

STUDIES OF THE VOLATILITY OF CESIUM AND IODINE

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ABSTRACT

Cesium and iodine are potentially volatile radionuclides which are present in both high-level and low-level wastes. Many volume reduction processes subject these wastes to elevated temperatures which are sufficient to cause volatilization to some extent. The volatilization of these radionuclides can have a major effect on off-gas system design and costs.

A laboratory apparatus was used to study the effects of temperature, pH, and drying gas on the volatilization of cesium and iodine from bead and powdered ion exchange resins. A small bed reactor having a volume of about 80 cc was used to hold the resin sample. The reactor was located inside a laboratory oven to control temperature. Drying gases of nitrogen and air were tested. Ion exchange resins were pretreated to be completely loaded with nonradioactive cesium and iodine.

In three separate tests, resins were heated from room temperature to temperatures of 140, 180, and 265°C. Cesium volatilization was below the limit of detection in all tests, that is, less than 0.2% of the cesium absorbed on the resins volatilized. Iodine volatilization was detected and found to be a function of temperature, pH, and drying gas. Significant volatilization of iodine occurred when the resins were in acidic solution and air was the drying gas. Iodine volatilization from resins in neutral or basic media with air as the drying gas was <0.3% (less than the limit of detection) when heated at 140°C. At temperatures of 180°C and 265°C, the iodine volatilization from powdered resins was 0.3% and 1.2%, respectively, and the volatilization from bead resins was 0.3% and 0.8%, respectively.

As an example of a waste processing application, a spray dryer system for volume reduction of low-level wastes was chosen. For this system, equipped with standard charcoal filters and operating at its usual temperatures of 265°C or less, the uncontrolled release limit for I-131 into air will be met when processing ion exchange resin waste containing a maximum of 0.13 μCi of I-131/cc of resin.

BACKGROUND

Many of the processes for volume reduction and preburial preparation of low-level and high-level radioactive wastes involve the application of heat to the wastes during processing. Temperatures for waste treatment may be moderate (100 to 500°C), as in the case of drying processes, or much higher (500 to 2000°C), as in the case of incineration or calcination processes. In the case of these high-temperature processes, much of the waste material is converted to a gas or finely divided powder; high-temperature, highly efficient off-gas treatment systems (e.g., HEPA filters or sintered metal filters) are required to clean the off-gas of radionuclides. In the case of drying processes, which operate at lower temperatures, less temperature-sensitive separation and filtration systems can be used prior to HEPA filtration. Since in either case radionuclide release limits must still be met, even a small degree of volatilization of radionuclides at processing temperatures may have a major effect on system design and operating conditions.

Cesium and iodine are two radionuclides that are found in significant quantities in both high-level and low-level waste. Cesium usually forms chemical compounds of limited volatility at moderate temperatures, but under certain conditions, it will form cesium

metal, which is easily volatilized. Cesium volatilization as high as 60% has been measured for immobilization of low-level waste in molten glass at 1300°C.¹ During pyrolysis of cation ion exchange resin, cesium has been detected in off-gas at temperatures above 450°C.² Iodine is usually bound to compounds in the iodide form, but it can be oxidized in acid solution to form triiodide ion, which decomposes to form elemental iodine. Both elemental iodine, I_2 , and hydrogen iodide, HI, are rapidly volatilized because they have an appreciable vapor pressure at room temperature. In neutral or basic solution, iodine is oxidized to iodate ion, which forms non-volatile compounds. During the reprocessing of nuclear fuel, iodine is expected to volatilize during fuel dissolution (an acid treatment process) and is then recaptured in the process off-gas system. This usually requires special iodine sorption media such as charcoal filters and zeolite beds.³⁻⁵ During tests in which simulated low-level wastes of sodium sulfate solution, boric acid slurry, and powdered ion exchange resin slurry were spray-dried at 90°C for volume reduction, cesium loss to the vapor phase was less than 0.02% for all three wastes. Iodine loss to the vapor phase was 0.2% for the sodium sulfate solution (neutral pH) but greater than 0.4% for both the boric acid solution (acidic pH) and the ion exchange resins.⁶ Thus, both cesium and iodine are potentially volatile

nuclides during waste treatment processing, and volatilization is a function of processing temperature and the processing chemistry.

In the studies presented here, controlled laboratory tests were conducted to distinguish the effects of temperature, pH, and drying atmosphere on the volatilization of these two nuclides.

APPARATUS

A schematic diagram of the apparatus used for these tests is shown in Fig. 1. The apparatus consisted of a heated tubular reactor constructed from a specially modified 100-ml graduated glass cylinder. A fritted-glass plate is located at the bottom of the reactor to hold the resin bed. Tests were typically done with two reactors, one for bead resins and one for powdered resins.

