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BALANCE AND BEHAVIOR OF GASEOUS RADIONUCLIDES RELEASED
DURING INITIAL PWR FUEL REPROCESSING OPERATIONS*

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Abstract

Five fuel pins, taken from a PWR fuel assembly with 32 000 MWD/t burn-up were chopped and dissolved in leak-proof equipment designed for accurate determination of the composition and quantity of gaseous elements released in these operations.

Analytical methods were specially developed to determine directly the noble gases, tritium and gaseous carbon compounds in the gas phase. Volatile iodine was kept as close as possible to the source by cold traps, then transferred to a caustic solution for quantitative analysis.

The quantities and activities of gaseous fission products thus determined were compared with predicted values obtained through computation. Very good agreement was generally observed.

I. Introduction

For a number of years the Commissariat à l'Energie Atomique has devoted a significant part of its R & D activities to the development of gaseous radioactive waste containment and trapping methods / 1 /, with a view to achieve minimal release and in any case, compliance with prevailing regulations.

The design of safe, efficient processes for dissolver off-gas purification in fuel reprocessing plants requires the accurate determination of the quantities of gaseous fission products involved, and their physical and chemical properties. It is important to establish the release process of such products during mechanical and chemical processing, as well as their distribution among the various liquid and gaseous flows.

The information is of special importance because it directly affects the design of equipment and ventilation systems.

It is also important to compare measured quantities and activities with computed data, in order to validate or adjust some of the basic input data used in computations.

For accurate analysis, it is essential to use whole fuel rods with clearly defined characteristics. Hence, the five rods treated were taken from a spent fuel assembly from the Dutch Borssele reactor, which was selected for the following reasons :

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- . the Borssele reactor is a typical pressurized water power reactor
- . the assembly had undergone three irradiation cycles ; burnup was approximately 32 000 MWD/t.
- . initial fuel enrichment was 3.1 %.

Assembly characteristics are therefore very close to those on which reprocessing and safety investigations are based. The results of this work can thus be transposed easily.

II. Gas sampling techniques

The experimental system designed for these investigations essentially consists of a leaktight chopper and dissolver connected to a sampling glove box.

However, since PWR fuel rod length exceeded shear capacity, the rods were first cut in two following recovery of internal gas.

Chopping (Figure 1)

Each half-rod was chopped into 15 mm lengths which were collected in a container used subsequently for dissolving.

After chopping, the released gas was pumped by a cryogenic system into a tubular trap cooled by liquid helium. Three flushing cycles eliminated the last traces of fission gases.

The trap was isolated, heated to 200°C to homogenize its contents, and a gas sample taken for analysis. Since the trap volume was accurately known, the amount of gas was calculated from accurate pressure and temperature readings.

Two - 50°C cold traps were placed between the chopper and the cryogenic pump to retain any iodine present.

Dissolution (Figure 2)

After chopping, the dissolver was connected to a reflux condenser. The gases released during dissolution passed through a - 50°C iodine trap, and to the sampling glove box, where they were homogenized and continuously recycled to the dissolver.

Dissolution occurred without recombination of nitrogen oxides, and only the dioxide was partly crystallized in the cold traps. To prevent any gas leakage, the system pressure was kept slightly below atmospheric by draining excess gas to a collection vessel under vacuum.

On termination of dissolution and gas release the collection vessel was isolated. Boiling is maintained for four hours for maximum iodine desorption from the dissolver liquor. Recycled nitrogen oxide was bubbled through the solution to prevent oxidation of iodine by nitric acid, with the formation of non-volatile compounds.

The quantity of gas released during dissolution was determined on the basis of :

