

## DEVELOPMENT AND IMPROVEMENT OF DEVICES FOR HYDROGEN GENERATION AND OXIDATION IN WATER DETRITIATION FACILITY BASED ON CECE TECHNOLOGY

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*Water detritiation facility based on CECE (Combined Electrolysis and Catalytic Exchange) technology needs an electrolyser for water conversion to hydrogen. Use of a conventional alkali electrolyser requires a very deep purification of hydrogen stream from alkali prior to injection to LPCE (Liquid Phase Catalytic Exchange) column. In some applications conversion of detritiated hydrogen back into water is required. This is usually performed via hydrogen catalytic oxidation in a recombiner. This paper presents results of study to improve hydrogen and oxygen purification for alkali electrolysers and develop a hydrogen recombiner based on use of hydrophobic catalyst.*

### I. INTRODUCTION

CECE technology has been acknowledged [1-5] as very attractive for tritium extraction from water and hydrogen flows. Two devices are necessary or often needed for the CECE facilities: an electrolyser for conversion of tritiated water to gaseous hydrogen and a device for conversion of detritiated hydrogen back to water.

Hydrogen conversion to water is based either on direct combustion with oxygen [2,3] or on catalytic oxidation [5,6]. The main requirement for such device is safe and stable operation for long period of continuous functioning. The catalytic oxidation is safer because no high temperature flame is involved and therefore is the preferable option. Therefore development and study of recombiner based on use of the hydrophobic (styrene copolymer divinylbenzene type) Pt catalyst is one of the subjects presented in this paper.

CECE facilities usually employ alkali electrolysers for water detritiation [3-5]. The hydrogen and oxygen streams generated in industrial alkali electrolyser contain alkali at the level of tens micrograms per 1m<sup>3</sup> of gas even after purification in the electrolyser's purification system.

Feeding hydrogen which contains noticeable concentration of alkali into LPCE column may lead to poisoning the hydrophobic catalyst and deterioration in the LPCE column performance. If hydrogen generated in the electrolyser shall be fed to isotope separation system, such as cryogenic hydrogen distillation, it has to be purified to very high purity standard. It is usually undertaken using a palladium permeator. Alkali present in the hydrogen can quickly poison or even destroy the palladium membrane in the permeator. Improvement of hydrogen and stream purification from alkali for alkali electrolyser is the second subject presented in this paper.

### II. RESULTS

#### II.A. Development and study of recombiner

##### II.A.I. Experimental Facility

Schematic diagram of the experimental facility for testing of a catalytic hydrogen recombiner is shown in the Fig. 1.

Recombiner 1 was made of stainless steel cylinder of 62mm inner diameter and 60cm height. It was equipped with three hydrogen inlet pipes located with the same distance between each other. Recombiner was fed with hydrogen generated in the electrolyzer 2. Water produced in hydrogen oxidation process down through the hydraulic hitch 3 into the tank 4. The water from tank 4 was pumped by pump 5 to the recombiner through the heat exchanger 6 controlling its temperature. Pipe 7 was for release of residual gas. Stoichiometric amount of oxygen to be injected to the recombiner was supplied by the same electrolyzer 2. Extra amount of oxygen was supplied from the external source.

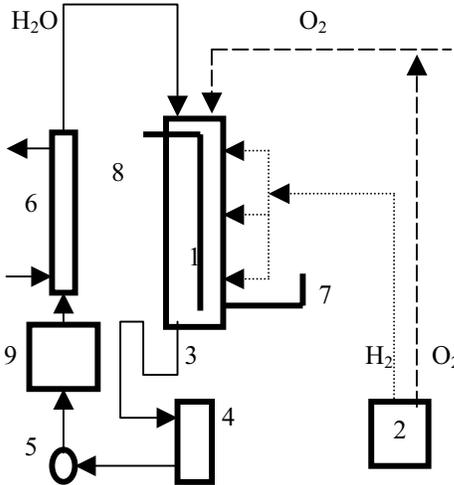


Fig. 1. Schematic diagram of the experimental facility for testing of catalytic hydrogen recombiner.

The pocket 8 for thermocouple was used for measuring the temperature along the recombiner. The feed-water was heated in thermostat 9 or cooled in the heat exchanger 6 when necessary.

The recombiner was filled with a mixture of hydrophobic platinum catalyst [7] and mini-spiral random packing of dimensions 2mm×2mm×0.2 mm made of stainless steel. Extent of hydrogen oxidation was monitored via measuring residual hydrogen concentration in the flow at the recombiner outlet. Detection limit for the gas analyzer was 2 vppm.

