OPTIMIZATION OF THE RATIO PACKAGE/ CATALYST FOR THE SIMULTANEOUS TRANSFER OF TRITIUM AND DEUTERIUM IN A WATER DETRITIATION FACILITY

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1. Introduction

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

The isotopic exchange process takes place between the pre-heated deuteriated and/or tritiated water that is fed in at the top of the column and deuteriated hydrogen that is fed in at the bottom.

The column has been filled with catalyst and inert packing (layers or mixed) according to the manufacturers specifications. The measurements of the time evolution of the deuterium and tritium 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 in respect to deuterium measurements. 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 was measured on-line by IR spectrometry. For tritium measurements a Liquid Scintillation Counter (LSC) was used

The next objective was to produce new catalysts with adequate shape which are mixed with appropriate packages with the goal to maximize the surface of package-catalyst mixtures contained in a specified volume. The performances for these mixtures were tested within the experimental facility for water detritiation at TLK.

The most suitable process for water detritiation is the Combined Electrolysis Catalytic Exchange (CECE) process, a combination of electrolysis and catalytic exchange of hydrogen isotopes in a Liquid Phase Catalytic Exchange (LPCE) column. Tritium is recovered in the gas phase from tritiated water and then injected in to a cryogenic distillation system for further enrichment

Detailed investigations of separation performances individually for catalysts and packings allow improving the catalyst-packing ratio in order to obtain higher performances of the LPCE column.

2. Model to determine the catalyst height / packing height ratio at simultaneously tritium and deuterium transfer

Usually, the tritium content in the feed water of a water detritiation facility is about 1Ci/l. It was considered that eventually the water can contain also deuterium in the range 0.1-5%.

In order to characterize with good accuracy the separation performances in a catalytic exchange column it is necessary to consider all the species that can appear in such a process. At low tritium and deuterium content the homonuclear species usually have a very small value. However the concentration of DT must be investigated for the tritium and deuterium concentration range from above.

2.1 Establishing the mass transfer coefficients

With the above considerations 8 molecular species were therefore contemplated i.e. H_2O, HDO, HTO, DTO, H_2, HD, HT and DT. Since the number of atoms in this component system is four, i.e. H, D, T and O, 8-4=4 chemical reactions are necessary for a full description of such a system. The following chemical reactions describe the isotopic exchange process among all involved molecular species:

$H_2O+HD \leftrightarrow HDO+H_2$ (a)

$H_2O+HT \leftrightarrow HTO+H_2$ (b)

$H_2O+DT \leftrightarrow DTO+H_2$ (c)

$HD+HT \leftrightarrow DT+H_2$ (d)

For a column such as under test in TLK, the following reactions describe the process in each section:

I. Catalytic section

Mass transfer coefficient k_1: $\mathbf{H_2O_v+HD \Leftrightarrow HDO_v+H_2}$

Mass transfer coefficient k_2: $\mathbf{H_2O_v+HT \Leftrightarrow HTO_v+H_2}$

Mass transfer coefficient k_3: $\mathbf{H_2O_v+DT \Leftrightarrow DTO_v+H_2}$

Mass transfer coefficient k_4: $\mathbf{HD+HT \Leftrightarrow DT+H_2}$

II. Scrubbing section

Mass transfer coefficient k_5: $\mathbf{H_2O_l+HDO_v \Leftrightarrow HDO_l+H_2O_v}$

Mass transfer coefficient k_6: $\mathbf{H_2O_l+HTO_v \Leftrightarrow HTO_l+H_2O_v}$

Mass transfer coefficient k_7: $\mathbf{H_2O_l+DTO_v \Leftrightarrow DTO_l+H_2O_v}$

Input data for the calculation of mass transfer coefficients are the column diameter, the column height, the number of layers of catalyst and of package, the height of the catalyst layer, the height of the package layer, the gas flow rate, the liquid flow rate, the column temperature, and the concentrations in the gas and in the liquid phase at the inlet and outlet of the column.

The vapor flow rate can be estimated from the condensate volume when it is assumed that all vapors fully condense at the condenser.

The concentrations in the vapor phase at the bottom of the column are calculated on the basis of thermodynamic equilibrium considerations with the liquid phase.