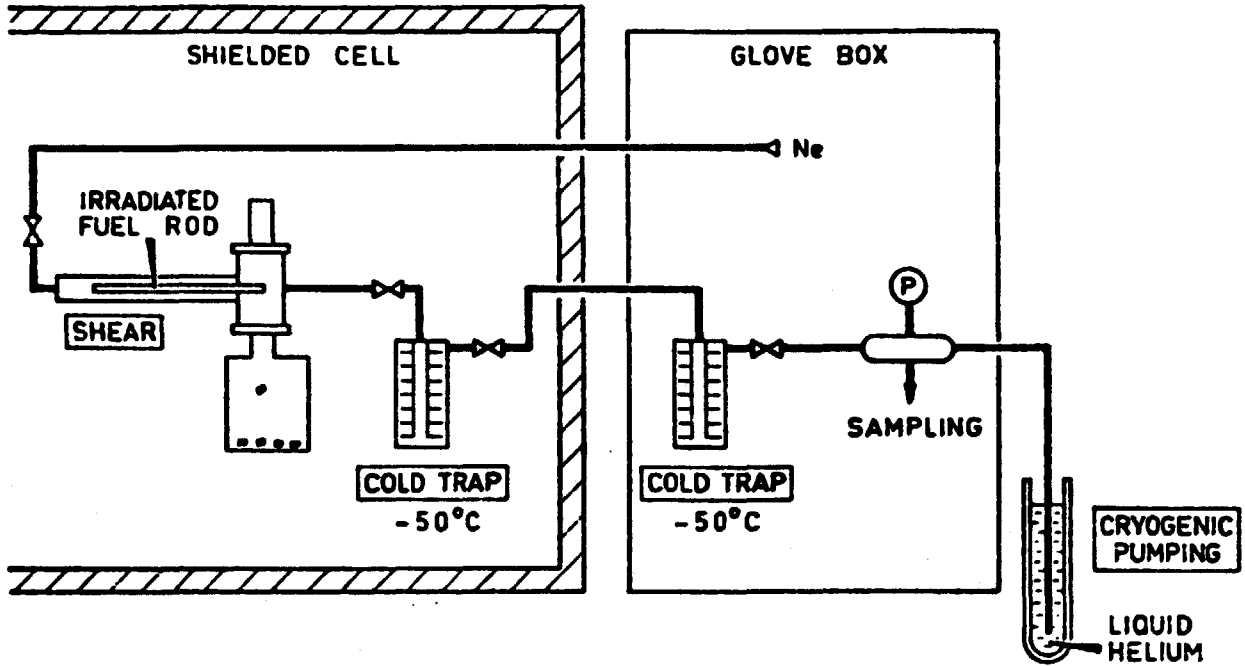


FIG. 1.- SHEARING

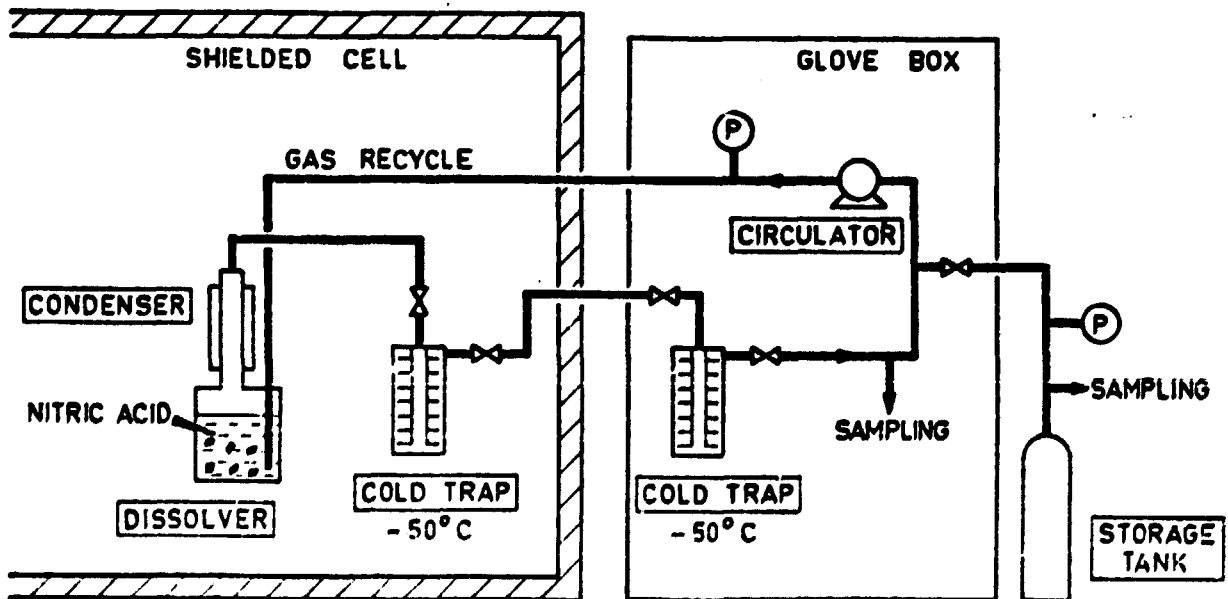


FIG. 2.- DISSOLUTION

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- . analysis of gas in the collection vessel
- . analysis of gas remaining in the dissolver system.

