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## **ABSTRACT**

At the Tritium Laboratory of the Forschungszentrum Karlsruhe (TLK) an experimental facility is running which is designed for the intercomparison of several hydrophobic catalysts for use in an Liquid Phase Catalytic Exchange (LPCE) column. The catalysts under comparison are from Russia, Belgium and Romania. The intercomparison is being performed by computing the Height eEquivalent of Theoretical Plates (HETP) and the mass transfer coefficients for HD transfer from gas to water using the measured values of the composition. The range of HD concentration in hydrogen as carrier gas was 1000ppm up to 2%. The gas and liquid composition at the bottom and at the top of the column and the condensed vapour composition at the top of the column are measured by mass spectrometry and IR spectrometry.

## **1. INTRODUCTION**

At JET, tritiated water is produced during the operation of the tokamak and from the Exhaust Detritiation System of the Active Gas Handling System. Much tritiated water is also expected to be produced during the decommissioning of JET. Hence a water detritiation system with a throughput of 20 000 kg/year needs to be developed and installed at JET. This system is based on an electrolyser for the conversion of water to hydrogen, a cryogenic distillation column for tritium enrichment and either a Liquid Phase Catalytic Exchange (LPCE) or Vapour Phase Catalytic Exchange (VPCE) column for the tritium recovery from gas. Parameter testing and selection of the most suitable catalyst for a LPCE column have become important goals.

A laboratory sized catalyst test installation is presently running at TLK. Three catalyst/packing combinations from different manufacturers from Russia, Belgium and Romania are currently being tested. Water and deuterium-hydrogen mixtures are employed in a counter-current mode to study the performances of the catalyst.

## **2. EXPERIMENTAL DESCRIPTION**

The intercomparison between different catalysts on the experimental facility at TLK (shown in Fig.1) was performed in an isotopic exchange column of 1200mm length and 40mm diameter with an active catalyst/packing height of approximately 900mm.

At the bottom and top of the column 15cm height of packing material was used with the aim to have the same temperature of the gas, liquid and vapor phase.

The isotopic exchange process takes place between the pre-heated water that is fed in at the top of the column and deuteriated hydrogen that is fed in at the bottom. The deuterium-depleted hydrogen is released at the top of the column and condensed vapours are returned into the column. The temperature of the isotopic exchange column, which has double walls, is held constant by an external heater.

The column has been filled with catalyst and inert packing (layers or mixed) according to the suppliers specifications. The heater for the feed water was necessary in order to have the same temperature for the water feed as the working temperature of the column. The boiler with adjustable

electrical power produced the water vapour for saturating the hydrogen at the temperature of the column. A constant water level is maintained in this boiler. The condenser with a high thermal exchange surface ( $0.1\text{m}^2$ ) operated at  $10^\circ\text{C}$  was installed to recover the majority of vapors from the saturated gas at the outlet.

The time evolution of the deuterium content in the liquid phase at the bottom of the column and in the gas phase at the top of the column are necessary to establish when the steady state is reached. For the column output, on-line measurements of the gas phase were performed by a Quadrupole mass spectrometer. For comparison, batch measurements at steady state conditions were performed with an Omegatron mass spectrometer. For the liquid phase, deuterium content both in the feed water at the top of the column and in the water from the boiler were measured on-line by IR spectrometry. At steady state the concentration in the liquid and gas phase at the bottom and the top of the column were used to establish the HETP and the mass transfer coefficients.

### 3. COMPOSITION MEASUREMENTS

The feed gases for the experiments with different contents of deuterium (mixtures of  $\text{D}_2$  and  $\text{H}_2$ ) were supplied by an industrial company. In order to achieve a good accuracy for measuring the HD and  $\text{D}_2$  content in the gas processed in the column, a suitable measuring procedure for the Quadrupole spectrometer was established. The analyses were made for the following ions, which can appear in the measurement process:  $\text{H}^+$ ,  $\text{H}_2^+$ ,  $\text{H}_3^+$ ,  $\text{HD}^+$ , and  $\text{D}_2^+$ . We have paid attention to develop a method in order to establish the contribution only for  $\text{HD}^+$  species to the total current  $I_3$  (which also contains the  $\text{H}_3^+$  contribution). In order to determine the ionisation probability for HD species, samples with different content of  $\text{H}_2$  and  $\text{D}_2$  were prepared by a partial pressure method of mixing. All the mixtures were totally equilibrated by passing the mixtures through a vessel of 10cm length and 2.5cm diameter filled with catalyst. Knowing the total amount of deuterium in the mixture, the amount of HD and  $\text{D}_2$  species was computed for total equilibrated gas. These values and the peak height for pure  $\text{H}_2$  and  $\text{D}_2$  were used to establish the ionisation probabilities for the HD species.

