send back and further treated into the CD cascade.



In order to finally process the bottom stream of the cryogenic distillation column of the water detritiation mobile unit (WDMU), the adoption of a TCAP system using an inverse column will be therefore considered in this work. In fact, in such a way both deuterium (raffinate) and tritium (product) enriched streams could achieve the required purity levels without any need to recycle them into the CD cascade.

Accordingly, the following analysis takes into consideration the results of the tests carried out by Heung et al. on TCAP systems in both basic configuration (using a palladium packed column and a PFR), see fig. 3, and new configuration where an inverse column is used to replace the PFR, see fig. 4 [20]. These tests, carried out with protium-deuterium mixtures, demonstrated that adopting the TCAP basic configuration purities levels over 98% for both raffinate and product streams could be achieved operating with a feed flow rate of 1 STP/cycle; however, in this operating mode the raffinate purity deteriorated at higher feed flow rate (3 STP l/cycle). When in this TCAP system the PFR was replaced by the molecular sieves (inverse column) it was possible to achieve significant better performances: namely, a raffinate purity 1% absolute higher than that obtained by the basic configuration operated at feed flow rate of 4 STP L /cycle. Furthermore, as previously discussed, the other main advantages introduced by the new configuration are the reduction of the tritium inventory (to 1/2) and of the heat load (25%). Accordingly, for the scope of this work the new configuration (fig. 5) will be considered. Its characteristics are:

- the Pd/k column packed in copper tubing (0.95 cm diameter and 6.35 m long) operated from -70 to +145 °C and pressure from 1 to 5500 torr,
- the inverse column (filled with 99 g of MS4A) in stainless steel tubing (0.95 cm diameter and 3.33 m long) temperature ranged from -190 to -90 °C and pressure from 1 to 9000 torr,
- heating via electrical resistances and cooling with liquid nitrogen,
- feed flow rate of about 8 STP L/h (assessment based on a cycle duration of about 0.5 h),
- raffinate and product purity of about 99%,
- reported inherent safe, robust and fault proof operation [39].

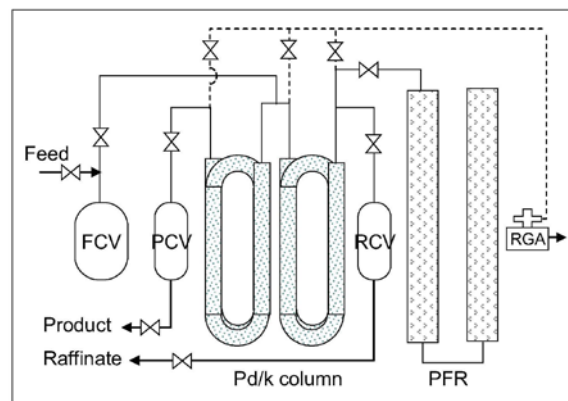


Figure 3: The Pd/k-PFR configuration.

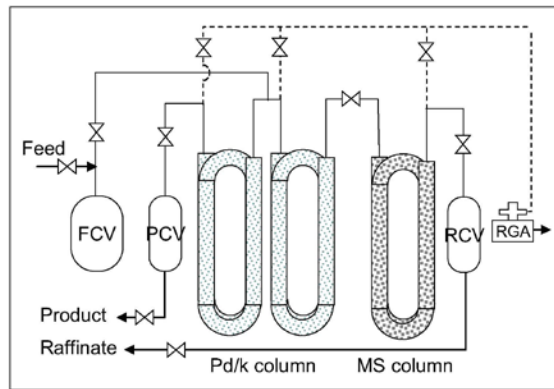


Figure 4: The Pd/k-MS configuration.

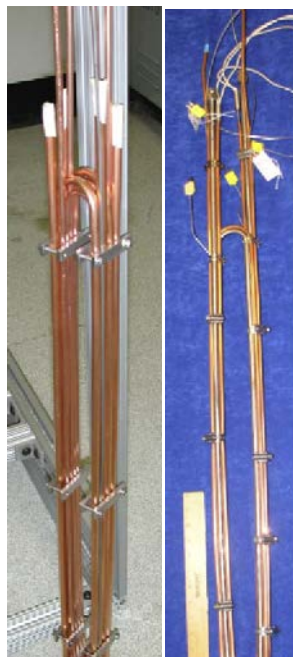


Figure 5: Pd/k (right) and MS (left) columns.

