IDENTIFICATION OF IODINE SPECIES RELEASED FROM FUEL USING A COMMERCIAL VOLATILE RADIOIODINE SPECIES SAMPLER

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ABSTRACT

Experiments have been carried out to verify the manufacturer's claims (1) for an "iodine species" sampler which differentiates between I_2, CH_3I and HOI, the main volatile forms of iodine expected in nuclear installations after radioactive releases from fuel. This sampler consists of five components: a filter paper to retain particulates; CdI_2 on a matrix of chromosorb-P to retain I and I_2; iodophenol on a matrix of activated alumina to retain HOI; 30-50 mesh silver zeolite for CH_3I; and lastly 40-50 mesh TEDA-impregnated (5%) charcoal to capture any iodine which escapes the preceding filter elements.

Calibration experiments used radioactively labelled CH_3I and I_2. 95.4% of the methyl iodide was trapped in the silver zeolite, and 87% of the I_2 in the CdI_2. These figures are almost identical to those of the manufacturer.

The sampler has been used to measure the iodine species released during oxidation in air of irradiated UO_2 fuel fragments, and Pickering elements. The identification of I_2 as the volatile form of iodine seems certain and logical since >93% of the released iodine was trapped in the first element of the sampler and little penetration occurred beyond this.

The only fission products ever observed downstream of a sampler have been the noble gases, and even these are trapped up to 50% by the charcoal back-up cartridge operating at room temperature.

In conclusion, the iodine species sampler performs very well and up to specifications for separating I_2 and CH_3I. It has been found extremely useful in preventing radioactive iodine releases from apparatus during destructive oxidation of fuel in hot cells.

INTRODUCTION

The chemical form of iodine released from fuel during oxidation has been measured after verifying manufacturer's claims (1) for an "iodine species" sampler which differentiates between I_2, CH_3I and "HOI", the volatile forms of iodine expected in nuclear installations after radioactive releases from fuel. This sampler consists of five components: a filter paper to retain particulates; CdI_2 on a matrix of chromosorb-P to retain I and I_2; iodophenol on a matrix of activated alumina to retain HOI; 30-50 mesh silver zeolite for CH_3I; and lastly 40-50 mesh TEDA-impregnated (5%) charcoal to capture any iodine which escapes the preceding filter elements. The sampler is marketed by RADeCO/SAI of San Diego.

This sampling system has been used to differentiate between organic and inorganic iodine in nuclear installations including TMI (2-4). At CRNL it has been used to monitor iodine releases during the oxidation of irradiated fuel in air. Under these conditions HOI is not expected since it is a product of the hydrolysis of I_2 in alkaline pH water. Problems of making a positive identification of HOI have been recently discussed (2,5). All that is certain is that an inorganic form of iodine of valence one can be formed when I_2 is hydrolyzed. The partition coefficient is probably $>10^4$.

In this paper results are presented and compared with manufacturer's data for I_2 and CH_3I. Further studies were then made of iodine released from irradiated Te, fuel fragments and a Pickering fuel element.

EXPERIMENTAL

Radioactive I_2 was prepared by irradiating a few mg of high purity tellurium (Johnson Mathey) in the hydraulic capsule facility of NRX, to give a mixture of iodine in tellurium. Neutron capture by Te-130 gives Te-131 which decays to give I-131. The irradiated tellurium was sealed in the glass sidearm of a glass tube through which argon flowed to the species sampler. The "TeI_2" was heated (in the sidearm) using a gas torch to induce decomposition to Te and I_2 at ~400 K (6). Two carrier free experiments were carried out, then in the third experiment excess I_2 was added to ensure that the I-131 became bound in I_2 by exchange.

I-131 labelled methyl iodide was obtained from I.C.N. This was injected through a rubber septum into an argon stream flowing directly to the species sampler.

Experiments to measure iodine releases during oxidation of UO_2 are described elsewhere (7).

RESULTS

In no experiment has iodine been confirmed as passing through a sampler.

METHYL IODIDE

The following distribution of iodine was observed when methyl iodide was injected into a sampler using an airflow of 30 mL/min for 1½ hours then 1 L/min for a further 3 hours.

Filter	Species	% Iodine Trapped
Paper	Particulate	0
CdI_2	I_2	0
Iodophenol	HOI	2.8
Ag Zeolite	CH_3I	95.4
Charcoal	Backup	1.8

No redistribution occurred after the first period of 1½ hours.

Good selectivity is shown in that only 4% of the methyl iodide was absorbed by traps other than that specific for methyl iodide. The manufacturers claim that less than 0.02% will be absorbed by preceding filter elements. This is obviously too optimistic, but the results are nevertheless impressive.

TELLURIUM IODIDE

The initial experiments aimed at checking the selectivity of the filters to small quantities of I_2, produced some interesting results. Carrier free iodine was prepared by irradiating Te, which was then gently heated to induce decomposition.

$$"TeI_4" \rightarrow Te + 2\ I_2$$

The following results were obtained.

