

ENDURANCE TESTS FOR WDS COPONENTS

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1. Introduction

The Water Detritiation System (WDS) of ITER is a safety related component since is the final barrier against tritium discharge into the environment. Therefore, its subcomponents have to be qualified and prediction on the time evolution of performances to be made.

Endurance tests at tritium low concentrations on Pt/PTFE catalyst have been performed by different research institutes. In this respect, ICIT extended the endurance tests with tritiated water of 100 Ci/kg for an LPCE column. With the experimental rig manufactured, ICIT investigated the time behavior of the catalyst. For ITER relevant operation condition, this experimental rig had a small LPCE column filled with the same type of catalyst as in the TLK LPCE column, and operated for one year with tritiated water of 100 Ci kg^{-1} .

The quality of the tritiated water was measured on a regularly basis at 1, 3, 6, 9 and 12 months and the time evolution of the fluoride content in the tritiated water was determinated.

2. Experimental rig setup

The main parts of the endurance test experimental rig, shown in Figure 1 and Figure 2, are the following:

- 1 - LPCE column;
- 2 - Process pump for tritiated water- Bran+Luebbe PS 100 (P1);
- 3 - Tritiated water vessel (V1)
- 4 - Electric heat exchanger for normal water (H101);
- 5 - Heat exchanger for tritiated water (V2);
- 6 - Normal water pump (P2);

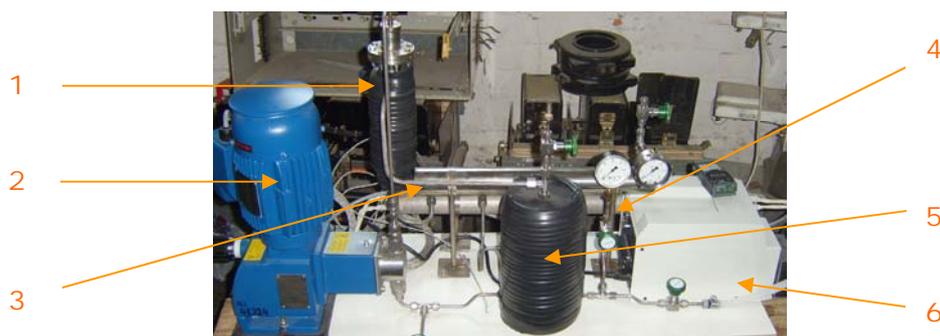


Figure 1. Experimental rig

All components of the rig, in contact with tritiated water, were made from polish pickling 316L stainless steel (the same material proposed to be use for the LPCE columns of WDS from ITER). All the technological pipes were acid pickling, to remove the oxides and impurities resulting from the machining and welding process. After that, the rig was subjected to pneumatic and hydraulic leakage tests at 3 bars. The LPCE column had a heating jacket with normal water, for maintaining the tritiated water at a constant temperature of 80⁰C. Inside the column was created an overpressure (1 bar of pure hydrogen). In order to ensure an equal distribution on the catalyst, the inlet of the tritiated water was made by a spreading system. The operating duty tests with distilled water, were performed to calibrate the temperature of the feedback control loop of the tritiated water from the LPCE column. In the H101, inside of three concentric 316L pipes are installed electric resistances of 700W power each one. One of these electric resistances worked permanently, one was used for regulating the water temperature and one was for back-up. Inside the V2 vessel there was a heating coil through which the process pump P1 circulated the tritiated water. In this way, the pre-heated tritiated water was introduced to regulate the system temperature at a specific value. The required flow rate of the tritiated water 5 l/h was regulated from the pump (P1) and flow rate of the heating water (P2) was calculated in order to obtain the necessary heat power for the electric resistances. All the experimental parameters were acquired with a Field-Point acquisition system using Lab-View software.

For this experiment, ICIT manufactured the necessary hydrophobic catalyst, of the same type as the one used in the TLK LPCE column. The tritiated water of 100 Ci/l was obtained into a reactor by burning an HT mixture on Al/Pd catalyst. In order to comply with the radioactive safety procedures, the experimental rig was installed and all the experiments were carry out in a tritium monitored glove box, at IFIN HH Bucuresti.