6 Comparison GC/TCAP with pros. and cons.

The analysis of the literature with particular focus to the JET experience for the GC systems and to the Savannah Rivers laboratories for the TCAP systems shows that, in general, both these two processes comply with the purity levels required for



the final purification of the cryo-distillation bottom stream proposed for the Water Detritiation Mobile Unit (WDMU).

More in details, both systems have been extensively tested by demonstrating their safe operation. Furthermore, these technologies as well as the materials used have been validated in industrial relevant environment corresponding to TRL levels of 6-7 and both these systems are scalable to the sizes required by the proposed application (WDMU).

The GC systems exhibits better separation performances since it can achieve purity level of the deuterium and tritium enriched streams (99.96% and 99.70%, respectively) higher than those of the TCAP process that, at its best, achieves purity of the raffinate and product stream just around 99%. This difference could be significant when assessing the economical value of the streams produced or considering the regulatory aspects for licensing the process. Process temperature are more favorable for GC (T_{amb} to 67 °C) than TCAP (-70 to +145 °C and -190 to -90 °C for the Pd-column and the inverse column, respectively).

These considerations are summarized in the Tables I and II.

In the end, although both systems (GC and TCAP with inverse column) comply the requirements for the application in the mobile water detritiation unit, the use of GC process has to be preferred according to the above discussion.



	<i>Streams' purity</i>	<i>Operating T</i>	<i>TRL</i>	<i>Safety</i>	<i>Sizes</i>
GC	> 99%	T _{amb} to 67 °C	6-7	inherent safety validated in experiments	compatible with mobile applications
TCAP with inverse columns	≈ 99%	-70 to +145 °C -190 to -90 °C	6-7	inherent safety validated in experiments	compatible with mobile applications

Table I: Comparison GC/TCAP (text)











	<i>Streams' purity</i>	<i>Operating T</i>	<i>TRL</i>	<i>Safety</i>	<i>Sizes</i>
GC					
TCAP with inverse columns					

Table II: Comparison GC/TCAP (symbols)



7 Conclusions

This report analyzes the state-of-art of water detritiation processes with particular focus on the hydrogen isotope separation systems based on the displacement gas chromatography and the thermal cycling adsorption process improved with the use of an “inverse column”. These processes have been evaluated critically in order to establish their application for the final purification of the DT stream recovered at the bottom of the cry-distillation column of a water detritiation unit designed for mobile applications.

In principle, both solutions (GC and TCAP with inverse column) exhibit safe and feasible operation, have achieved a good technological level and are capable to meet the main design specifications required by the Water Detritiation Mobile Unit (WDMU), namely raffinate and product streams of purity > 99% and feed flow rate of 5 L/h ($\pm 50\%$). However, the use of GC has to be preferred since this system can operate with modest temperature cycling and exhibits a purity of the produced streams (close to 100%) higher than the TCAP system ($\approx 99\%$).

Bibliography

[1] Chao Chen, Jingwei Hou, Jiamao Li, Xiaojun Chen, Chengjian Xiao, Qiang Wang, Yu Gong, Lei Yue, Linjie Zhao, Guangming Ran, Xiaolong Fu, Xiulong Xia, Heyi Wang, A water distillation detritiation facility and its performance test, Fusion Engineering and Design 153 (2020) 111460



- [2] Y. Iwai, et al., Recent activities on water detritiation technology in JAEA, Fusion Eng. Des. 109–111 (2016) 1447–1451.
- [3] K.R. Kim, et al., Operational analysis of a liquid phase catalytic exchange column for a detritiation of heavy water, Sep. Purif. Technol. 54 (3) (2007) 410–414.
- [4] M. Zamfirache, et al., Final status of water detritiation system (WDS) for Cernavoda Tritium removal facility (CTRF), Fusion Eng. Des. 136 (2018) 1038–1040.
- [5] I. Cristescu, et al., Investigation of simultaneous tritium and deuterium transfer in a catalytic isotope exchange column for water detritiation, Fusion Eng. Des. 61–62 (2002) 537–542.
- [6] A.N. Perevezentsev, et al., Development of a water detritiation facility for JET, Fusion Eng. Des. 61–62 (2002) 585–589.
- [7] I. Cristescu, et al., Commissioning of water detritiation and cryogenic distillation systems at TLK in view of ITER design, Fusion Eng. Des. 82 (15–24) (2007) 2126–2132.
- [8] S. Welte, et al., Setup and commissioning of a combined water detritiation and isotope separation experiment at the Tritium Laboratory Karlsruhe, Fusion Eng. Des. 88 (9–10) (2013) 2251–2254.
- [9] J.M. Miller, et al., Design and operational experience with a pilot-scale CECE detritiation process, Fusion Sci. Technol. 41 (3P2) (2002) 1077–1081.
- [10] M. Hammerli, W. Stevens, J. Butler, Combined electrolysis catalytic exchange (CECE) process for hydrogen isotope

separation, Separation of Hydrogen Isotopes, ACS Symposium Series Vol. 68 (1978).