Filter	Species	% Iodine Trapped
CdI_2	I_2	1.4
Iodophenol	HOI	5.3
Ag Zeolite	CH_3I	5.2
Charcoal	Backup	88.1

Rather than producing I_2, it appeared that a penetrating volatile and unreactive compound of tellurium and iodine was volatilized. The chemical filters were unable to react with the halogen.

In order to check this, the experiment was repeated but the irradiated tellurium was heated more strongly to induce greater decomposition to the elements.

The following results were obtained.

Filter	Species	% Iodine Trapped
CdI_2	I_2	27.0
Iodophenol	HOI	42.4
Ag Zeolite	CH_3I	30.6
Charcoal	Backup	0.06

The iodine was now in a form more amenable to chemical trapping but was still at most 27% I_2. This did not provide a check of the selectivity or efficacy of the system for I_2.

IODINE GAS

Following the failure to prepare carrier free radioactive iodine, it was decided to use I_2 with a small amount of labelling.

Results are given in this section for an experiment in which radioactive I_2 was volatilized by heating irradiated tellurium with excess crystals of I_2. The iodine distribution in the sampler was as follows:

Filter	Species	% Iodine Trapped
CdI_2	I_2	86.6
Iodophenol	HOI	6.6
Ag Zeolite	CH_3I	6.2
Charcoal	Backup	0.6

Remarkably good agreement is obtained with the manufacturer's efficiency of 87.3 $\pm$ 4.5%, for I_2 generated from aqueous solution by neutralizing an acidic solution of iodate.

IODINE RELEASED FROM A DEFECTED FUEL ELEMENT DURING OXIDATION IN AIR

A 3½-month old Pickering NGS element, 155 MW.h/kg U, with one artificial defect was oxidized in a flowing air stream at 900°C for 2½ hours. Under these conditions, oxidation of iodide to iodine would not be unexpected. Although only a small quantity of volatile iodine escaped from the fuel element, 97% of this reached the iodine sampler giving the following distribution:

Filter	Species	% Iodine Trapped
Paper	Particulate	0.15
CdI_2	I_2	99.50
Iodophenol	HOI	0.35 Ag
Zeolite	CH_3I	0.002
Charcoal	Backup	0

Although traces of Te-132 could be seen upstream, none was detected in or near the sampler.

IODINE RELEASED FROM FUEL FRAGMENTS DURING OXIDATION IN AIR

Fragments of fuel from an NRU filler element, 465 MW.h/kg U, were oxidized at 900°C in a flowing air stream. The following distribution was obtained in an iodine sampler, which trapped 20% of the calculated fuel inventory of iodine.

Filter	Species	% Iodine Trapped
CdI_2	I_2	93.8
Iodophenol	HOI	2.8
Ag Zeolite	CH_3I	2.99
Charcoal	Backup	0.25
Cold Trap	Backup (probably external contamination)	0.10

No Te-132 was observed in or near the sampler.

DISCUSSION

Manufacturers' claims regarding the separation of CH_3I and I_2 have been verified, using labelled CH_3I and I_2.

Experiments which attempted to make carrier free iodine by irradiating high purity Te, did not produce I_2, but rather a volatile and unreactive species, presumably a compound of Te and I. In other circumstances, away from a defined two element system, the results could have been interpreted as due to a mixture of CH_3I, I_2 and HOI. Obviously the sampler must be used with caution on unknown systems, and chemical interpretation and/or another method should be sought to verify results.

The identification of I_2 as the volatile form of iodine released from fuel during high temperature oxidation seems certain and logical since this was trapped in the first element of the sampler and little penetration beyond this occurred. Also no Te was observed. A mass spectrometer is currently being set up to independently confirm this observation of I_2.

From a safety point of view, the sampler effectively formed an impenetrable barrier for iodine between highly active fuel and the hot-cell air. No penetration of a sampler was ever observed at flow rates up to 2 L/min over three days. The manufacturer claims that samplers can be used at flow rates up to 0.1 L/s.

The only fission products observed downstream of a sampler are the noble gases and even these are trapped up to 50% by the charcoal backup cartridge operating at room temperature. On occasion, iodine was observed downstream of samplers, but this was always found to be due to external contamination.

CONCLUSIONS

The RADeCO/SAI iodine species sampler performs very well and up to specifications for separating I_2 and CH_3I. It has been found extremely useful in preventing radioactive iodine releases from apparatus during destructive oxidation of fuel in hot cells. Iodine appears to be released as I_2 when irradiated fuel is oxidized at high temperatures. Whenever possible, confirmatory evidence of speciation should be sought using another method as results using the sampler are always subject to interpretation. When irradiated Te was volatilized, a compound of Te and I was distributed throughout the sampler. Release of such a compound from irradiated fuel would obviously prevent use of the sampler for iodine species identification; however, significant Te activity has never been observed when sampling iodine from oxidized fuel.

Future work will study "HOI" and the volatility of iodine from fuel in radiation fields.

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