2.2 Method to compute the optimum ratio between catalyst and packing

The procedure to establish the catalyst-packing ratio for the WDS as required by JET and ITER is presented below. The following activities are developing according to this procedure:

1. The separation performances, mass transfer coefficients and Height Equivalent of Theoretical Plate (HETP) for five types of catalyst have been determined. The performances were investigated in a Vapor Phase Catalytic Exchange (VPCE) process. Four types of catalysts were delivered by ICIT- Rm. Valcea, Romania and another one was prepared at TLK. The four types of ICSI catalysts were selected after preliminary investigations in respect to BET surface.
2. The separation performances of four types of packing were determined as well. The evaluations were made under specific working conditions for JET and ITER. Three types of packings have been delivered by SULZER and one type by ICIT Rm. Valcea.

The first measurements have been made with a tritium activity of 1 Ci/Kg and a deuterium content up to 5% D/(D+H) in the liquid streams, and up to 1 Ci/m^3 in the gaseous streams. For the most promising catalyst-packing mixture layered in the optimum ratio, the measurements will be continued at higher tritium activity.

In order to compare the ratio catalyst/packing predicted by the model necessary to obtain a specific decontamination factor along a separation column with the value of the decontamination factor experimentally determined, one experiment is on going.

In Figure 1 is presented the variation of decontamination factor versus height of catalyst bed for a specified column height and operation conditions. For this evaluation has been considered 900 Kmol/m3h the value for isotopic mass transfer coefficient and 500 Kmol/m3h respectively for distillation, and 5 cm for the lengths of packing layers.

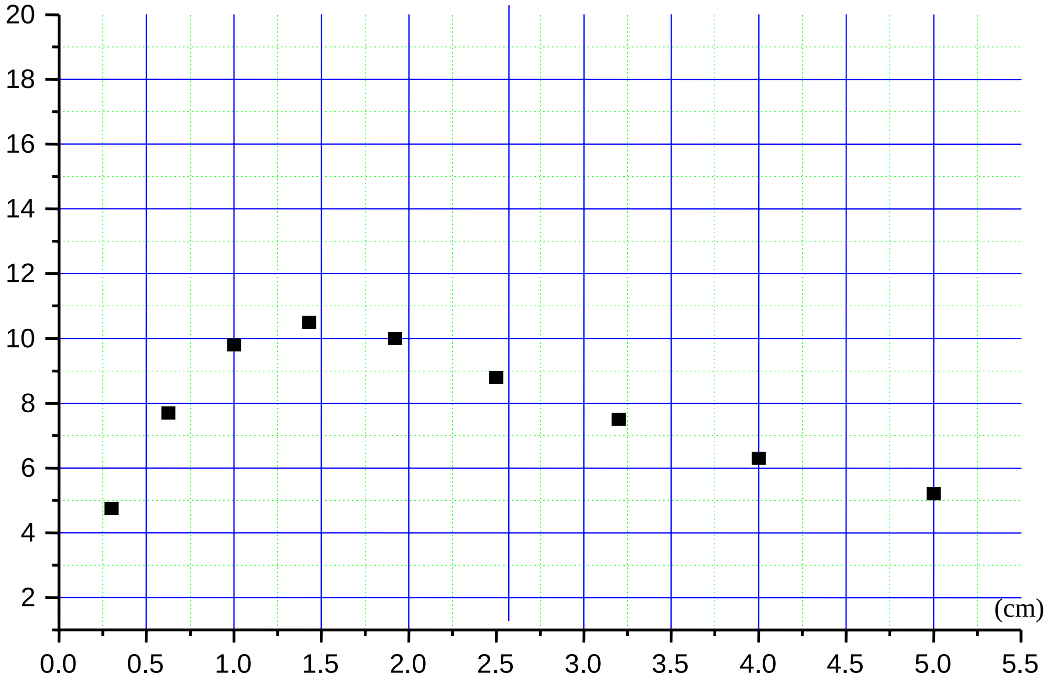

Figure 1 Decontamination factor versus height of catalyst bed

3. Preliminary tests for simultaneous tritium and deuterium transfer in a LPCE process

The separation performances, expressed as HETP and mass transfer coefficients for different catalysts on the experimental facility at TLK were determined in an isotopic exchange column of 1200 mm length and 40 mm diameter with an active catalyst-packing height of approximately 900 mm.

The isotopic exchange process takes place between the pre-heated tritiated and deuteriated water fed in at the top of the column and deuteriated hydrogen fed in at the bottom of the column. The hydrogen stream with different content of tritium and deuterium is released at the top of the column and condensed vapours are returned.

The columns have been filled with catalyst and inert packing (as layers or as mixture) according to the manufacturer specifications. The isotopic exchange column has an outer jacket, through which thermo stated water flows to maintain a constant temperature along the column. In addition, the heater for the feed water and the heater of the boiler are power controlled. The boiler ensures heating and saturation of the hydrogen with water vapour.