3. Experiments inputs

- For the LPCE column we manufactured and used 150 g Pt/C/PTFE catalyst;
- Vessel V1 was filled with 900 ml of HTO with a radioactive concentration of 3,28 TBq (88,5 Ci)/l;
- Vessel V2 was filled with approximately two liters of distilled water;
- Tritiated water flow rate in the LPCE column – 5 l/h;
- Temperature of the tritiated water in the LPCE column – 80⁰ C;
- Pressure inside of the LPCE column - 1 bar (pure H₂)

4. Experiments determinations

Catalyst and HTO samples were investigate at 1, 3, 6, 9, 12 months.

- Analysis of the pH and fluoride ion total concentration for the tritiated water;
- Determination of radiation-induced modifications in the catalyst exposed

The stability of the isotopic exchange catalyst was analysed by:

- evaluating the absorbed dosed in tritiated water solutions;
- simulating by quantum chemical methods the behaviour of the isotopic exchange catalysts which were exposed to tritiated water;

- stimulating radiolytic processes by exposing the catalyst immersed into water to a gamma radiation field;
- mechanical behaviour of the isotopic exchange catalyst in the presence of tritiated water.

5. Process description

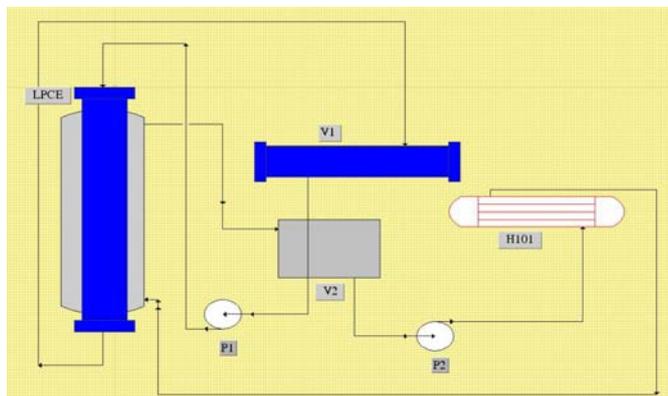


Figure 2. Block diagram of the experimental rig for catalyst endurance test

The normal water enters through the bottom of the column jacket, get out from the upper part and filled the V2 vessel. Pump P2 circulates the normal water from V2 vessel through the H101 heater to the column jacket, and the cycle is repeated. From V1 vessel, the tritiated water is circulated by the P1 pump, through the heating coil from V2 vessel into the LPCE column. The tritiated water temperature is measured in three points, at the inlet, middle and outlet of the column. If the average temperature obtained from these three measurements, is different from 80°C, the feedback control loop decrease/increase the power supply to the regulating resistance from H101.

6. Catalyst manufacture process

The endurance tests were performed with the same type of catalyst as in the TLK LPCE column. The catalyst was produced by ICIT through platinum deposition on an activated charcoal support, before mixing it with PTFE (polytetrafluoroethylene) used as hydrophobic material. The catalyst molded into the cylindrical shape ($\Phi = 2,5 \text{ mm}$, $L = 15 \text{ mm}$) was baked into a controlled atmosphere glass column at 355-360°C in order to improve its the mechanical stability.



Figure 3. Pt/C/PTFE catalyst

7. Results

1. The calculus of the absorbed doses when isotopic exchange catalysts were exposed to tritiated water

1.1 The calculus of the absorbed doses in tritiated water solution

Doses and doses flow absorbed in tritiated water solution through auto-irradiation were calculated as follows:

$$D_{bloc} = \frac{1}{100} \cdot \frac{Ed}{m} \cdot \Phi_{total} = \frac{1}{100} \cdot \frac{Ed}{m} \cdot \Lambda_0 \cdot \frac{(1 - e^{-\lambda t})}{e^{-\lambda t}} = \frac{1}{100} \cdot \frac{Ed}{m} \cdot \Lambda_0 \cdot \frac{(1 - e^{-\frac{0,693t}{T_{1/2}}})}{e^{-\frac{0,693t}{T_{1/2}}}}$$

- where D_{bloc} = the absorbed dose in tritiated block water expressed in rad (10^{-2} Gy);
 A = the activity expressed in Bq;
 m = sample mass expressed in g;
 Ed = β radiation average energy of tritium expressed in erg;
 t = exposure time expressed in s;
 l = tritiated water thickness layer expressed in μm ;
 Φ_{total} = total β radiation flow emitted during the exposure;
 A_0 = initial activity expressed in Bq;
 λ = tritium disintegration constant;
 $T_{1/2}$ = tritium reducing time to one half.