[11] Sicking, G. Isotope effects in metal-hydrogen systems. *J. Less Common Met.* 1984, 101, 169–190

[12] Wiswall, R.H.; Reilly, J.J. Inverse Hydrogen Isotope Effects in Some Metal Hydride Systems. *Inorg. Chem.* 1972, 11, 1691–1696.

[13] A. Pozio, S. Tosti, Pd-Ag Electrical Resistivity in Hydrogen and Deuterium: Temperature Effect, *Materials* 2019, 12, 3551; doi:10.3390/ma12213551

[14] Yuting Liu, Wenqing Wu, Guanghui Zhang, Manquan Fang, Wenyong Jing, Yifu Xiong, Renjin Xiong, Tao Tang, Study of separation factor and product extraction ratio in hydrogen isotope separation with displacement chromatography, *Fusion Engineering and Design* 165 (2021) 112246

[15] X. Deng, D. Luo, X. Qian, Development of separation materials containing palladium for hydrogen isotopes separation, *J. Isot.* 23 (2010) 53–58.

[16] A.B. Sazonov, EP. Magomedbekov, Estimate of the efficiency of hydrogen-metal hydride (intermetallic compound) systems in the separation of the three-isotope mixtures H-D-T, *Atom Energy* 89 (2000) 736–744.

[17] S. Fukada, K. Fuchinoue, M. Nishikawa, Hydrogen isotope separation by displacement chromatography with palladium, *J. Nucl. Sci. Technol.* 32 (1995) 556–564.

[18] X. Deng, D. Luo, C. Qin, X. Qian, W. Yang, Hydrogen isotopes separation using frontal displacement chromatography with Pd-



Al₂O₃ packed column, Int. J. Hydrogen Energy 37 (2012) 10774–10778.

[19] D. Ducret, A. Ballanger, J. Steimetz, C. Laquerbe, O. Baudouin, P. Sere Peyrigain, Hydrogen isotopes separation by thermal cycling absorption process, Fusion Eng. Des. 58-59 (2001) 417–421.

[20] L.K. Heung, H.T. Sessions, A.S. Poore, W.D. Jacobs, C.S. Williams, Next-generation TCAP hydrogen isotope separation process, Fusion Sci. Technol. 54 (2008) 399–402.

[21] Andrew D. Shugard, George M. Buffleben, Terry A. Johnson, David B. Robinson, Isotope exchange between gaseous hydrogen and uranium hydride powder, Journal of Nuclear Materials 447 (2014) 304–313

[22] A. Yawny, G. Friedlmeier and J. C. Bolcich, Hydrides for Hydrogen-Deuterium separation, Int. J.

[23] Arnulf Maeland and Ted B. Flanagan, Lattice Constants and Thermodynamic Parameters of the Hydrogen-Platinum-Palladium and Deuterium-Platinum-Palladium Systems, The Journal of Physical Chemistry, Volume 68, Number 6, June, 1964, 1419-1426

[24] Kuniaki Watanabe, Masao Matsuyama, Tohru Kobayashi, Shigeru Taguchi, Gas chromatographic separation of H₂-D₂ mixtures by Pd-Pt alloy near room temperature, Journal of Alloys and Compounds 257 (1997) 278-284

[25] Kuniaki Watanabe, Masao Matsuyama, Tohru Kobayashi, Wei Min Shu, Hydrogen isotope separation by gas chromatography



using Pd–Pt alloy, Fusion Engineering and Design 39–40 (1998) 1001–1008

[26] R. Lasser, A.C. Bell, N. Bainbridge, D. Brennan, L. Doerr, J.L. Hemmerich, S. Knipe, R. Stagg, The preparative gas chromatographic system for the JET Active Gas Handling System—tritium commissioning and use during and after DTE1, Fusion Engineering and Design 47 (1999) 301–319

[27] Yuting Liu, Wenqing Wu, Guanghui Zhang, Manquan Fang, Wenyong Jing, Yifu Xiong, Renjin Xiong, Tao Tang, Study of separation factor and product extraction ratio in hydrogen isotope separation with displacement chromatography, Fusion Engineering and Design 165 (2021) 112246