II.A.II. Results of Testing

Two series of tests were carried out. The first one was carried out with excess of oxygen 20% or larger than required for the stoichiometric reaction. Hydrogen was fed to the recombiner through one inlet pipe only. The results of the tests are shown in the Table 1.

During all these tests the operation of the recombiner was stable. The observed length of reaction temperature zone did not exceed 1.5cm.

The second series was carried out with stoichiometric ratio of oxygen to hydrogen flows. Results of the tests are shown in the Table 2.

The following was observed in the second series:

a) reaction zone in the recombiner working with stoichiometric ratio of hydrogen to oxygen is much wider than for the recombiner operated with excess of oxygen. The measurements show that temperature of the packing was approximately constant along the whole

TABLE I. Results of the tests with oxygen flow above stoichiometric ratio

Time, min.	0	60	120	150	160	180-240
O <sub>2</sub> flow rate, L/h	150	180	210	220	270	310
H <sub>2</sub> flow rate, L/h	180	240	300	325	410	500
T <sub>water</sub> at the inlet, °C	53	52	60	55	55	56
T <sub>water</sub> at the outlet, °C	65	74	77	75	78	79
T in the reaction zone, °C	81	82	82	83	83	84

TABLE II. Results of the tests with stoichiometric amount of oxygen

Time, min.	0	30	50	70	90	100-150
O <sub>2</sub> flow rate, L/h	95	120	120	180	250	250
H <sub>2</sub> flow rate, L/h	190	240	240	360	500	500
T <sub>water</sub> at the inlet, °C	53	55	40	42	48	30
T <sub>water</sub> at the outlet, °C	62	66	58	68	78	63
T in the reaction zone, °C *	61	64	57	67	76	59

\*- temperature along the full length of the thermocouple pocket (position 8 in the Figure 1),

length of the packed bed and is slightly smaller than a temperature of water leaving the recombiner. This was different from results observed in tests with overstoichiometric oxygen flow;

b) during the recombiner operation pressure in the recombiner fell periodically to 5mb-7mb below atmospheric pressure as was seen on water hydraulic hitch of the exhaust pipe 7 . Because the pipe 7 was open for atmosphere for most operating time, the ambient air can enter the recombiner at that times;

c) even at the stoichiometric ratio between hydrogen and oxygen flows, the recombiner operation was stable and controllable,

d) no hydrogen was detected at the recombiner outlet. The same was for tests with oxygen flow being larger than stoichiometric ratio.

The experience gained during the recombiner testing shows that a recombiner of the described construction is efficient for complete hydrogen oxidation. Moreover, it has large resource for increase of throughput. Maximum flow of hydrogen fed into the recombiner was 0.5m<sup>3</sup>/h and was through one inlet pipe only. At this hydrogen flow and with oxygen flow in excess of stoichiometric ratio a length of the reaction zone did not exceed 1.5cm. This means that the recombiner would process 1.5m<sup>3</sup>/h of hydrogen if all three inlet pipes will be engaged for hydrogen feeding.

**II.B. Purification of Electrolytic Hydrogen from Alkali**

*II.B.I. Experimental Procedure*

Our preliminary tests showed that a simple hydrogen bubbling through water leads to purification of electrolytic hydrogen at least from droplet aerosol of alkali. For detailed investigation of the purification process the test facility, which principal scheme is shown in the Fig. 2, was used.

The test facility includes alkali electrolyzer (1), counter-current gas purification column (2), water collector (3), water flow meter (4), pressure tank (5) filled with water and connected with the purification column (2) via gas line, pressure regulator (6), and fine filters (7) and (8). The electrolyser electrolyte contained 25w% of KOH. Two purification columns, one of 20mm inner diameter with packed bed of 23cm height and second of 28mm inner diameter with packed bed of 98cm height, were tested. Both columns were made of stainless steel. The diameter of fibers, which the filter material was manufactured from, was 1.5 μm [8]. The filter material provides high holding capacity for aerosol particles of size larger than 0.2μm.

