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**SAMPLING AND ANALYZING TRITIUM RELEASE
FROM THE PUREX STACK**

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**ATLANTIC RICHFIELD HANFORD COMPANY
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Date: July 14, 1972

To: G. E. Benedict
K. H. Henry

From: V. L. Schuelein *V. L. Schuelein*

Subject: SAMPLING AND ANALYZING TRITIUM RELEASE
FROM THE PUREX STACK

A request was made by Purex Processing to sample and analyze the tritium released from the Purex stack. The analyses show that over 90 percent of the emitted tritium is in either the ammoniacal or elemental form, probably elemental. The rate of emission varies widely depending on the point in progress of the dissolution.

The Purex stack air was sampled for tritium in the 293-A Building by breaking the iodine monitor sampling line (Figure 1).

Figure 2 shows the tritium sampling apparatus.

The gas was first pulled into a catch flask where excess water was collected. This water was not analyzed since only tritium in the gaseous phase was of interest. From here the gas enters the first CO₂-acetone cold trap where all water is condensed. This sample contains all tritium associated with water vapor, HTO. The NO_x fumes which have escaped the first cold trap are removed in a caustic scrubber because they could have detrimental effects upon the Cu-CuO furnace. The ammoniacal tritium is collected on a 4A molecular sieve. This same sieve could also collect elemental tritium and water introduced by the caustic scrubber; but it should be more preferential to ammonia. It is at this point, therefore, that errors in discriminating between the two different forms of tritium could occur. Assuming the elemental hydrogen and titrated hydrogen have escaped the molecular sieve, it will go into a 475 °C Cu-CuO furnace where it will be converted to water vapor. At this temperature any ammoniacal tritium which escaped the molecular sieve would also be

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converted to water. This is the second source of error for discrimination between ammoniacal tritium and elemental tritium. Although we are sure it would be quite small, any other forms of tritium, such as organic, would probably be collected at this point. In summary, the gas samples are collected at three points:

- The tritium associated with water, HTO, is condensed in the first cold trap.
- The tritium associated with the ammonia, NH_2T , is collected in the 4A molecular sieve.
- The elemental hydrogen, HT, is collected in cold trap No. 3 after conversion to water by the Cu-CuO furnace.

[These samples are designated by "MS".]

[These samples are designated by "F".]

Tritiated ammonia was measured only on the Zirflex run and the one charge to "A" dissolver.

Standards were run for all possible phases of the operation. The liquid scintillation instrument was calibrated and a new efficiency curve drawn. The efficiency of the precipitation distillation procedure was checked by using a uranyl nitrate solution spiked with tritium standard. The efficiency of the cold traps was checked by putting a weighed tube of Drierite[®] after the cold trap. During the experimental phase this weight was checked after each sample. No water was ever found to escape the cold trap. The efficiency and necessary temperature operating range for the hydrogen-to-water conversion Cu-CuO furnace were determined in a laboratory-scale operation shown in Figure 3. The molybdenum trioxide shown in the laboratory-scale operation was not used in the plant setup because it was found to be too insensitive.

* Drierite--trade name of J. T. Baker Chemical Company.

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Results

The results in Tables I and II show an unusually large percentage of elemental tritium (TH) or tritiated ammonia (NH_2T) instead of the accepted combined HTO-form. Although the sampling procedure was essentially the same for the aluminum-clad fuel, a difference does exist. In the monitored aluminum-clad fuel (Table III), no attempt was made to determine the amount of tritium combined in the ammonia-form. The molecular sieve eliminated excess oxides of nitrogen not removed by the caustic scrubber and excess water vapor from the caustic scrubber. The molecular sieve was changed, therefore, depending on the number of hours used instead of every time a sample was taken. This affected the total tritium found in the second cold trap and biased it low. Since on all three sampling periods the Cu-CuO furnace was operated at 450 to 475 °C, any ammonia as well as any elemental tritium which passed through the molecular sieve would be converted to water. If the sampling time was very short, elemental tritium could be held up on the molecular sieve until it was displaced by ammonia or water. The Zirflex run and the one charge from "A" dissolver were monitored for ammonia by changing the molecular sieve on every sample.

During the monitoring of tritium in Zirflex fuel, tritium was also analyzed on several aqueous waste and process streams. These streams were found from previous sampling programs to contain the bulk of the process stream tritium. They are A-26 NH_3 scrubber crib flow, X-C acid absorber product, A-10 process condensate crib flow, and the U-8 acid fractionator condensate. These results are shown in Table IV.

Tritium was continuously monitored on one charge of aluminum-clad fuel in "A" dissolver to determine a total tritium emitted per tritium charged. It also appeared from previous work with Zirflex and normal fuel tritium emission data that a peak

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would be observed at the start of the first cut. Although due to equipment failure we missed the most important sample, a peak for elemental tritium emission was still firmly established (Figure 4). Peaks were observed for the molecular sieve samples, NH_2T (Figure 5) and for the first cold trap, tritiated water, Figure 6.