[28] Qian, Xiaojing, Deli Luo, Cheng Qin, G. Q. Huang and W. Yang. “FTP / P 106 Gas Chromatography Separation of H₂-D₂-Ar Using Pd / K.” (2010) - https://www-pub.iaea.org/mtcd/meetings/PDFplus/2010/cn180/cn180_papers/ftp_p1-06.pdf

[29] G. Neffe, U. Besserer, J. Dehne, E. Hutter, H. Kissel, R.D. Penzhorn, J. Wendel, H. Brunnader, Routine operation of the gas chromatographic isotope separation system of the Tritium Laboratory Karlsruhe, Fusion Engineering and Design 39–40 (1998) 987–993

[30] C. H. Cheh, Large Scale Gas Chromatographic Demonstration System for Hydrogen Isotope Separation, Fusion Technology Volume 14, 1988 pages 567-573, <https://doi.org/10.13182/FST88-A25194>

[31] W.T. Shmayda, M.D. Wittman, R.F. Earley, J.L. Reid, N.P. Redden, The Laboratory for Laser Energetics’ Hydrogen Isotope





Separation System, Fusion Engineering and Design
109–111 (2016) 128–134

[32] D. Ducret, A. Ballanger, J. Steimetz, C. Laquerbe, O. Baudouin, P. Sere Peyrigain Hydrogen isotopes separation by thermal cycling absorption process, Fusion Engineering and Design 58 – 59 (2001) 417 – 421

[33] J. E. Klein (Editor), L. K. Heung, D. W. Howard, M. W. Lee, T. Motyka, A. S. Poore, and J. H. Scogin, Conceptual Design for Consolidation TCAP, Report WSRC.TR-97-00340, 24 October 1997, Savannah River Technology Center, <https://www.osti.gov/servlets/purl/4820>

[34] X. Steve Xiao, L.K. Heung, H.T. Sessions, S. Redd, Advances in Hydrogen Isotope Separation Using Thermal Cycling Absorption Process (TCAP), [https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&ved=2ahUKEwiC-rfq0eT5AhVQXfEDHajvAp4QFnoECAUQAQ&url=https%3A%2F%2Fenergy.gov%2Fsites%2Fprod%2Ffiles%2F2015%2F08%2Ff26%2FSRNL-STI-2013-00230%2520Rev1_Advances%2520in%2520TCAP%2520\(Xiao\).pdf&usg=AOvVaw1C3s5IDVNIQoqv5FITED4a](https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&ved=2ahUKEwiC-rfq0eT5AhVQXfEDHajvAp4QFnoECAUQAQ&url=https%3A%2F%2Fenergy.gov%2Fsites%2Fprod%2Ffiles%2F2015%2F08%2Ff26%2FSRNL-STI-2013-00230%2520Rev1_Advances%2520in%2520TCAP%2520(Xiao).pdf&usg=AOvVaw1C3s5IDVNIQoqv5FITED4a)

35 [35] Elliot A. Clark, Materials Performance in Prototype Thermal Cycling Absorption Process (TCAP) Columns (U), Report WSRC.TR-92-552-552, 21 November 1992, Savannah River Technology Center, <https://doi.org/10.2172/10161885>

[36] Junbo Zhou, Xiang Zhang, Shan Hao, Wenjia Huan, Dynamic simulation of Thermal Cycling Absorption Process with twin

columns for hydrogen isotopes separation,
International Journal of Hydrogen Energy 39 (2014)
13873-13879

[37] Li Deng, Changan Chen, Guoqiang Huang, Yan Shi, Yong Yao, Jun Hu, Kelin Chen, Yongtao An, Jiangfeng Song The oil bath thermal cycling absorption process design and separation process research, Int. Journal of Hydr. En. 48 (2023) 22132-22140, <https://doi.org/10.1016/j.ijhydene.2023.01.236>

[38] George Ana, Alina Niculescu, Anisia Bornea, Marius Zamfirache, Mirela Draghia, TCAP Hydrogen Isotope Separation Process Under Development at ICSI Rm. Valcea, IEEE TRANSACTIONS ON PLASMA SCIENCE, VOL. 46, NO. 7, JULY 2018

[39] Xin Xiao, Benton Randall, Henry T. Sessions, Robert Allgood, Dave Babineau, Thermal Cycling Absorption Process Overview, Presentation of Savannah River National Laboratory, <https://www.energy.gov/sites/prod/files/2019/06/f63/Thermal-Cycling-Absorption-Process-Overview.pdf>

