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EXPERIMENTAL STUDY OF THE TRITIUM DISTRIBUTION IN THE EFFLUENTS RESULTING FROM THE SODIUM HYDROLYSIS

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Within the framework of the dismantling of fast breeder reactors in France (PHENIX, SUPERPHENIX, RAPSODIE), several processes are under investigation regarding sodium disposal. One of them, called ELA (radioactive sodium waste treatment process), is based on the implementation of the sodium-water reaction, in a controlled and progressive way, to remove residual sodium mainly from the sodium purification systems called cold traps. This sodium contains impurities such as sodium hydride, sodium oxide and tritiated sodium hydride. The hydrolysis of these various chemical species leads to the production of a liquid effluent, mainly composed of an aqueous solution of sodium hydroxide, and a gaseous effluent, mainly composed of nitrogen (inert gas), hydrogen and steam. The tritium is distributed between these effluents, and, within the gaseous effluent, according to its forms HT and HTO. HTO being 10,000 times more radiotoxic than HT, a precise knowledge of the mechanisms governing the phase distribution of tritium is necessary. Indeed, it will help to design the process needed to optimize the treatment of the off-gas before its release into the environment.

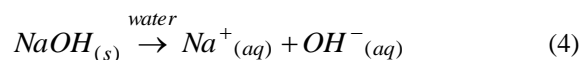
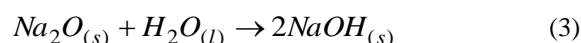
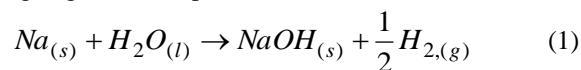
This paper presents the first experimental results from a parametric study on the tritium distribution between the various effluents generated during hydrolysis operations. This parametric study has been performed in a laboratory scale hydrolysis process designed at the CEA Cadarache.

I. INTRODUCTION

Liquid sodium, used as a coolant fluid in Sodium Fast Breeder Reactors (SFBR), can contain several impurities such as oxygen or hydrogen, present from the start or introduced during certain servicing or handling operations on components or fuel assemblies. Another contaminant that can be found in the sodium is the tritium, a radioactive hydrogen isotope, mainly produced by fission reactions. In order to operate in safe conditions, the sodium is purified in devices called cold traps, in

which the crystallization of the sodium oxide (Na₂O), sodium hydride (NaH) and co-crystallization of tritiated sodium hydride (NaT) is induced by cooling. The crystals thus formed are trapped on a woven steel wool support. When these devices need to be dismantled, the residual sodium and impurities must be removed.

Various methods have been proposed or developed in the past to remove residual sodium from cold traps.¹ One of them rests on the implementation of the sodium-water reaction (SWR) to remove films or clusters of residual sodium. As described in previous paper (Ref. 2), this reaction is almost instantaneous, highly exothermic^a and is characterized by the generation of large volumes of hydrogen gas and the production of soda.



In order to use these reactions in a controlled and progressive way, a process called ELA (Enceinte de Lavage en Actif), is under development mainly for the cleaning of cold traps from the prototype fast breeder reactor PHENIX. This process is continuously controlled by limiting the water flow rate in the vessel to avoid over pressure, hydrogen and temperature excursions.

In order to design the process, a precise knowledge of the composition of the effluents is needed. Indeed, the

^a The heat generated by a mole of sodium is, respectively for each reaction, $\Delta_r H^0_1 = -141 \text{ kJ}\cdot\text{mol}^{-1}_{\text{Na}}$, $\Delta_r H^0_2 = -82 \text{ kJ}\cdot\text{mol}^{-1}_{\text{Na}}$, $\Delta_r H^0_3 = -76 \text{ kJ}\cdot\text{mol}^{-1}_{\text{Na}}$ and $\Delta_r H^0_4 = -45 \text{ kJ}\cdot\text{mol}^{-1}_{\text{Na}}$. $\Delta_r H^0_4$ is the heat of solution of NaOH at infinite dilution.

tritium distribution between the gaseous and liquid effluents, and within the gaseous effluent, according to its chemical form HT(g) or HTO(g), is critical for designing the elements needed to treat the off-gas before its release into the environment.

The sodium wastes expected to be hydrolyzed in ELA should contain a large majority of tritium as tritiated sodium hydride NaT. By analogy with the reaction (2), the chemical phenomena involved in the hydrolysis of NaT should lead to the production of gaseous tritium in its HT(g) form only. However, HTO(g) has been identified in the gaseous effluent produced by hydrolysis operations performed at the CEA Cadarache, and sometimes in an important amount (up to 90 % of the tritiated gaseous products).