In this respect, the presence of a boiling liquid phase and the fact that system temperatures were not accurately known prevented accurate determination of the real gas volume. To overcome this difficulty, an accurately known quantity of carbon-13 and natural isotopes of krypton and xenon was introduced into the dissolver system. The quantities of carbon-14 and noble gases released from the fuel were then readily computed by isotopic analysis.

Finally, the two cold traps were isolated and gradually heated. Nitrogen flushing entrained the iodine to a caustic solution in two absorbers placed in series. A third absorber, filled with methanol, was provided to trap any methyl iodide present.

III. Gas analysis methods

Much work has been devoted to the development of highly sophisticated gas sample analysis methods.

The gas concentration and specific activity of tritium and carbon-14 were measured in a single chromatographic analysis, although the activity of Krypton 85 was higher by a factor of 10^4 to 10^6 (figure 3).

A HP 5880 chromatograph featuring a liquid nitrogen cryogenic system was used. Stable gases were detected by a catharometer and active gases by a Panax type, low background noise circulation counter.

A porapak-Q column was used to separate H_2 , N_2 , Ar, CO and NO at a constant temperature of $-65^\circ C$, and then Kr, CO_2 , N_2O and Xe at programmed temperatures up to $60^\circ C$.

Tritium and ^{14}CO measurements were easy because these gases are eluted before Krypton 85. As for $^{14}CO_2$, thorough krypton decontamination was necessary.

As soon as CO_2 elution began, the gas flow was diverted to a Porapak - N column for good separation of residual krypton 85 and $^{14}CO_2$ which was then easily measured.

During CO_2 analysis, N_2O and Xe were retained in the Porapak - Q configuration. The column was reconnected to the system on completion of CO_2 elution.

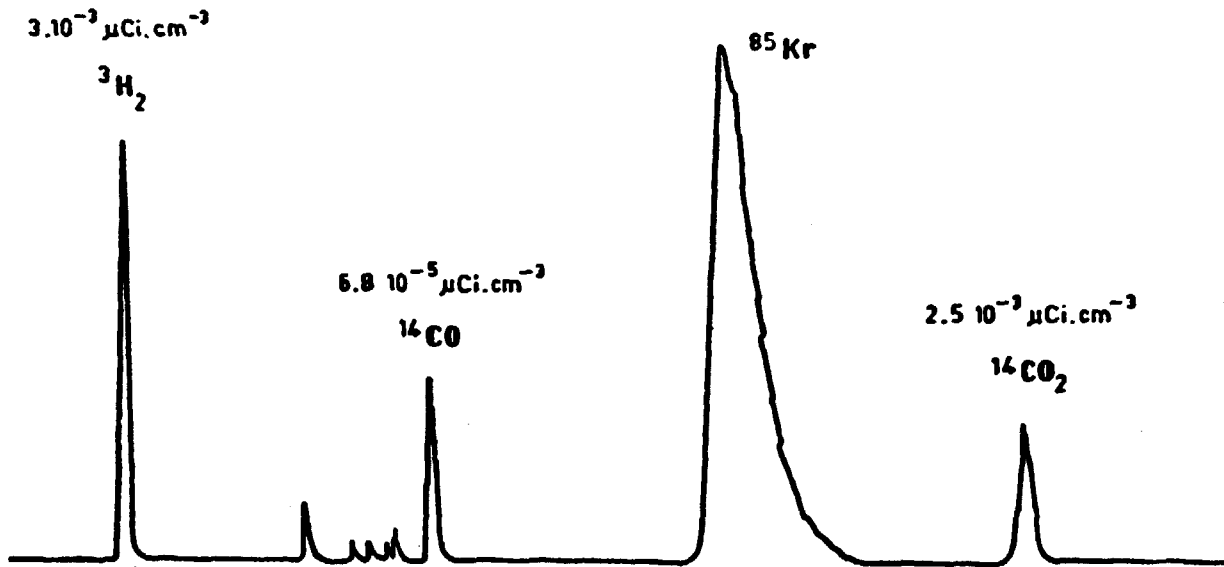
Krypton 85 activity was measured directly by gamma spectrometry, using a Ge-Li detector.