The deflection caused by Point 3 in Figures 4, 5, 6, and 7 is explained by it being taken at the very start of the first cut before tritium evolution was at its highest level. This is further explained in Figure 8. It is interesting to note that the peaks are widely separated, occurring after 7 to 9 hours of processing for the tritiated ammonia. The total tritium curve, Figure 7, is almost identical with the elemental tritium curve since 99 percent of tritium appears to be in this state. These curves are drawn as the data are presented, with no extrapolation.

Figure 8 presents a postulated explanation of and a curve for the total tritium emission from one charge of normal fuel. Starting with an emission of zero at time zero, the rate builds quickly until the mid-point of coating removal where it starts to fall back to near zero when coating removal is complete. The first cut causes another spurt of emission which builds to a peak about half-way through the first cut. Here the emission begins to taper off as the charge goes into the second cut and decreases to nearly zero during cooling and jetting of the dissolved uranium. The evolution starts again with the second cut but never reaches the level it had before. To aid in reading the tritium emission curves, Figure 9 was prepared which gives the times samples were taken in relation to the number of processing hours and the particular phase of dissolution.

Conclusion

The total amount of tritium is not in question, but the molecular form is. The unfortunate fact

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is that one form of tritium, elemental, is harmless because it quickly dissipates into the upper atmosphere; while the other form, ammoniacal, is most definitely of ecological concern because it can be assimilated into the life cycle. Since the forms in question make up more than 90 percent of the evolved tritium, some important questions should be answered:

1. Is the tritium count found in the molecular sieve material actually tritiated and no tritiated ammonia is being given off?
2. Is tritiated ammonia the primary contributor to the tritium found in the second cold trap; and little or no elemental tritium is being given off?

The tables and figures are attached.

This work was done with the cooperation and coordination of W. J. Grady who has since left the Company.

VLS:e

Att. (13)

TABLE I
TRITIUM ANALYSIS OF ONE CHARGE ALUMINUM-CLAD FUEL--"A" DISSOLVER

Date	Sample Description	Number	Operation		Time		Gas Flow ft		$\mu\text{Ci}/\text{ft}^3$	$\mu\text{Ci}/\text{ml}$
			Time	Cut	Taken	Total Hr	Rate	Total		
02/22/72	Gas		1855+0100	Coats	1855	3.08	1.5+1.0 1.25 ave.	3.85		
	Tritiated water	1			↓				8.8×10^{-3}	
	Tritiated hydrogen	1C							3.41	
	Tritiated ammonia	MS1			2200				3.91×10^{-3}	
	Gas		1855+0100	Coats	2205	2.92	1.7+1.9 1.8 ave.	5.25		
	Tritiated water	2			↓				2.7×10^{-2}	
	Tritiated hydrogen	2C*							$4.0 \times 10^{-1*}$	
	Tritiated ammonia	MS2			0100				4.9×10^{-2}	
	D-2	2553								5.2×10^{-3}
	D-2	2567								4.1×10^{-2}
02/23/72	Gas		0300+1520	1st Cut Part 2	0300	3.8	1.8	7.6		
	Tritiated water	3			↓				$2.5 \times 10^{-2**}$	
	Tritiated hydrogen	3C							$9.6 \times 10^{-1**}$	
	Tritiated ammonia	MS3			0710				$4.3 \times 10^{-2**}$	
	D-5	2736								1.11
	Gas		0300+1520	1st Cut Part 2	0722	3.55	2.0	7.1		
	Tritiated water	4			↓				1.7×10^{-3}	
	Tritiated hydrogen	4C							3.58	
	Tritiated ammonia	MS4			1055				2.5×10^{-1}	
	D-5	2785								1.04
02/23/72	Gas		0300+1520	1st Cut Part 3	1115	4.1	2.	8.2		
	Tritiated water	5			↓				4.3×10^{-4}	
	Tritiated hydrogen	5C							3.01	
	Tritiated ammonia	MS5			1520				4.4×10^{-2}	
	D-5	2896								1.14
02/25/72	Gas		0830+Start of "C" dissolver	2nd Cut 1st Sample	0830	1.7	2.2	3.7		
	Tritiated water	6			↓				$<2 \times 10^{-4}$	
	Tritiated hydrogen	6C							1.87	
	Tritiated ammonia	MS6			1010				2.1×10^{-2}	
	D-5	3370								1.14
02/29/72	Gas		1035+1710	Coats	1045	4.	1.75	7.		
	Tritiated water	7			↓				5.9×10^{-3}	
	Tritiated hydrogen	7C							3.85	
	Tritiated ammonia	MS7			1445				2.0×10^{-2}	
	D-5	3272								7.5×10^{-2}
03/15/72	Gas		0907+1522	Coats	0955	3.1	1.5	4.65		
	Tritiated water	8			↓				1.4×10^{-2}	
	Tritiated hydrogen	8C							2.52	
	Tritiated ammonia	MS8			1300				1.4×10^{-2}	
	D-5	5448								

Glass wool melted.
Air filter leaked.