In the phenomenological model developed in this study, any conversion of HT(g) into HTO(g), by oxidation or by isotopic exchange reaction, has been dismissed². It is assumed that HTO is produced by the chemical reactions in liquid state and that part of this HTO(l) changes into HTO(g) either by evaporation or by vaporization. A more precise description of the phenomena involved is provided in Ref. 2.

In order to validate some of the hypotheses proposed in this scenario, a laboratory scale process has been designed at the CEA Cadarache. Experimental results of a parametric study on the tritium distribution in the effluents are presented and discussed in this paper. This study is carried out in order to provide a numerical model of the phenomena involved in such an operation to predict the composition of the effluents produced, especially regarding tritium contamination.

II. LABORATORY SCALE HYDROLYSIS PROCESS

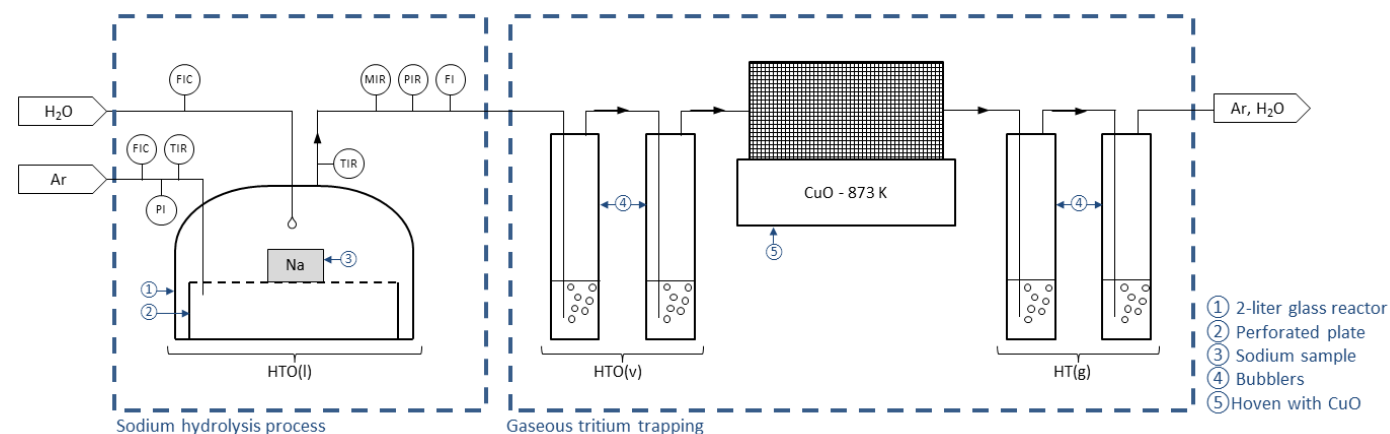


Fig. 1. Laboratory scale hydrolysis process.

Due to technical limitations, specific activities of the samples and experimental conditions are not representatives of ELA. Another difference between the experimental device used for this study and ELA rests on the means used to perform the hydrolysis operations. Water is not spread under the sodium but above it, drop by drop. Nevertheless, the results of this parametric study should validate some of the hypotheses proposed to explain the tritium distribution.

The different parts of the process are described in the following paragraphs and presented in Fig. 1.

II.A. Hydrolysis Reactor

The main part of the experimental device is a 2-liter glass reactor into which small amounts of sodium (up to 15 g) are hydrolyzed. The sodium is maintained on a perforated metallic plate that allows the liquid effluent produced to flow toward the bottom of the reactor for future collection. In order to dilute the hydrogen produced, the vessel is swept by a flow rate of Argon. Water is added drop-by-drop over the sodium by means of a syringe pump. Flowmeters, pressure sensors, thermocouples and a moisture sensor are used to perform mass and energy balances.

II.B. Gaseous Tritium Trapping System

At the outlet of the reactor, tritiated water vapor HTO(g) is trapped into a first series of bubblers. The remaining gaseous tritium, in its HT(g) form, is then converted into HTO(g) by an oxidation reaction with CuO at a temperature of 873 K, before being trapped into a second series of bubblers. For each experiment, tritium collected in the liquid effluents in the reactor and in the bubblers is quantified by liquid scintillation counting.