1.2 The calculus of absorbed doses at the interface of isotopic exchange catalysts which were exposed to tritiated water

The catalyst was exposed to ionizing-radiations field which were emitted by the disintegration of tritium atoms from the HTO. Due to the very low β radiation emitted by tritium, the direct measurements of the dose absorbed by the isotopic exchange catalysts using classical techniques are actually impossible. In order to determine the absorbed dose at the isotopic exchange catalyst interface, a calculus model was developed.

The absorbed dose flow was calculated using the formula:

$$\Phi = \sum_{i=0}^{i=60} \Phi_i = \sum_{i=0}^{i=60} \phi_i \cdot \alpha_i \cdot \gamma_i$$

Where:

Φ_i = radiation flow emitted by tritium atoms from the tritiated water volume delimited by the surfaces of two semispheres;

α_i = emission coefficient in the direction of the catalyst on a semispherical calotte surface;

y_i =attenuation coefficient of the β -radiation, which is emitted by tritium, from the water volume delimited by the surfaces of two semispheres, absorbed in the volume given by the interior semisphere surface in the tritiated water layer.

Based on the data which were previously presented, dose flow value was calculated using the formula:

$$d = \frac{9,131 \cdot \pi \cdot 37 \cdot n \cdot 10^{-22}}{3m} \sum_{i=0}^{i=60} (3i^2 + 3i + 1) e^{-i/5.77078} \cdot \left(1 - \frac{i}{\sqrt{i^2 + 1}} \right)$$

In this case the absorbed dose flow can be calculated by taking into account the radioactive concentration of the tritiated water (n) expressed in GBq/l.

$$d = n \cdot 89,71 \text{ mrad/s} = n \cdot 331.9 \text{ } \mu\text{Gy/s}$$

In Table 1, the absorbed doses at the interface of the isotopic exchange catalyst are presented.

Table 1. The values of the doses absorbed into the isotopic exchange catalyst superficial layer.

Radioactive concentration [GBq/L]	d [mGy/s]	Calculated dose [kGy]				
		1 day [kGy]	1 month [MGy]	3 months [MGy]	6 months [MGy]	12 months [MGy]
370	122	10.6	0.3	1.0	1.9	3.8
740	246	21.2	0.6	1.9	3.8	7.6
1110	368	31.8	1.0	2.9	5.7	11.5
1480	491	42.5	1.3	3.8	7.6	15.3
1850	614	53.1	1.6	4.8	9.6	19.1
3700	1228	106.1	3.2	9.6	19.1	38.2
37000	12284	1061.3	31.8	95.5	191.0	382.1

2. Simulation by quantum chemical methods of the behaviour of the isotopic exchange catalysts which were exposed to tritiated water

Radiochemical yields (G) were associated to the possibility of homolytic break up action. Thus, G represents the amount (G_i) of homolytic break up of each chemical bound from LUMO's peripheral orbital coverage area. G_i is directly proportional with LUMO orbital coverage per chemical bound and inversely proportional with the chemical bound strength.

$$G = \sum G_i = \sum a \cdot \frac{A_{LUMO_i}}{BE_i}$$

Where: a – represent a parameterization constant deduced from experimental values, A_{LUMO_i} represents the value of the LUMO orbital coverage degree per chemical bound, and BE_i represents the bound energies for each evaluated chemical.

Based on the obtained results, we have determined the following values for polymeric bound break up: $G = 3.033$, G (F direct emission)=0,214 and G (F total emission)= 6.214.

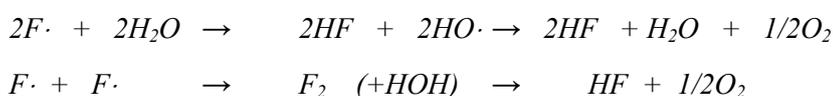
Table 2. Bound energies values, LUMO orbital coverage, and individual G values

Chemical bound	BE	ALUMO	G_i	Chemical bound	BE	ALUMO	G_i
C1-F	110.5	0.005	0.0045	C1-C2	64.18	0.02	0.0312
C2-F	110.7	0.01	0.0090	C2-C3	53.42	0.03	0.0562

C3-F	124.3	0.02	0.0161	C3-C4	60.18	0.08	0.1329
C4-F	120.2	0.03	0.0250	C4-C5	5.83	0.15	2.5729
C5-F	120.2	0.03	0.0250	C5-C6	60.21	0.08	0.1329
C6-F	124.3	0.02	0.0161	C6-C7	53.45	0.03	0.0561
C7-F	110.7	0.01	0.0090	C7-C8	64.23	0.02	0.0311
C8-F	110.4	0.005	0.0045				

Due to the solid structure of PTFE, the resulted F atoms from the primary process migrated heavily in the material. This process facilitated the recombining processes, namely the addition of F atoms to the free radicals which were formed, respectively to vinylic groupings induced in the break up action. This is why the G value (-F total) was diminished and the estimated value was of approx. 3, similar to G break up value.