A metered drying/carrier gas (about 50 ml/min) passed through a copper preheat coil and then into the glass reactor. For the tests with bead resins, the gas passed through the resin bed and through the top of the reactor. For the tests with the powdered resins, the pressure drop through the resin bed was too large to permit gas flow through the reactor without entraining the resin bed. In this case, the carrier gas was passed over the top of the powdered resin bed, and heating was accomplished only by conduction through the glass reactor walls. Plugs of glass wool were placed at the top of each reactor tube to avoid any possibility of entrainment of resin particles in the gas stream. The two parallel reactors were constructed and located inside a laboratory convection drying oven. A photograph of the heated tubular reactors is shown in Fig. 2.

Gas exiting the oven passed through a water-cooled condenser, a distilled water scrubber (containing 100 ml of liquid), and a 1 normal NaOH scrubber (also containing 100 ml of liquid). Condensate and scrubber samples were analyzed for cesium and iodine content using X-ray fluorescence. This technique is sensitive to about 25 ppm for each species.

Small diameter (0.8 mm) thermocouples were positioned in the resin bed and recorded bed temperature. All fittings were made of stainless steel, glass, and Teflon tubing to minimize loss of cesium or iodine.

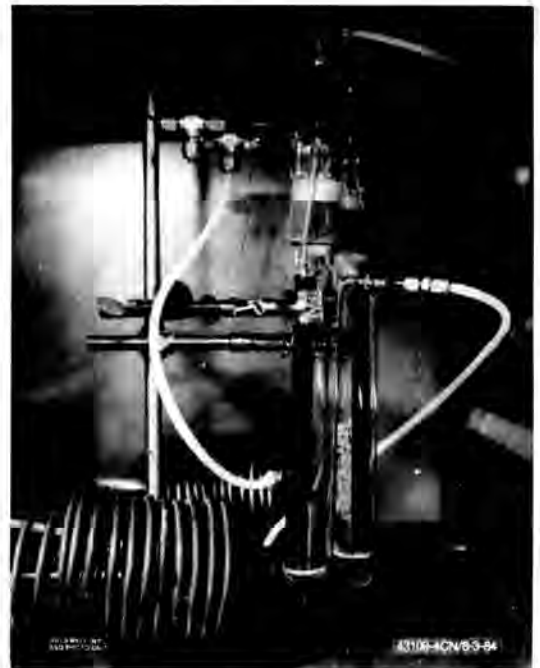


Fig. 2. Photograph of the heated tubular reactors used for cesium and iodine volatility tests.

The apparatus was leak-checked prior to testing to prevent loss of sample.

IODINE AND CESIUM LOADING

The first step in the testing was to load the resins with iodine and cesium. The same procedure was followed for all samples. The proportions of material are shown in Table I. All weights were determined on a digital balance which had a sensitivity of 0.01 g.

The powdered resins used were Epicor PD-1 anion resins (hydroxide form, 68 wt. % water as-received) and Epicor PD-3 cation resins (hydrogen form, 58 wt. % water as-received). Bead resins were Amberlite INR-78 anion resins (hydroxide form, 67 wt. % water as-received) and Amberlite INR-77 cation resins (hydrogen form, 52 wt. % water as-received). Water content was

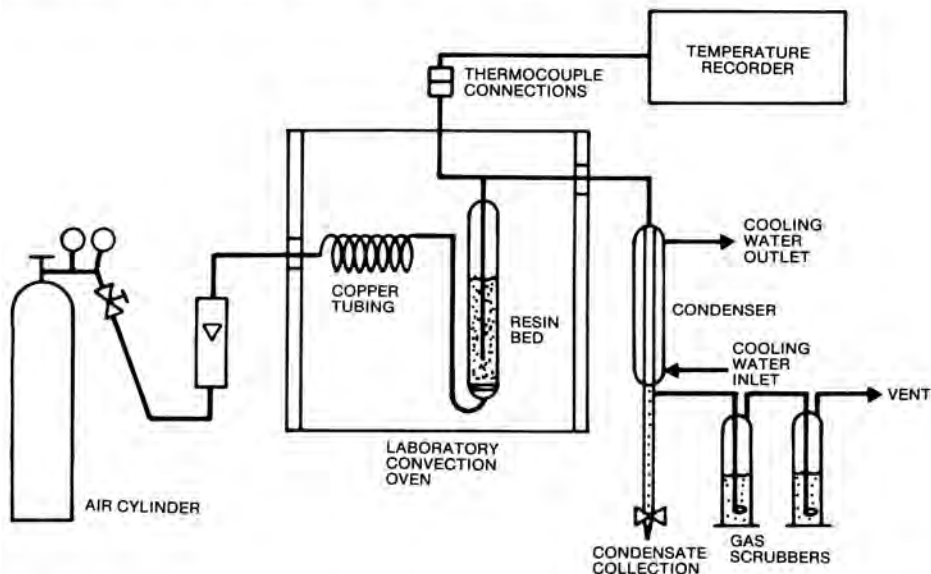


Fig. 1. Volatility test apparatus.