III. PARAMETRIC STUDY ON THE TRITIUM DISTRIBUTION IN THE EFFLUENTS

III.A. Description of the Experiments

A series of experiments have been performed in order to study the influence of water flow rate, argon flow rate, initial mass and specific activity of the sample.

The sodium hydrolyzed in this study is from the secondary loop of the reactor PHENIX. Small cylindrical

samples with an initial mass of approximately 5 or 10 g are used.

Argon flow rate is varying from 1.00 to 4.50 l·min⁻¹ and water flow rate from 5.0 to 17.5 ml·h⁻¹.

III.B. Results and Discussion

Experimental results are gathered in Table I. Argon flow rates, water flow rates, initial mass of the samples, total specific activities and tritium distributions are presented for a series of thirteen experiments.

TABLE I. Results of the Parametric Study on the Tritium Distribution in the Effluents Resulting from a Sodium Hydrolysis

Q_{Ar} (l·min ⁻¹)	Q_{H_2O} (ml·h ⁻¹)	m_{sample} (g)	$S_{A, tot}$ (Bq·g ⁻¹)	$S_{A, HTO(l)}$ (Bq·g ⁻¹)	$S_{A, HTO(g)}$ (Bq·g ⁻¹)	$S_{A, HT(g)}$ (Bq·g ⁻¹)
1.00	5.0	6.3	17.6	10.2 [58 %]	1.5 [9 %]	5.9 [33 %]
2.25	5.0	3.8	37.2	25.2 [68 %]	4.7 [13 %]	7.4 [19 %]
3.00	5.0	4.2	15.6	10.2 [65 %]	2.1 [13 %]	3.3 [22 %]
3.75	5.0	3.5	38.6	28.0 [73 %]	3.4 [9 %]	7.2 [18 %]
4.50	5.0	5.4	27.2	18.0 [66 %]	2.8 [10 %]	6.5 [24 %]
4.50	7.5	4.0	32.6	23.3 [71 %]	2.6 [8 %]	6.6 [21 %]
4.50	10.0	6.3	26.8	16.8 [63 %]	2.9 [11 %]	7.1 [26 %]
4.50	12.5	5.7	27.5	13.4 [49 %]	2.6 [9 %]	11.5 [42 %]
4.50	15.0	5.7	28.3	16.6 [59 %]	6.0 [21 %]	5.7 [20 %]
4.50	17.5	5.7	16.3	9.3 [57 %]	2.9 [18 %]	4.1 [25 %]
3.00	10.0	5.8	59.0	37.6 [64 %]	7.6 [13 %]	13.8 [23 %]
3.00	10.0	10.9	68.5	43.8 [64 %]	6.9 [10 %]	17.8 [26 %]
3.00	10.0	10.6	104.1	65.1 [63 %]	10.3 [10 %]	28.7 [27 %]
N/A	N/A	6.4	134.9	74.1 [55 %]	12.3 [9 %]	48.5 [36 %]

III.B.1. Influence of the Total Specific Activity on the Tritium Distribution

An influence of the total activity on the tritium distribution, according to its chemical form (HT or HTO), seems to be observed in the Fig. 2a and is confirmed in the Fig. 2b, where experimental results of the tritium distribution gathered from former experiments also performed at the CEA have been added to the study. The concentration of HTO seems to rise until the achievement of a limit for high total activities, whereas the concentration of HT continues to rise.

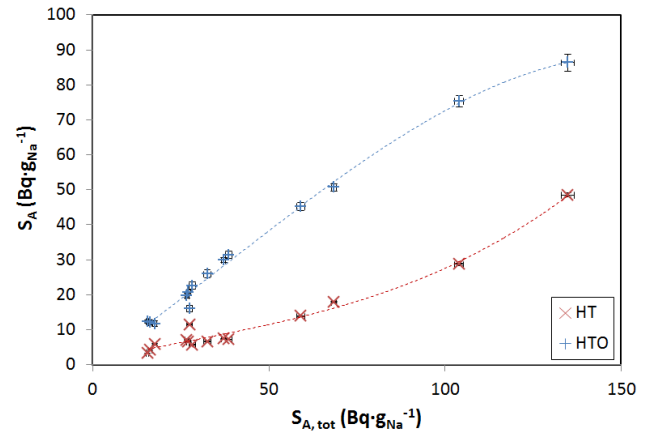


Fig. 2a. Influence of the total specific activity on the tritium distribution.

