

## RETENTION OF IODINE ON DUCT SURFACES

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The behaviour of fission-product iodine in a reactor exhaust duct and filtering system is of continuing interest. At CRNL parts of the research reactors are cooled with air which is released from a stack located 770 m beyond the absolute filters. Gases are transferred to the stack through a large duct. Occasionally, small amounts of iodine are released to the system from an experimental reactor loop. These nuclides have been used in the present study to measure the hold-up of iodine in the system.

### Introduction

The behaviour of airborne radioactivity is of interest in evaluating the hazard from continuous or accidental discharge of fission products from a nuclear reactor. One of the factors affecting the amount released to the environment is the fractional deposition on containment surfaces. This report deals with the mechanism of deposition on specific surfaces and with re-emission from them.

The research reactors at CRNL are operated as test facilities in which the fuel material, cladding and the cooling conditions can be altered. A test loop, inserted in a single NRX fuel channel, is isolated from the reactor cooling system. In some cases the loop circuit may be vented to the main air duct; rare gases and halogens from a failed fuel element can then be discharged from the stack. The remaining fuel rods in NRX are water cooled and do not vent to the atmosphere.

Iodine-131 is particularly important in assessing the hazard from nuclear reactors. It has a fairly long half-life and escapes readily from ruptured fuel and the element is essential to man. The remaining fission product iodines have shorter half-lives and contribute proportionally less to the integrated dose, but they are useful for investigating the behaviour of the element in a dynamic system.

Various chemical forms of gaseous  $^{131}\text{I}$  have been recognized in addition to the elemental form<sup>1, 2</sup>. Perhaps the most troublesome of these is methyl iodide<sup>3, 4</sup>, but hypiodous acid, HOI, is released under moist conditions at high pH<sup>5, 6</sup>. Both of these are difficult to remove from the gas phase.

Elemental iodine should deposit on duct surfaces but the more penetrating forms, which generally comprise about half the total, are unreactive and are not retained on surfaces to an appreciable extent. Assuming that the retention of  $\text{I}_2$  is reversible and that the mean life on the surface is the order of days, there should be an observable difference between the 8.065 d  $^{131}\text{I}$  and the other isotopes which are retained on the surface. At the stack one should see the sum of the following components: a) All isotopes present in the

penetrating form; b)  $^{131}\text{I}$  which has been deposited on the surface and subsequently released; c)  $^{133}\text{I}$  and possibly  $^{135}\text{I}$  in the elemental form which has undergone partial or substantial decay before escaping from the surface. Iodine-134 (52.3 m) should only be transported to the stack in the penetrating, i. e. non-elemental form.

### Methods

A flow diagram of the ventilation system is shown in Figure 1. The absolute filters are located at a short distance from the NRX reactor. The duct is constructed of mild steel 1.2 m diameter by 770 m long and is painted on the inside with one coat of Zincilate 410. This provides a sacrificial coating of zinc which protects the underlying metal.

Samples were collected by drawing a measured amount (0.1 to 2 m<sup>3</sup>) of air through a canister. Collection times varied from five minutes to two hours depending on the nature of the experiment. In experiments designed to measure the chemical form of iodine the sample was collected with a freshly prepared May pack<sup>2</sup>. In all other cases a polyethylene capsule, 12 mm x 50 mm, filled with activated charcoal, was used to collect the sample. The order and efficiency of components in the May pack is given in Table 1. Uptake of hypiodous acid by copper screens and charcoal was determined in this study. McCormack<sup>7</sup> reports that more than 70% of the HOI is retained by the carbon paper. In the present case less than 11% is found on the other components of the May pack, so more than 89% must be retained by the paper.