Because the irradiation was performed in water vapours medium, F emission was associated to HF formation:



3. Radiolytic processes simulation by exposing the catalyst immersed into water to a gamma radiation field

The stimulation of the isotopic exchange catalyst behaviour in the presence of HTO was performed by exposing the catalyst immersed into ultrapure water to a gamma radiation field emitted from a source of Co-60. The samples were introduced into HDPE (NALGEN) vials and exposed to a dose flow of 1.58 kGy/h. The absorbed doses were of 50, 100, 150, 200, 440 and 2000 kGy.

Radiation-induced modifications were carried out by FTIR spectrometry using ATR TENSOR 27 (Bruker) spectrometer.

HF emission was analyzed by determining the pH and fluoride ion from the immersion water. The determinations were performed using a pH meter-ionometer WTW INOLAB MULTI 720 with pH micro- electrode and fluoride ion selective electrode in a range $1-10^{-6}$ mol/l.

The identification of radiation-induced modifications using IR spectrometry

In order to validate the suggested model by quantum chemical simulation, the IR analysis of the irradiated samples was carried out with a view to identify the specific radiation-induced grouping lines COOH, OH and C-H. The obtained spectra were intercompared with the results obtained for CF₃COOH and Cl₃CH.

Spectral analysis confirmed the presence of COOH, C(=O)-H or CF₂H groupings. Thus, the specific unassociated carboxylic OH strip (3470 cm^{-1}), as well as the trifluoride acetic acid characteristic strips (2600 cm^{-1} , 1783 cm^{-1} , 1447 cm^{-1} , 813 cm^{-1}) were identified. The drops from the fields 2930 cm^{-1} and 2850 cm^{-1} which were presented in the control sample, grown in intensity and can be attributed to C-H aldehydic groupings or more probably to F₂C-H.

Fluoride ion emission analysis

The results obtained from the spectral analysis are also confirmed by the HF emission analysis using pH-analysis and fluoride ion concentration in watery solutions (Table 1.).

Table 3. F radiation-induced emission into the isotopic exchange catalyst.

Sample	Dose [kGy]	pH	F ⁻ conc [mol/l]	Nr. F mol/g	G(F)
PTFE : H ₂ O	50	3.3	1.90E-03	4.37E-05	3.28
PTFE : H ₂ O	100	3.5	1.66E-03	8.30E-07	3.12
PTFE : H ₂ O	150	3.4	5.32E-03	2.32E-06	3.06
PTFE : H ₂ O	200	3.1	6.35E-03	1.59E-06	2.99
PTFE : H ₂ O	440	2.8	5.56E-03	1.86E-06	2.37
PTFE : H ₂ O	2000	1.8	1.52E-02	5.06E-06	1.42

The study of the isotopic exchange catalyst behaviour in the presence of tritiated water

150 g of catalyst and 900 ml of HTO with a radioactive concentration of 3,28 TBq (88,5 Ci)/l were introduced in the installation in order to execute endurance tests.

Catalyst and HTO samples were subject to the following exposure periods: 1, 3, 6, 9, 12 months.

Tritiated water was analyzed by determining pH and fluoride ion total concentration.

The catalyst was decontaminated by multiple washings using deionised water, methylic alcohol and finally dried for 24 hours, stocked in a vacuum exicator.

The radiation-induced modifications were analyzed by IR spectrometry.

Tritiated water characterization

Tritiated water was characterized by determining pH and fluoride ions.

In order to determine pH and the F⁻ content from the tritiated water samples we used a pH-meter/Inolab potentiometer pH 720, manufactured by WTW GmbH Company-Germany, to which we added a selective ion electrode, with a solid membrane for F⁻ DC219-F, manufactured by Mettler Toledo Company.

Selective ion electrode calibration

In a 150ml high density polyethylene vessel we measured 100 ml of the lowest concentrated F⁻ standard solution, on which we added 2 mL electrolyte solution (ISA). The solution was homogenized by magnetic stirring and after approximately 1 minute the potential value was read. After the stabilization, in order to obtain a new concentration, the solution was adjusted to an exact volume.