The method for measuring concentration of alkali in hydrogen outgoing from the column 2 was based on collection of alkali aerosol particles on filters 7 and 8. The filter used in the experiment was then washed in 10cm<sup>3</sup> of water at a temperature of approx. 95°C to dissolve the alkali. The potassium concentration in resulting solution was measured by ionometric method using K<sup>+</sup>-selective electrode. The preliminary tests showed that alkali concentration in the water used for the second washing of the filter material was below the detection limit of the ion-selective electrode, which was about 5.6μg. Thus, concentration of alkali aerosol which could be measured according to this technique depends on the amount of gas passed through the filter. For example, if the volume of gas passed through the filter was 10 Nm<sup>3</sup> then alkali concentration in the gas 0.56 μg/Nm<sup>3</sup> or larger can be detected.

*II.B.II. Results*

Results of the experiments for study of hydrogen purification efficiency in a counter-current column fed with pure water are shown in the Table 3. In all the tests stainless steel packing was pretreated to increase its wetting towards water.

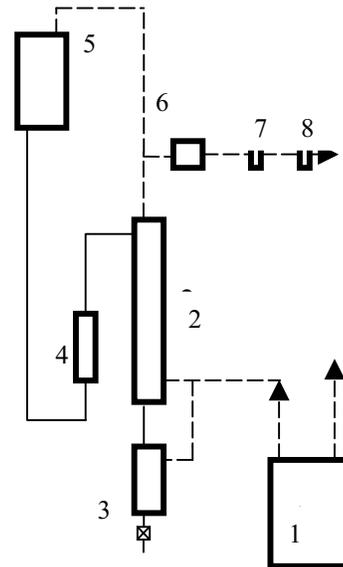


Fig.2. Principal scheme of the facility to study purification of hydrogen from alkali

The following conclusions can be made from review of the data in Table 3:

- a) Purification of hydrogen in column operated in a film mode demonstrated a small purification factor (DF).
- b) Column operated in flooded mode shows purification factor larger than that for column in film mode. Purification factor is nearly independent of hydrogen flow rate but rises with increase of height of flooded bed.
- c) Use of millipore ceramic gas distributor, which allowed formation of small hydrogen bubbles, led to increase in purification efficiency.
- d) Value of concentration in gas at the column outlet ( $C_{exit}$ ) achieved in the column equipped with the gas distributor was nearly independent of height of flooded bed. For example, the same KOH concentration was observed at the outlet of packed bed after decreasing height of flooded bed by a factor of 4.5.

From our point of view KOH concentration of  $\approx 6 \mu\text{g}/\text{Nm}^3$  in hydrogen is the lowest content of KOH aerosol which can be achieved by cleaning electrolytic hydrogen in a flooded counter-current column at a temperature of 293K-296K. Further purification might be possible only with use of final fine filter.

Special test was carried out to determine concentration of alkali in hydrogen purified in a counter-current column followed by the final fine filter. The flooded mode of column operation with using of gas distributor was employed for this test. In this test  $14 \text{Nm}^3$  of hydrogen was purged through the purification system shown in the Figure 2. The amount of alkali collected on the second fine filter (position 8 in the Figure 2) was analysed but found below the detection limit. This means that concentration of alkali aerosol in hydrogen at the first filter outlet was smaller than  $0.4 \mu\text{g}/\text{Nm}^3$ . This value is lower than any residual KOH concentration in hydrogen reported for commercial alkali electrolyzers (e.g. made by Norsk Hydro Electrolyzers and Vandenberg Hydrogen Systems).

TABLE III. Experimental results on purification of hydrogen in a counter-current column (column was operated at temperature 293K to 296K and atmospheric pressure)

$G_{\text{H}_2}$ , $\text{Nm}^3/\text{h}$	$U^*$ , $\text{m/s}$	$L_{\text{H}_2\text{O}}$ , $\text{g/h}$	H, $\text{m}$	$C_{\text{entr}}$ , KOH $\mu\text{g}/\text{Nm}^3$	$C_{\text{exit}}$ , KOH $\mu\text{g}/\text{Nm}^3$	DF= $C_{\text{entr}}/$ $C_{\text{exit}}$
Column operated in film mode						
0.22	0.20	120	0.23	320	200	1.6
Column operated in flooded mode						
0.22	0.20	120	0.23	330	110	3.0
0.38	0.34	200	0.23	120	42	2.9
0.22	0.10	120	0.98	280	25	11.2
Column operated in flooded mode and equipped with gas distributor						
0.22	0.10	120	0.98	315	6.3	50
0.38	0.17	200	0.98	100	6.4	15.6
0.38	0.17	200	0.22 **	90	6.8	13.3

\*- linear velocity of gas in the column, \*\*- overall height of packing bed in the column was 0.98 m, but height of flooded bed was 0.22 m

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