Table 1

		$\text{I}_2$	Particulate	HOI	$\text{CH}_3\text{I}$	Ref.
4 Copper screens	100 mesh	97%	nil	<3%	nil	8, 9
1 Glass fibre filter	Type GFA	3%	99%	<2%	nil	9
1 Gelman carbon paper	Type ACG/B	nil	nil	>70%	1%	7
Barnebey-Cheney #513						
Activated charcoal	60g	nil	nil	<6%	99%	7

Air samples were taken at the four locations shown in Figure 1. In order to minimize loss of iodine prior to counting, the individual components were sealed in polyethylene envelopes. Sample 1 was collected through a metal tube inserted six inches into the duct so is probably not representative of the mean concentration at that point.

All the nuclides were determined simultaneously by gamma spectrometry. A 125 cc Ge(Li) detector with 2.3 keV resolution was used for most of the experiments. This was coupled to a 4096 channel analyser. Details of the method of computation were given in an earlier report<sup>10</sup>. With this system the isotopes of iodine, bromine, xenon, rubidium and cesium could be resolved easily in a single count. Repeated measurements were made to verify half-life and to check for interfering lines such as the 529.5 keV gamma transition of 2.4 h  $^{83}\text{Br}$ . In this case the maximum error in the determination of the 20.8 h  $^{133}\text{I}$  was 3% in the first hour. The energies of the lines which were selected for quantitative determinations are given in Table 2 together with the preferred gamma branching ratios.

### Results

#### Chemical Composition of Iodine

A typical result from the analyses of the May packs is given in Table 3.

TABLE 2  
Selected Gamma Ray Energies

Mass	Half -Life	Preferred $\gamma$ Line	$\gamma$ per Disintegration
131	8.065 d	364.49 keV	0.790
132	2.284 h	667.8	0.999
133	20.8 h	529.9	1.00
134	52.3 m	847.04	1.00
135	6.68 h	1260.45	1.00
82	35.34 h	554.23	0.73
		776.45	0.83

These samples were collected at location 2, immediately after the absolute filters. Corrections have been applied for incomplete uptake of  $I_2$  on the copper screens (97%) and for retention by the particulate filter (see Table 1). The species held by the charcoal paper is largely hypoiodous acid<sup>7</sup>, though high molecular weight alkyl iodides may be collected with this fraction.

The five iodine isotopes show a remarkably similar distribution on the May pack. This is in contrast to Keller et al<sup>11</sup> who recently observed large isotopic differences under conditions of high humidity. However, in both instances the fraction found in the elemental form was lowest for  $^{131}I$ .

TABLE 3  
Chemical Composition of Iodines and Bromine

Mass No.	131	132	133	134	135	82
Elemental	26.1%	29.7%	31.1%	31.2%	29.7%	17.7%
Particulate	1.8	2.4	2.1	2.3	2.3	2.0
HOI/HOBr	64.6	60.3	63.1	61.0	63.4	60.1
$CH_3I/CH_3Br^*$	7.5	7.6	3.8	5.4	4.2	21.2

\*This represents an upper limit; species which are not completely held by earlier components in the pack will be collected and counted as methyl iodide or bromide. Relative humidity = 35%.

#### Retention of Iodine-131

The concentration of  $^{131}I$  at various points in the duct was measured in three separate experiments. The purpose of this series was to establish the extent to which this nuclide was retained on surfaces under conditions of near constant release. The first three runs in Table 4 followed long periods with the reactor operating at constant power.

Iodine-131, corrected for air flow at the sampling point, shows little variation along the length of the duct with the reactor operating (samples 2, 3 and 4); it follows that there is negligible removal of  $^{131}I$  in the duct system. The results also suggest that  $^{131}I$  is not removed by the absolute filters. The apparent increase from the first to second sampling point is caused by poor mixing and non-representative sampling at the first location.

There tends to be a release of extra fission products at shutdown which is still evident 15 hours later (Table 4). Some of the excess  $^{131}I$  is retained on the duct surface, thus at  $t_0 + 15$  hours the concentration is lower at the stack (location 4) than at the filters (location 2).