Chromatography was also used for hydrocarbon detection with a flame ionization detector, and also for methyl iodide detection with an electron-capture detector.

The isotopic composition of noble gases was measured by mass spectrometry, a method also frequently used for quantitative analysis of krypton and xenon by isotopic dilution, using a mixture of ^{80}Kr and ^{124}Xe as a tracer.

Complete analysis involved the following steps :

PROPORTIONAL COUNTER



CATHAROMETER

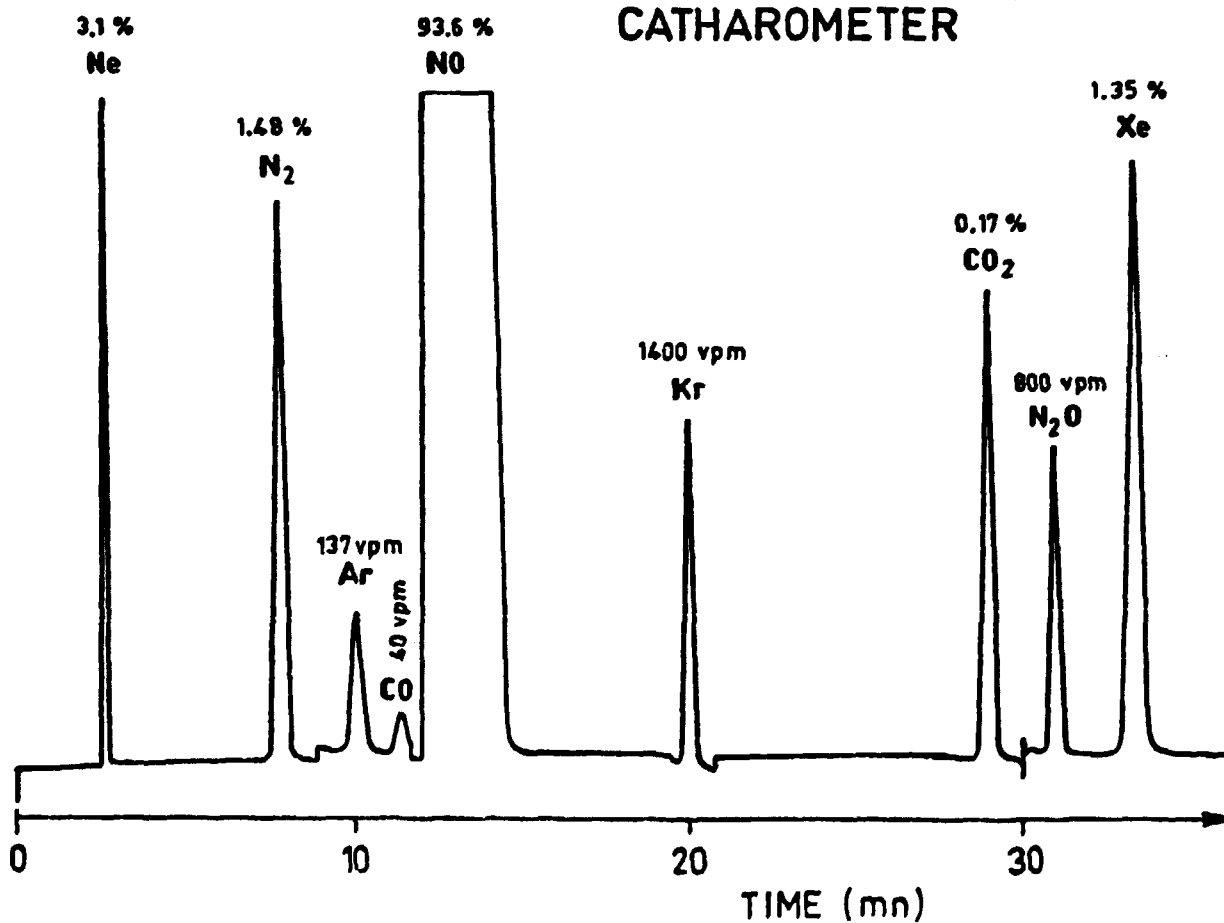


Figure 3 : Typical chromatogram

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- . preparation and analysis of tracer mixture by reverse dilution, using a mixture of natural krypton and xenon.
- . isotopic measurement of the test gas
- . isotopic measurement of the test gas/tracer mixture