After each measurement, the electrode was washed with distilled water and gently wiped using a filter paper.

Through successive dilutions from the 1000 ppm standard solution we prepared 2 solutions having the concentration close to the one of the samples.

Based on the performed measurements, the calibration curve presented in Figure 4 was drawn.

The analysis of the tritiated water radioactive samples

From the testing installation regarding the resilience of the catalyst which was exposed to tritiated water in a dynamic system, tritiated water samples with volumes of 2 mL were extracted.

For the radioactive samples, the measurements were carried out after 1, 3, 6, 9, 12 months from the catalyst exposure time in tritiated water with a radioactive concentration of 90 Ci/l.

Sample's pH was determined using InLab 423pH microelectrode.

In order to determine F⁻ ion content, the samples were prepared as follows:

2 mL of tritiated water were diluted into 8 mL of deionized H₂O to which 0.200 mL of electrolyte is added as to not modify the system operation parameters.

Concentration value was calculated with a 2.5 correction factor.

The obtained results are presented in Figure 5 and Table 4.

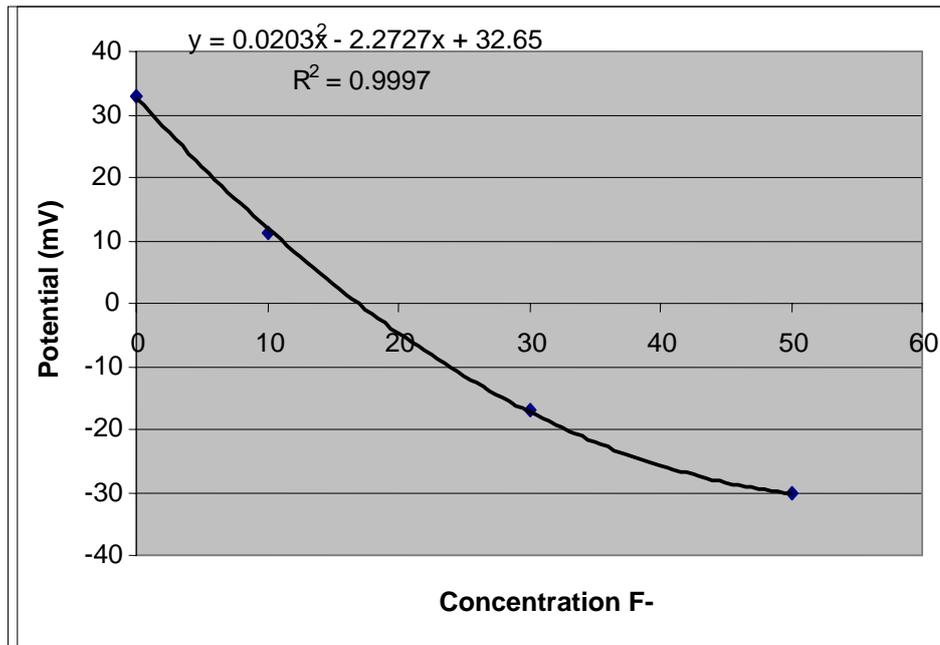


Figure 4 Calibration curve for determining F⁻ from the H₂O samples

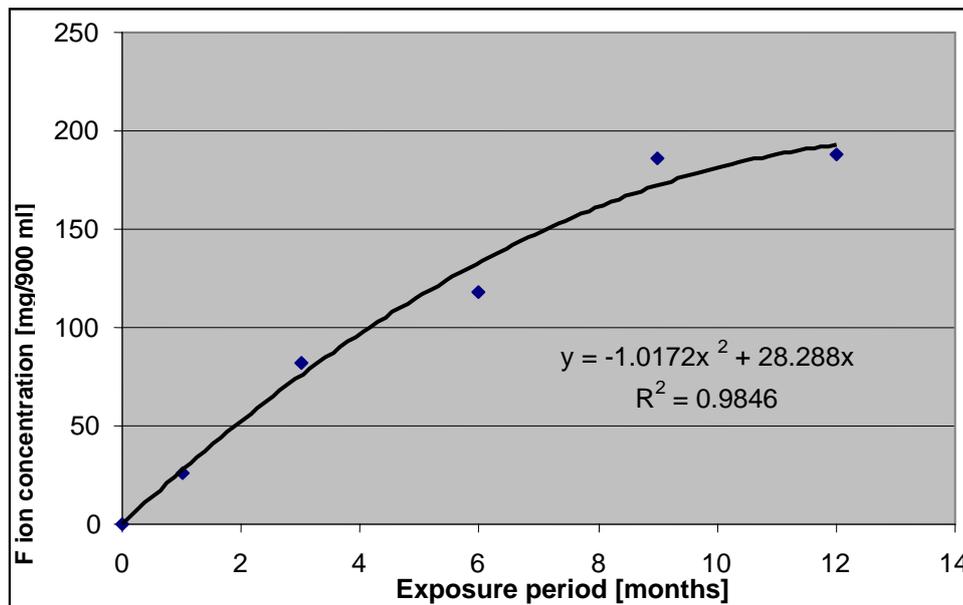


Figure 5. Variation of fluoride ions concentration on HTO in terms of exposure period

Table 4. Determination of the radiation-induced effects in PTFE by HTO exposure to 3,28 TBq (88.5 Ci)/l concentration

Exp. period. [months]	pH	F ion concentration in HTO [ppm]	F total emission [mg]	Relative loss referred to PTFE	F loss relative percentage [% F emitted/F total PTFE]
0	5.6	0	0	0	0.00
1	5.26	29.44	26.5	0.0002	0.017
3	5.7	90.67	81.6	0.0007	0.052
6	5.9	126.80	118.2	0.0010	0.075
9	5.7	207.22	186.5	0.0016	0.118
12	5.6	209.22	188.3	0.0016	0.119

8. Collaborative work

Activities related to this task were performed in collaboration with the “Horia Hulubei” National Institute of Physics and Nuclear Engineering (IFIN – HH) starting with May 2007. Part of this work was performed during the two-month Mobility Secondment of M. Vladu at Forschungszentrum Karlsruhe – Tritium Laboratory, Germany.

9. Conclusions

The results obtained by mathematical modelling, show an exposure to very high doses of the superficial layer of the isotopic exchange catalyst for contact periods exceeding 30 days. The determined absorbed doses are much higher than the stability limit of the PTFE polymers (0,3 MGy).

The analysis of the primary and secondary radiolytic processes by quantum chemical simulations indicates different degradation mechanisms, associated with similar effects, respectively:

- the break up of the main polymeric bound and