TABLE 4

## Iodine-131 Concentrations at Various Points in the Duct

Experiment	Sampling Point				Time from Shutdown
	1	2	3	4	
1	4.35	6.85	6.64	6.59 nCi/m <sup>3</sup>	*
2	3.88	6.48	6.15	6.31	*
3	3.78	5.39	-	5.46	*
3a	5.54	8.61	-	7.28	15 h
3b	3.19	5.04	-	5.18	20 h
3c	2.03	2.45	-	2.85	40 h

\*Reactor Operating, Flow = 52,670 m<sup>3</sup>/h.

TABLE 5

## Iodine-133/Iodine-131 Activity Ratios

Experiment	Sampling Point				Time from Shutdown
	1	2	3	4	
1	5.2	5.0	4.1	4.2	*
2	5.4	5.2	4.6	4.5	*
3	10.2	9.3	-	5.0	*
3a	1.8	1.1	-	1.7	15 h
3b	1.3	1.6	-	2.0	20 h
3c	1.0	1.7	-	2.3	40 h
3d	0.8	2.6	-	2.4	60 h

\*Reactor Operating. Ratios are corrected for radioactive decay from time of shutdown as applicable.

Other Isotopes of Iodine

Table 5 shows the retention of <sup>133</sup>I, one of the four isotopes of iodine with half-lives shorter than eight days. Ratios to <sup>131</sup>I permit use of results from the first sampling point. In Table 6 the data for <sup>133</sup>I and other nuclides are normalized to facilitate intercomparison.

Under steady state conditions at constant reactor power there is moderate retention of <sup>133</sup>I on the duct. The results in Table 6 show little dependence on half-life though <sup>133</sup>I is slightly higher than <sup>134</sup>I and <sup>135</sup>I at the stack end of the duct. Tellurium-132 (78 h) is found beyond the absolute filters and this causes <sup>132</sup>I to be high and variable.

Release Following Reactor Shutdown

The foregoing were steady state experiments; the reactor loop had operated at constant flux for periods of up to three weeks. Following shutdown, it was observed that <sup>131</sup>I levels remained relatively constant (see Table 4), but the 6.68 h <sup>135</sup>I and 20.8 h <sup>133</sup>I dropped by an order of magnitude (Table 5). This rapid change provided an opportunity for observing desorption from the duct surface. Results are given in Table 7.

Bromine-82

Bromine-82 is a shielded nuclide which has a very low fission yield so would not normally be observable with the other halogens. In NRX it is probably produced by an n,  $\gamma$  or n, p reaction on bromine or krypton.

TABLE 6

Concentrations of Iodine and Bromine Isotopes Relative to  $^{131}\text{I}$  (Normalized)

Isotope	Half-Life	Exp. 1 Sampling Point				Exp. 3 Sampling Point			
		1	2	3	4	1	2	3	4
133	20.8 h	1	0.95	0.78	0.80	1	0.91	-	0.58
135	6.68 h	1	0.99	0.75	0.74	1	0.92	-	0.52
132	2.28 h	1	1.1	1.0	1.0	1	1.6	-	2.0
134	0.87 h	1	0.97	0.74	0.75	1	0.93	-	0.50
82	35.34 h	1	0.67	0.69	0.68	1	0.53	-	0.51

TABLE 7

Duct Concentrations After Shutdown Relative to  $^{131}\text{I}$  (Normalized)

Isotope	Experiment	Sampling Point			*Reactor Operating
		1	2	4	Time from Shutdown
133	3	1	0.91	0.58	*
	3a	1	0.62	0.90	15 h
	3b	1	1.2	1.4	20 h
	3c	1	1.7	2.3	40 h
	3d	1	2.6	2.4	60 h

Discussion

Morris and Nicholls<sup>1,2</sup> measured the deposition velocity on copper and galvanized steel and found that there was rapid uptake with a much slower rate of removal. In the present case the metal surface of the duct has a coating of granular zinc onto which the iodine deposits. This layer of  $^{131}\text{I}$  can be displaced with inactive iodine<sup>3</sup>, showing that the exchange is reversible.