Although the procedure may seem complex, the number of manipulations is reduced by using a single tracer mixture. The quantities of krypton and xenon can be readily calculated from measured values of $^{80}\text{Kr}/^{86}\text{Kr}$ and $^{124}\text{Xe}/^{136}\text{Xe}$ isotopic ratios.

This method only requires a few ml of gas, which is an overwhelming advantage in active gas analysis. Mixtures are prepared by a purely barometric method, and all transfers performed using liquid helium. Utilization of a highly accurate pressure sensor (0.1 m bar) yields results with less than 1 % error in a concentration range of a few hundred vpm.

IV. Behavior of gaseous fission products

All the results are given for 1 - year cooling time.

Noble gases

The quantities of gas collected at the various stages of fuel pin processing are given in table I. Krypton and xenon released during chopping respectively account for 4.4. % and 3.8 % of the total quantity collected. A fraction of the gas was measured during the first cut of the clad, and corresponded to the fraction of noble gases present in the gas plenum ; the balance, i.e., 1 % to 2 % of the total, was released during chopping. This operation is relatively ineffective in opening the micropores in which gas remains trapped.

PIN		1	2	3	4	5	MEAN
Kr	SHEARING %	2.6	3.3	5.3	5.8	5.0	4.4
	DISSOLUTION %	97.4	97.8	94.7	94.2	95.0	95.6
Xe	SHEARING %	2.2	2.8	4.6	5.1	4.3	3.8
	DISSOLUTION %	97.8	97.2	95.2	94.9	95.7	96.2

TABLE I. NOBLE GAS DISTRIBUTION

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BURN-UP Gwd/t _v	KRYPTON		KRYPTON - 85		XENON	
	g/t _v	Adjusted to 33 Gwd/t	Ci/t _v	Adjusted to 33 Gwd/t	g/t _v	Adjusted to 33 Gwd/t
31.0	342	364	8930	9510	5250	5590
31.8	340	353	9030	9370	5240	5440
31.6	333	348	8660	9040	5110	5340
31.5	322	337	8750	9170	4930	5160
31.0	346	368	9250	9850	5300	5640
MEASUREMENTS (MEAN)		354		9390		5430
CALCULATED		370		9150		5430
$\frac{M-C}{C} \%$		- 4.3		+2.6		0

TABLE II -- NOBLE GAS CONTENT

The experimentally determined krypton and xenon masses and krypton 85 activities are shown in Table II. Average values show good agreement with computed values, and the maximum discrepancy, found for the mass of krypton was only 4.3 %. The next table gives the average isotopic composition of noble gases.

Kr		Xe	
82	0.2 %	130	0.1 %
83	11.5 %	131	8.2 %
84	30.8 %	132	20.7 %
85	6.3 %	134	28.4 %
86	51.2 %	136	42.6 %

Table III : isotopic composition of noble gases

Iodine

Our procedure permits the detection of volatile iodine from 10^{-4} g, i.e., less than 0.1 % of the mass contained in each half-rod.

Iodine release during chopping was less than this detection limit.

It is well known that fission-generated iodine in oxide fuel combines with the more electro-positive elements, especially cesium, of which a large amount is present. / 2 /.

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Since cesium iodide is not volatile, at least at standard reprocessing temperatures, it seems normal that no iodine is released during shearing.

It is only when the fuel is dissolved that practically all the iodine is released by oxidation of iodides under the combined actions of nitric and nitrous acids in the dissolver solution.