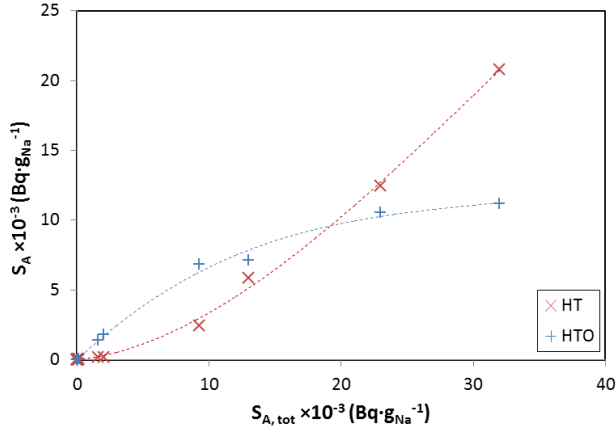


Fig. 2b. Influence of the total specific activity on the tritium distribution (extended with additional experimental results).

III.B.2 Influence of the Water and Argon Flow Rates on the Distribution of HTO between the Effluents

According to the experimental results plotted on Fig. 3, water flow rate seems to have an influence on the distribution of HTO. As expected in the phenomenological study, the higher the water flow rate is, the higher the overall hydrolysis reaction rate should be which leads to a higher quantity of energy released to vaporize the tritiated water.

In the studied range of parameters, argon flow rate, related to the evaporation of HTO, seems to have no influence on the phase change of tritiated water according to the results plotted on Fig. 4.

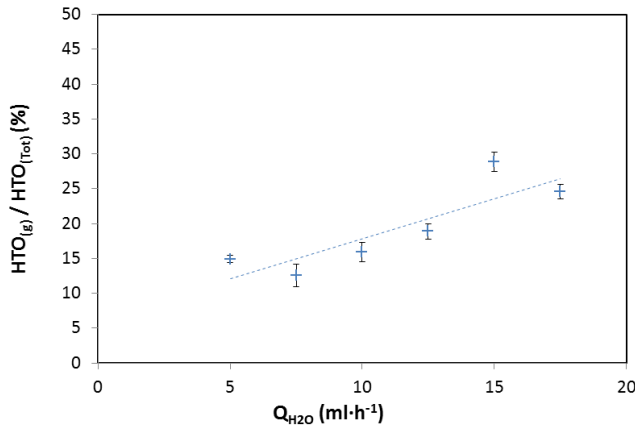


Fig. 3. Influence of the water flow rate on the distribution of HTO.

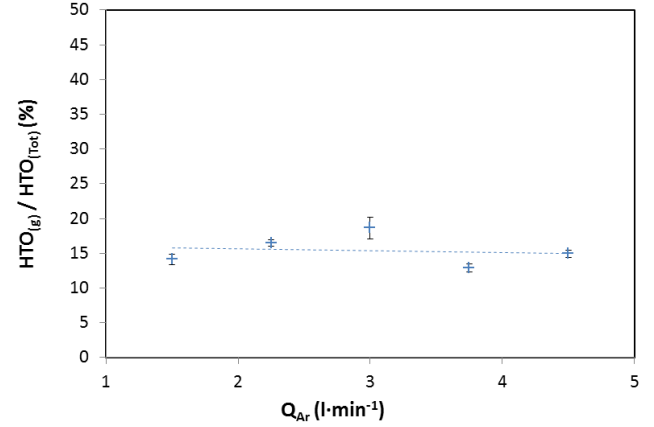


Fig. 4. Influence of the argon flow rate on the distribution of HTO.

IV. CONCLUSIONS AND PERSPECTIVES

The first experimental results of a parametric study on the tritium distribution between the effluents resulting from a sodium hydrolysis have been gathered in this paper. This experimental study was carried out at the CEA Cadarache. An important influence of the total tritium concentration in the sample hydrolyzed has been highlighted. As for the phenomena suspected to be responsible for the phase change of tritiated water, in the studied range of parameters, vaporization induced by the heat of reactions seems to be dominant over the evaporation induced by the inert gas flow rate.

To complete this primary experimental study, other experiments will be performed with samples with higher specific activities. Additional tests to study more precisely the influence of the inert gas flow rate are also planned.

These experimental results will be used to validate a numerical model for the tritium distribution currently under development at the CEA.

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