The advantage of the Omegatron mass spectrometer is that it can distinguish ions with very close masses, like  $\text{D}_2$  and He or HT and  $\text{D}_2$ . A calibration procedure for mixtures of hydrogen and deuterium in the concentration range 1 to 10%  $\text{D}_2/\text{D}_2+\text{H}_2$  was established. Pure  $\text{H}_2$ , pure  $\text{D}_2$  and several mixtures were compared using the Omegatron and Quadrupole mass spectrometers. The gas mixtures were prepared by a partial pressure method of mixing.

For measurements of water with deuterium content up to 5%, the absorption peak corresponding to  $2500\text{cm}^{-1}$  wavelength was used in the IR measurements. At this level of deuterium content only the HDO molecules have a major contribution to the peak, the contribution of the  $\text{D}_2\text{O}$  molecules can be neglected. The sensitivity for different optical path lengths of the measuring cell was determined. As a result, a cell with  $25\mu\text{m}$  path length had the highest sensitivity, and this cell was used in the measurements. In order to calibrate the instrument, several samples of known composition of HDO were prepared by partial volume mixing. With these values a calibration curve for mixtures in the

range 1000ppm- 5% was drawn. The water samples from the bottom of the column and the condensed vapour samples from the top were analysed and the deuterium concentration values were determined using the calibration curve.

#### 4. MODEL FOR THE SIMULATION OF COLUMN PERFORMANCES

The objective of the model is to establish the deuterium enrichment performances in the catalytic exchange column. To describe the performance of the separation process two approaches were considered:

- A graphical approach (classical) that uses the operating line and equilibrium curve for the process.
- An analytical approach that solves the transport equations characterising the isotopic exchange process.

To make the model broadly applicable it was developed to include non-negligible  $D_2$  and  $D_2O$  concentrations. Six molecular species were therefore contemplated i.e.  $H_2O$ ,  $HDO$ ,  $D_2O$ ,  $H_2$ ,  $HD$  and  $D_2$ . Since the number of atoms in this component system is three, i.e. H, D and O,  $6-3=3$  chemical reactions are necessary for a full description.

The following three chemical reactions describe the isotopic exchange process among all involved six molecular species:



The temperature dependence of the equilibrium constants corresponding to these reactions has been estimated from spectroscopic data employing the corresponding partition function.

In the columns under test package and catalyst occupy alternating layers indicating that:

- in the scrubbing section (filled with package) mainly the isotopic equilibration between the liquid and vapour takes place.
- in the catalytic exchange section (filled with catalyst) mainly the isotopic exchange reaction between the vapour and the gas occurs.

In order to calculate the transfer of the heavier isotope (D in this case) from the gas to the liquid phase, the mass balance in an element of height  $\delta z$  was considered and assumed that there is no change in the hold-up of the heavier isotope in the geometrical element. In this way the variation of the concentration of interest with height can be expressed as function of each input concentration both in the gas-vapour phase (for catalytic section) and vapour-liquid phase (for scrubbing section) [4, 5].

For each of the reactions a corresponding transfer equation can be written. It is apparent that some molecular species participate in several reactions. Therefore the contributions of all reactions must be incorporated in the isotopic transfer expression for each species.

Input data for the calculation of the transfer coefficients are column diameter and height, the number

of catalyst and package layers, the height of catalyst and package layer, the gas and liquid flow rate, column temperature and the deuterium concentration in the gas and liquid phase at the inlet and outlet of the column. Output data are the mass transfer coefficients and the concentration spectrum on gas, liquid and vapor phase along the column.

## 5. COMPARATIVE RESULTS OF THE INVESTIGATED CATALYSTS

The following testing conditions were accomplished during the experiments:

- gas flow rates equivalent to linear gas velocities in the column between 0.1 and 0.2m/s for the various catalysts;
- molar gas/liquid flow rate ratios in the range 2 – 4;
- operation temperature established by the catalyst manufacturers.

In table 1 are presented the main characteristics of the catalysts that are under testing at TLK.

The experimental results of the investigation are presented in Table 2.

Table 2 Experimental results

From the experimental results, the following can be noticed

- a). The feed in gas at the bottom of the column and the feed in water at the top of the column have constant concentrations of HD (1.964%-1.98%) and 140ppm HDO respectively.
- b). The HDO concentration in the vapor phase at the top of the column was dependent on the performances of the catalyst-packing and for all the experiments was in the range 1200-6400 ppm.
- c). The HD concentration in the output gas was in the range 4400-7000 ppm.

In table 3 the performances of three catalysts tested until now at TLK are summarised.