- the HF significant emission

The simulation of radiolytical processes by exposure to gamma radiation fields, emitted by a Co-60 source, confirms the degradative mechanisms deduced by quantum chemical simulations. These effects are low (ppm) for an absorbed dose of (0,2 MGy).

The study of the isotopic exchange catalyst behaviour in the presence of tritiated water was carried out by analyzing the tritiated water and the exposed catalyst.

The analysis of the tritiated water was carried out with a view to determine the content of HF (pH determinations) and F⁻ ion (F total)

The determined pH values were in the range of 5,5-6,0. We did not identify the presence of HF resulting from the primary or secondary radiolytic process. The presence of HF in HTO samples was contradictory to the results obtained by quantum chemical simulations and by exposure to gamma radiation fields.

The absence of HF in the samples was due to the fact that HF reacted with stainless steel, the material used in manufacturing the testing installation.

HF a highly corrosive agent (it even damages the glass) reacts with the metallic alloy forming metallic fluorides. This behaviour can be evidenced by determined F⁻ ions concentration values and can be associated with the catalyst colour change and brownish-yellow colour of the tritiated water which was extracted from the testing installation.

F⁻ ion concentration increased during the exposure period. The dependence on the exposure time was not linear, there was a flattening tendency of the curve to long exposure periods (absorbed doses).

Radiochemical yields (ppm F emitted/F total from PTFE) attained values between 170 ppm on 30 days exposure periods and 1190 ppm on 1 year exposure.

The catalyst exposed to HTO presented significant changes in the mechanical properties (colour) and chemical structure (determined through FTIR spectrometry).

The altering of the mechanical properties is important, starting from short exposure periods (1 month).

The chemical structure was changed by inducing some groupings COOH, CO, OH ascribed to primary and secondary radiolytical processes. The absence of modification regarding the characteristic strips of C-F bounds denotes a quite small share. The result obtained by determining F emission reflects a degradative process of approx. 0,2%, an unnoticeable change through FT IR analysis.

In conclusion, PTFE-based catalyst has a quite low stability in the presence of HTO, with a radioactive concentration of approx. 100 Ci/l. Radiolytical processes lead to HF formation and structural modifications of the hydrophobe support. Nevertheless, relatively minor structural modifications lead to significant modifications of the mechanical properties.

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