More than 99 % of the iodine can be readily eliminated from the dissolution liquor and carried into the off-gas. Insufficient desorption may be caused by :

- . insufficient oxidation of the iodides due to the lack of nitrous acid. This acid, resulting from NO_2 absorption, shows little stability in a boiling solution.
- . lack of carrier gas, so that molecular iodine cannot be carried into the off-gas.
- . formation of non-volatile compounds such as HI_3 , due to the oxidizing action of boiling concentrated nitric acid. However, these compounds are probably reduced to the elementary form by nitrous acid.

In our experiment, operating conditions were such that the above difficulties were avoided. The analysis of Iodine 129 in the fuel solution confirmed that the residual amount was under 1 %.

Initially an attempt was made to evaluate the amount of methyl iodide present through analysis of Iodine 129 in the ethanol solutions through which the gas stream flowed. Although this compound was not detected, the trapping efficiency remains highly questionable.

An analytical method is currently being developed for the direct determination of organic iodine compounds in the gas. Early results appear to show that only traces of these compounds are present. This, however, is subject to confirmation by further tests.

Nevertheless, the formation of organic iodides seems to be related to the presence of organic impurities in liquid or gaseous reagents. The products used in our experiments were of high purity, which suggests that organic iodides are only formed in very small quantities.

The table IV shows the total quantity of iodine as well as iodine 129 activity. Disregarding one incorrect value due to experimental error, very good agreement is observed with predicted quantities computed using a CEA code.

These results also allow the estimate of the respective proportions of isotopes 127 and 129. Calculations show that Iodine 129 accounts for an average 82 % of total iodine.

Carbon 14

Volatile carbon compounds consist almost entirely of CO_2 . Carbon monoxide CO is only 1 % to 2 % of the amount of dioxide. No traces of light hydrocarbons (to C_6) were detected in the off-gas.

Measured carbon-14 activity was 0.24 Ci.t.^{-1}

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BURN-UP Gwd/t	TOTAL IODINE		IODINE -129	
	g / t _u	Adjusted to 33 Gwd/t	mCi / t _u	Adjusted to 33 Gwd/t
31.0	201	214	28.2	30.0
31.8	215	223	30.6	31.8
31.6	122*	-	17.9*	-
31.5	204	214	29.5	30.9
31.0	202	215	30.0	31.9
MEASUREMENTS (MEAN)		216		31.2
CALCULATED		223		31.4
$\frac{M-C}{C}$ %		-3.1		-0.6

* Erroneous measurement (loss of iodine during experiment)

TABLE IV... IODINE CONTENT

Carbon-14 only accounts for 0.1 % of the total carbon measured, in monoxide as well as dioxide form.

The amount of CO₂ collected was approximately 80 l STP.t_u⁻¹. The gas released during chopping contained less than 1 % of the total CO₂.

BURN-UP Gwd/t	CARBON -14		TRITIUM	
	mCi / t _u	Adjusted to 33 Gwd/t	Ci / t _u	Adjusted to 33 Gwd/t
31.0	223	237	147	156
31.8	229	238	418	434
31.6	230	240	81	85
31.5	246	258	66	69
31.0	228	243	173	184
MEAN		243		186

TABLE V... CARBON-14 AND TRITIUM CONTENTS

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Tritium

Tritium quantities measured and shown in table V only relate to the fraction contained in the fuel, not including tritium in the zirconium clad.

The fraction of tritium gas released during chopping was very small and variable, representing 10^{-6} to 10^{-4} of the total tritium measured.

During dissolution, more than 99.5 % of the tritium was measured in the dissolution liquor, and 0.2 to 0.4 % was determined in the form of tritiated hydrogen in the gas phase.

Total tritium activity varied widely, from 66 to 420 Ci.t_U⁻¹ (180 Ci.t_U⁻¹ on the average). This spread of results is highly surprising ; it is generally estimated that in LWR fuel, 40 % of the tritium formed remains in the oxide / 3 /. It is also unlikely that such differences in tritium behavior could be accounted for by dissimilarities in thermal conditions affecting different rods in a single fuel assembly.

Experimental error is ruled out by the fact that results are consistent from one half-rod to the other. Furthermore , the tritium in the gas, determined by entirely different methods, shows fluctuations of the same magnitude.

A complete tritium balance will also require determination of tritium trapped in the clad. Attempts are currently being made to achieve tritium desorption by heating the hulls in a sealed oven.

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