The evolution of the deuterium content with time in the liquid phase at the bottom of the column and in the gas phase at the top of the column is followed until steady state is reached. For the column output, on-line measurements of the gas phase were performed by a Quadrupole mass spectrometer. For comparison, samples were taken at steady state conditions for analysis with an Omegatron mass spectrometer. For the liquid phase the deuterium content in both the feed water at the top of the column and in the water from the boiler was measured in-line by FTIR spectroscopy.

For simultaneous tritium and deuterium transfer, two possible processes have been investigated in the experiments performed at TLK:

I. Tritium transfer from tritiated water to gaseous hydrogen. The LPCE column was fed at the top with tritiated water and at the bottom the LPCE column was fed with hydrogen.

II. Isotopic transfer between tritiated water and deuteriated hydrogen gas, when tritium is transferred from the liquid to gas and deuterium is transferred in the opposite direction from gas to liquid. For this case the LPCE column was fed at the top with tritiated water and deuteriated hydrogen was fed at the bottom of the column.

The separation performances of three catalyst-packing combinations from different manufacturers (SCK-CEN Belgium, Mendeleev University Russia, Institute of Cryogenics and Isotopic Technologies (ICIT) Romania-TLK) have been investigated for the following experimental conditions: the temperature of the LPCE column was 70^0C, gas flow rates equivalent to linear velocities of 0.1 m/s and 2 was the molar gas to liquid flow rate ratio.

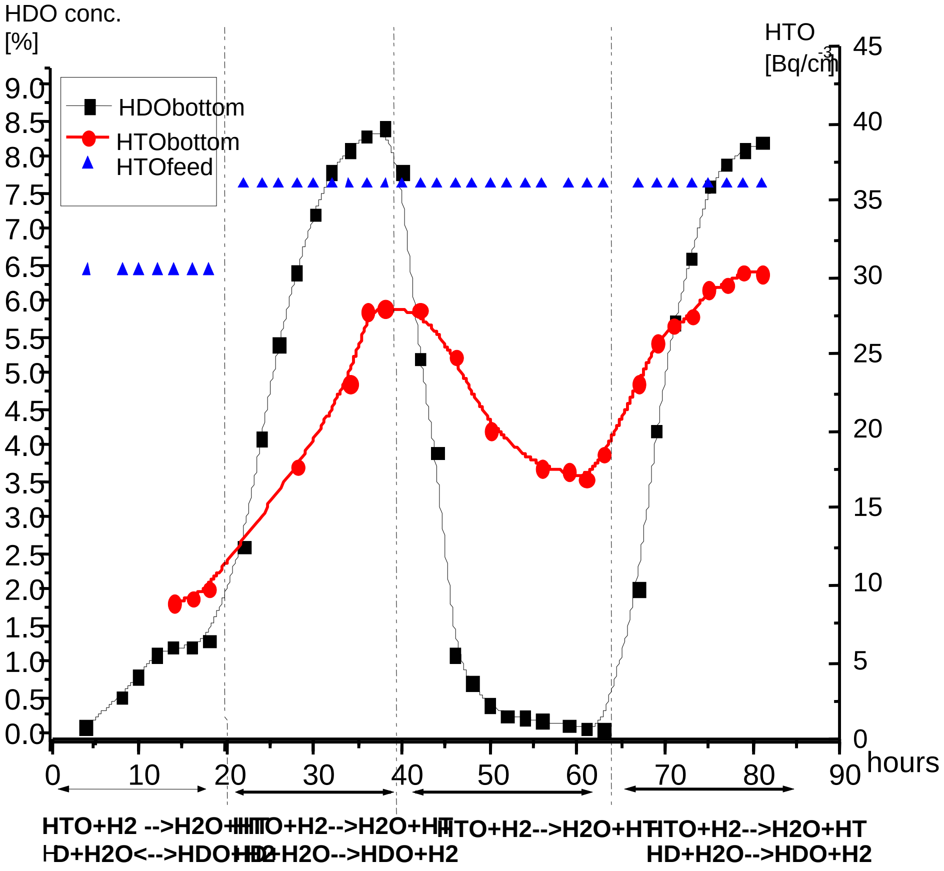

Figure 2. Time evolution of deuterium and tritium concentration in liquid phase at the bottom of the column

In Figure 2 the typical evolution for the catalysts under tests with respect the HDO concentration and tritium activity at the bottom of the LPCE column is presented. For case I the tritium activity in the feeding water was in the range 30 to 36 Bq/ml and for case II the deuterium content in the feeding hydrogen was approximately 4 % D/(D+H).

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