The data indicate that only the elemental form is exchanging. If R is the fraction retained on the duct then T, the fraction which is not retained is given by  $T = 1 - R$ . Values of T can be obtained from  $^{134}\text{I}$  and  $^{135}\text{I}$  concentrations at location 4 (Table 6). The observed retention, R, is 0.26 for the first experiment and 0.49 for the third. May pack results show that 30% and 50% of the iodine present is in the form of  $\text{I}_2$  at these times.

Most of the molecules on the surface of the duct at a given time will be  $^{131}\text{I}$  because this isotope has the longest half-life. At an observed activity ratio of nine to one the numbers of atoms of mass 131 and 133 are equal in the gas phase. Normally the 52 min  $^{134}\text{I}$  is a factor of ten less abundant.

The mean life of a molecule on the surface before escape by exchange can be estimated from the data in Table 6. Most, though not all, of the 20.8 h  $^{133}\text{I}$  decays while held on the surface. Let us assume that the fraction exchanging is the same for all isotopes and that in the case of 52 min  $^{134}\text{I}$  this fraction decays completely on the surface. Now if  $R_0$  is the fraction retained on the duct which undergoes complete decay and  $R_t$  is the fraction undergoing partial decay before escape, the fraction of  $^{133}\text{I}$  which remains is

$$\frac{N_t \lambda}{N_0 \lambda} = \frac{R_0 - R_t}{R_0}$$

but  $N_t \lambda = N_0 \lambda e^{-\lambda t}$

where  $\lambda = 0.693/20.8 \text{ h}^{-1}$ .

$N_0$  = number of atoms at zero time.

$N_t$  = number of atoms at t.

Solving for  $t$  gives values of 46 and 53 hours for the two experiments in Table 6. Thus the mean life of iodine on the surface is 2.1 days.

Iodine-135 has a half-life of 6.68 h and the amount remaining after 2.1 days decay is 0.6%. As practically all of the  $^{135}\text{I}$  on the surface decays in situ, one would expect the same retention as in the case of  $^{134}\text{I}$ . The data in Table 6 confirm this result.

It is evident from Table 7 that the  $^{133}\text{I}$  concentration is increasing along the duct following shutdown. The relative level at sampling point 4 reaches a value  $2\frac{1}{2}$  times the inlet concentration at  $t_0 + 60$  hours. Hence this nuclide must be coming from the metal and filter surfaces. The release probably occurs by an exchange reaction involving  $^{131}\text{I}$ . At  $t_0 + 20$  h the abundance of this isotope in the gas phase is over 95%, while the abundance of  $^{133}\text{I}$  is higher on the surface than in the gas phase. Exchange at this time will enhance the concentration of the isotope in the gas phase.

The outlet concentration of  $^{133}\text{I}$  is again the sum of two components: a penetrating fraction reduced in concentration by a factor of 10 following shutdown, and an exchanging fraction which escapes from the surface after partial decay. Note that the latter is deposited before shutdown at the higher concentration. Then the increase at the stack is:

$$Q = \frac{(1-R) F + R e^{-\lambda t}}{F} \quad \text{where } Q = \frac{\text{outlet}}{\text{inlet}}$$

$$= \frac{(0.48 \times 0.1) + 0.52 \times 0.21}{0.1} \quad F = \text{decrease in } ^{133}\text{I} \text{ after shutdown}$$