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TABLE III
TRITIUM ANALYSIS, ALUMINUM-CLAD FUEL
GAS AND D-5

<u>Date</u>	<u>Sample</u>	<u>Operation</u> <u>Cut</u>	<u>Dissolver</u>	<u>μCi/ft</u>	<u>D-5</u> <u>ID</u>	<u>D-5</u> <u>μCi/ml</u>
09/21/72	1F*	1, 2	A, B	14.6	72-1-165, 166 Comp. #9134	3.25
	2	1, 2	A, B	0.026	Same as 1F*	3.25
09/23/71	3	2	B	1.08 ⁻⁴	72-1-171, 172 Comp. #9356	3.00
	3F	2	B	19.04		
09/27/71	4	1, 2	B	1.86 ⁻⁴	72-1-182 Comp. #9859	2.10
	4F*	1, 2	B	6.56		
09/28/71	†5	1, 2	A & B	1.47 ⁻³	72-1-185 #18	2.10
	†5F*	1, 2	A & B	6.47		
09/28/71	6	1, 2	B, A	3.07 ⁻⁴	72-1-185 #18	2.10
	6F*	1, 2	B, A	11.1		
09/29/71	7	1	A	1.91 ⁻²	72-1-188 #151	2.16
	7F*	1	A	7.18		
09/29/71	8	2	A	4.84 ⁻⁴	72-1-188 #151	2.16
	8F*	2	A	0.441		
09/29/71	†9	Coats	B	2.10 ⁻²	72-1-189 #206	2.29
	†9F*			2.97 ⁻⁴		
09/29/71	10	1	A	3.12 ⁻³	72-1-191 #301	2.17
	10F	1	A	2.15		
09/30/71	11	3 and heels	A	1.44 ⁻³	72-1-191 #301	2.17
	11F*		B	3.47		
09/30/71	†12	Heel	A	3.50 ⁻³	72-1-192 #347	1.90
	†12F*	Heel		1.25	(Heels)	
09/30/71	13	XC acid adsorber product		1.75 ⁻²	μCi/ml	

* "F" refers to those samples taken after the Cu-CuO furnace. This should all be elemental tritium.

† Fluctuation in air volume noted (quantitatively unreliable).

TABLE IV
TRITIUM ANALYSIS OF ZIRFLEX FUEL
AQUEOUS WASTE AND PROCESS STREAMS

<u>Sample ID</u>	<u>Number</u>	<u>µCi/ml</u>
E-3	6569	1.1 x 10 ⁻¹
E-3	9992	1.1 x 10 ⁻¹
E-3	43	1.4 x 10 ⁻²
E-5	153	2.8 x 10 ⁻²
E-5	6648	2.6 x 10 ⁻²
E-5	7354	1.6 x 10 ⁻²
E-5	54	1.9 x 10 ⁻²
X-C	6005	5.6 x 10 ⁻²
X-C	6102	4.6 x 10 ⁻²
X-C	6439	2.0 x 10 ⁻²
X-C	6710	7.2 x 10 ⁻²
X-C	6576	1.8 x 10 ⁻²
X-C	7351	4.7 x 10 ⁻⁴
X-C	7553	5.9 x 10 ⁻²
X-C	82	3.4 x 10 ⁻²
U-8	6004	2.6 x 10 ⁻¹
U-8	6101	2.6 x 10 ⁻¹
U-8	6442	5.9 x 10 ⁻¹
U-8	6579	2.7 x 10 ⁻¹
U-8	6713	2.5 x 10 ⁻¹
U-8	7352	4.3 x 10 ⁻¹
U-8	7554	3.7 x 10 ⁻¹
U-8	83	7.2 x 10 ⁻¹
A-10	6440	2.7 x 10 ⁻¹
A-10	6711	5.6 x 10 ⁻¹
A-10	7349	7.5 x 10 ⁻¹
A-10	7551	3.3 x 10 ⁻¹
A-10	84	1.46
A-36	6007	2.2 x 10 ⁻²
A-36	6100	2.3 x 10 ⁻²
A-36	6441	7.3 x 10 ⁻³
A-36	6578	3.1 x 10 ⁻²
A-36	6712	1.0 x 10 ⁻²
A-36	7350	5.1 x 10 ⁻³
A-36	7552	6.0 x 10 ⁻²
A-36	85	7.3 x 10 ⁻³ *

* December Composite.

FIGURE 1
DISSOLVER OFF-GAS TREATMENT

COATING REMOVAL

ELEMENT DISSOLUTION

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FIGURE 2
TRITIUM SAMPLING APPARATUS

FIGURE 3
LABORATORY TEST SAMPLING APPARATUS

FIGURE 4
SECOND COLD TRAP--TRITIATED HYDROGEN

FIGURE 5
MOLECULAR SIEVE--TITRIATED AMMONIA

FIGURE 6
FIRST COLD TRAP--TRITIATED WATER

FIGURE 7
TOTAL TRITIUM

FIGURE 8
TOTAL TRITIUM EMISSION--POSTULATED CURVE

FIGURE 9
TRITIUM SAMPLING OF ONE CHARGE ALUMINUM-CLAD FUEL

DATE
FILMED

9/9/94

END