According to the computed values for catalysts performances it can be seen that:

- The HETP and the mass transfer coefficients for isotope exchange ( $K_S$ ) and distillation ( $K_D$ ) are strongly dependent both on the G/L ratio (the operating line) and columns temperature by vapor flow-rate and isotopic exchange equilibrium constant.
- At G/L~4 the HD concentration in the input and output gas are relatively closed for all the catalysts: 7000 ppm for SCK-CEN catalyst, 6940 for Mendeleev Univ. catalyst, 6400 for ICIT-FZK catalyst. Due to the temperature influence in the equilibrium constant and to the vapor flow rate, the differences in the HETP and the mass transfer coefficients are comparatively large.
- At G/L~2 the global performances of the catalyst- packing for the ICIT-FZK column are higher (31cm HETP comparing with 52cm and 84cm). Analysing the corresponding mass transfer coefficients it can be seen that these performances are due to a better performance of the packing material.



## CONCLUSIONS

Considering the performances for tritium separation are similar to the ones for deuterium separation [6], the present experimental results show that any of the catalyst-packing materials investigated can assure a decontamination factor of 5000-10000, as required by JET, for a column height of ~9m.

For more and detailed investigations a new catalytic isotope exchange facility is presently under construction in the controlled area of TLK in order to investigate the transfer process of hydrogen isotopes from gas to water using tritiated water. The throughput will be of 1/2 that for specified for JET and the method will be Combined Electrolysis Catalytic Exchange process (CECE) with a Liquid Phase Catalytic Exchange (LPCE) column.

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Catalyst	SCK-CEN	ICIT-FZK	Mendeleev Univ, Russia
	Platinum 1wt%	Platinum ~1.5%	Platinum ~0.8%
	carbon 19wt%	carbon 15%	Copolymer of styrene and divinyl benzene
	PTFE 80wt%	PTFE 83.5%	
	Pellets	Granular 2mm diam × 4mm	Pellets
Packing	Mini-spirals	Wire mesh	Mini-spirals
	Stainless steel	Phosphor-bronze	Stainless steel
	2mm diam × 2mm		2.2 × 2.2 × 0.2mm
Filling ratio (Catalyst/packing)	1:3	1:2,5 sandwich method	1:4 sandwich method
Temperature	~40°C	60°C - 80°C	60°C

JG03.335-1c

Table 1: Catalyst characteristics

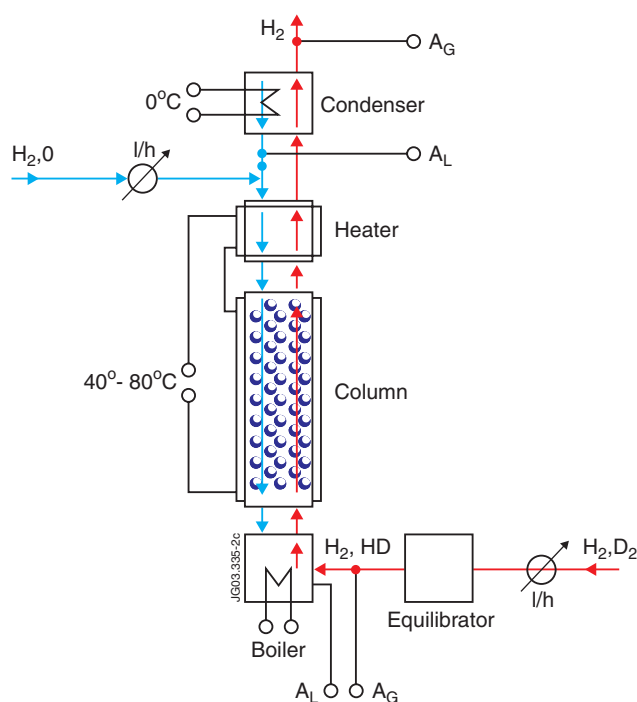


Figure 1 Catalyst test installation

Column	G/L	Concentrations at the bottom %		Concentrations at the top (ppm)	
		Liquid HDO	Gas HD	Vapor HD	Gas HD
Mendelev Catalyst	1.85	2.84	1.98	6400	5160
	3.71	5.06	1.96	4740	6940 4800
SCK-CEN Catalyst	1.79	2.4	1.97	4600	6960
	3.28	4.46	1.98	3200	7000
ICIT-FZK Catalyst	1.7	2.04	1.98	1200	4400
	3.35	4.84	1.98	4500	6400

JG03.335-4c

Table 2: Experimental results

	G/L	HETP (cm)	KS (kmol/m <sup>3</sup> h)	KD (kmol/m <sup>3</sup> h)
Mendelev	1.85	52	248	143
SCK-CEN	1.79	84	128	54
ICIT-FZK	1.7	31	350	214
Mendelev	3.71	27	314	245
SCK-CEN	3.27	45	183	88
ICIT-FZK	3.35	26	330	280

JG03.335-5c

Table 3: Catalyst performances