$$= 1.6 \quad \lambda = 0.693/20.8 \text{ h}^{-1}$$

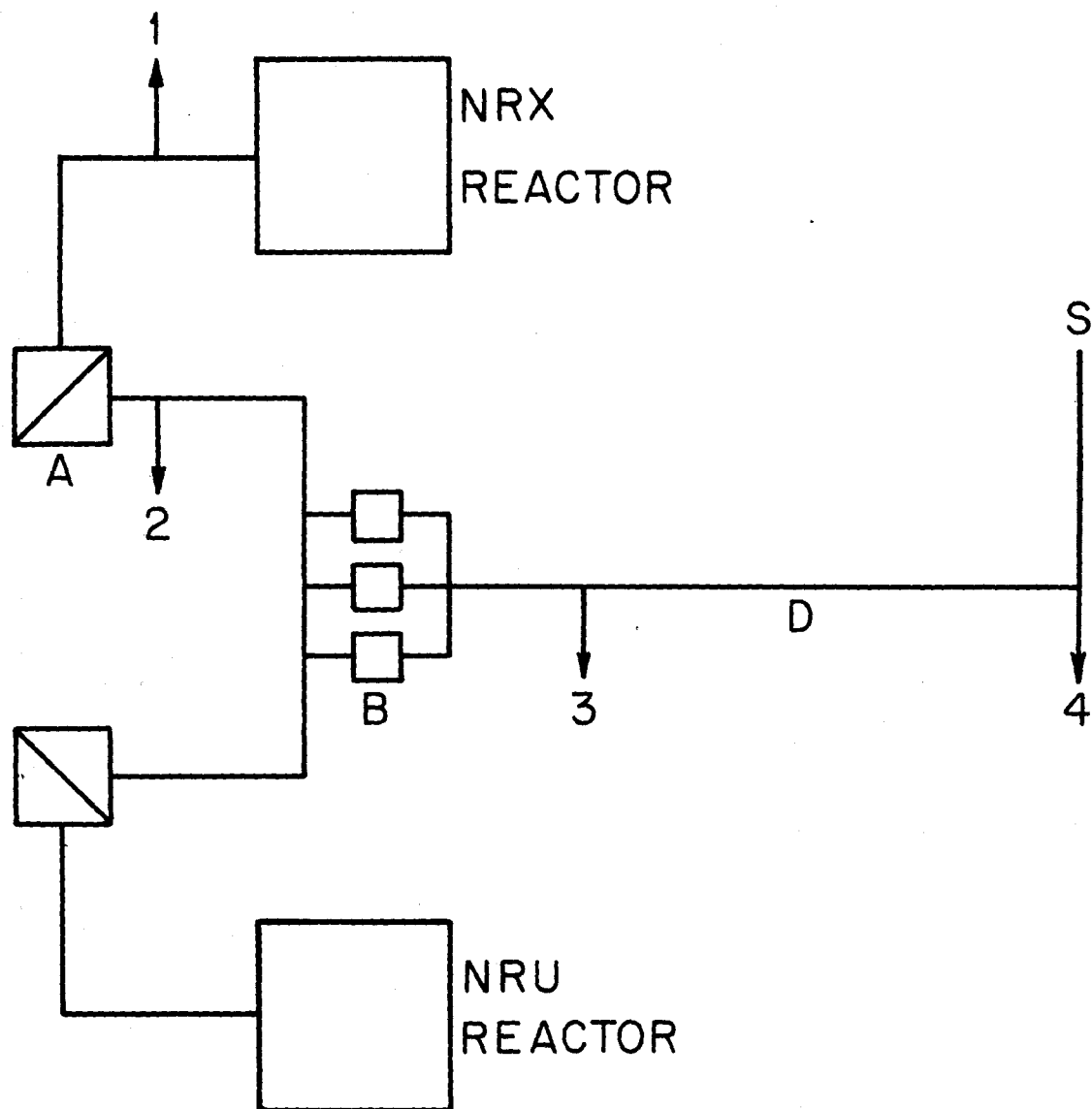
$$t = 2.1 \text{ d}$$

This value can be compared with an observed average of 1.7 from measured concentrations. The agreement supports the calculated mean residence time of 2.1 days.

#### References

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A - ABSOLUTE FILTERS  
 B - MAIN FANS  
 D - DUCT  
 S - STACK  
 1,2,3,4 SAMPLE POINTS

Figure 1. Schematic diagram of the reactor ventilation system