TABLE I

Preparation of Test Resins

Measured Quantity	Epicor Powdered Resins	Amberlite Bead Resins
Anion resin, g "as-rec'd"	13.00	14.00
Cation resin, g "as-rec'd"	26.00	28.00
CsNO ₃ , g	15.21	16.38
NaI, g	11.70	12.61
H ₂ O, g	150.00	150.00
pH before washing	1.2	1.1
pH after washing	3.4	2.7

determined by heating the resins in a laboratory oven for 24 h at 120°C. The resins in these tests were mixed in proportions to simulate a 2:1 mixed bed of cation:anion resins.

The salts were dissolved in the water in two separate flasks using magnetic stirrers. The resin batches were then added to the respective solutions, and the mixtures were stirred for about 24 h to effect the iodine and cesium exchange. The resin batches were then filtered and washed with deionized water five times to remove all unexchanged iodine and cesium. The filtrates and wash solutions were collected and analyzed for iodine and cesium content. It was assumed that all iodine and cesium not in the filtrate and wash solutions was absorbed by the resins. The quantity of inorganic salts of cesium and iodine was sufficient to load the resins with 6 milliequivalents of iodine per gram of anion resin and 3 milliequivalents of cesium per gram of cation resin.

Tests were conducted by placing batches of resins in the reactors, and then deionized water was poured into the resulting beds so that the water levels were above the top of the resin levels. Typically, 43 g of water were added to each bed. Carrier gas (nitrogen or air) was then started through the resin beds and heating was begun. Condensate was collected from the resins and the test was continued until drying was complete and the oven, the powdered bed, and the bead resin bed had been isothermal at the test temperature for about 15 min.

Typical heating curves for these tests are shown in Fig. 3. The temperature of the resin beds shows the characteristic pause at 100°C, the boiling point of water, while drying of the beds occurred. The powdered resin bed showed a more rapid temperature rise than did the bead bed after the 100°C level had been attained.

EFFECT OF pH AND DRYING GAS

Initial tests were carried out to determine the effect of drying gas and resin bed pH on volatility. A drying temperature of 140°C was used in these tests. In one test, nitrogen gas was passed through the resin beds; in a subsequent test, air was used. Samples of condensate and scrubbers were collected and analyzed. The purpose of this drying gas comparison was to determine if the oxygen in air enhanced the volatilization of iodine. As shown in Table II, it was found that the iodine showed little volatilization from resin beds at 140°C with either drying gas. On the basis of this test, it was decided to use air as the drying gas in subsequent tests.

TABLE II

Effect of Drying Gas on the Volatilization of Iodine at 140°C

Resin Type	Drying Gas	Iodine Volatility (%)
Bead	Nitrogen	<0.3
	Air	<0.3
Powdered	Nitrogen	<0.3
	Air	<0.3

A test was then made using bead resins with ions in solution around the resins, i.e., no deionized water wash was used. In this test, the solution was a mixture of dilute HNO₃ -9 wt. % CsNO₃ -7 wt. % NaI. This solution was strongly acidic, having a pH of about 1.1. Significant quantities of iodine evolved as heating was begun. This iodine was observed visually and by odor. Heating of a neutral solution of 5 wt. % NaI to 140°C in air did not show any iodine volatilization.

EFFECT OF DRYING TEMPERATURE ON VOLATILIZATION

Volatilization of cesium and iodine as a function of temperature was measured at drying temperatures of 140, 180, and 265°C. Air was used as the drying/carrier gas in these tests. Three separate tests were performed, one at each temperature. In each test, beds of powdered resins and bead resins were dried. Condensate and wash samples were collected, and the cesium and iodine content was analyzed. The results of these tests are given in Table III.

The temperature volatilization data indicate that cesium volatilization is less than 0.2% at resin drying temperatures of about 265°C or less. Iodine begins to show increased volatilization as the temperature rises from 180 to 265°C. The increase in iodine evolution indicates that the measured iodine in the drying gas is due to loss from the resins and is not residual iodine left from incomplete washing of the resin beads. However, the amount of iodine volatilized is still small, increasing from 0.3% to 1.2% for the powdered resins and from 0.3% to 0.8% for the bead resins.

The distribution of iodine in the loaded resins, the resin condensate, and the carrier gas scrubber solutions is given in Table IV. The resin condensate typically contained small amounts of iodine, varying from 7 to 16 mg in all of the samples. When volatilization did occur (the 265°C test), the water scrubber contained 31 mg from the powdered resins and 40 mg from the bead resins. The sodium hydroxide scrubber contained 52 mg of iodine from the 265°C test, which may be indicative of some HI evolution. However, the bead resin hydroxide sample from the same test only contained 10 mg of iodine. Thus, there was no distinctive trend which would indicate the preferential evolution of I₂ or HI.

OFF-GAS SYSTEM DESIGN

Although the volatilization of iodine at temperatures of less than 265°C is only 1.2%, some precautionary iodine filters will be required in the off-gas treatment systems of volume reduction systems. This is shown in the following example. The spray dryer system to volume reduce low-level ion exchange resin

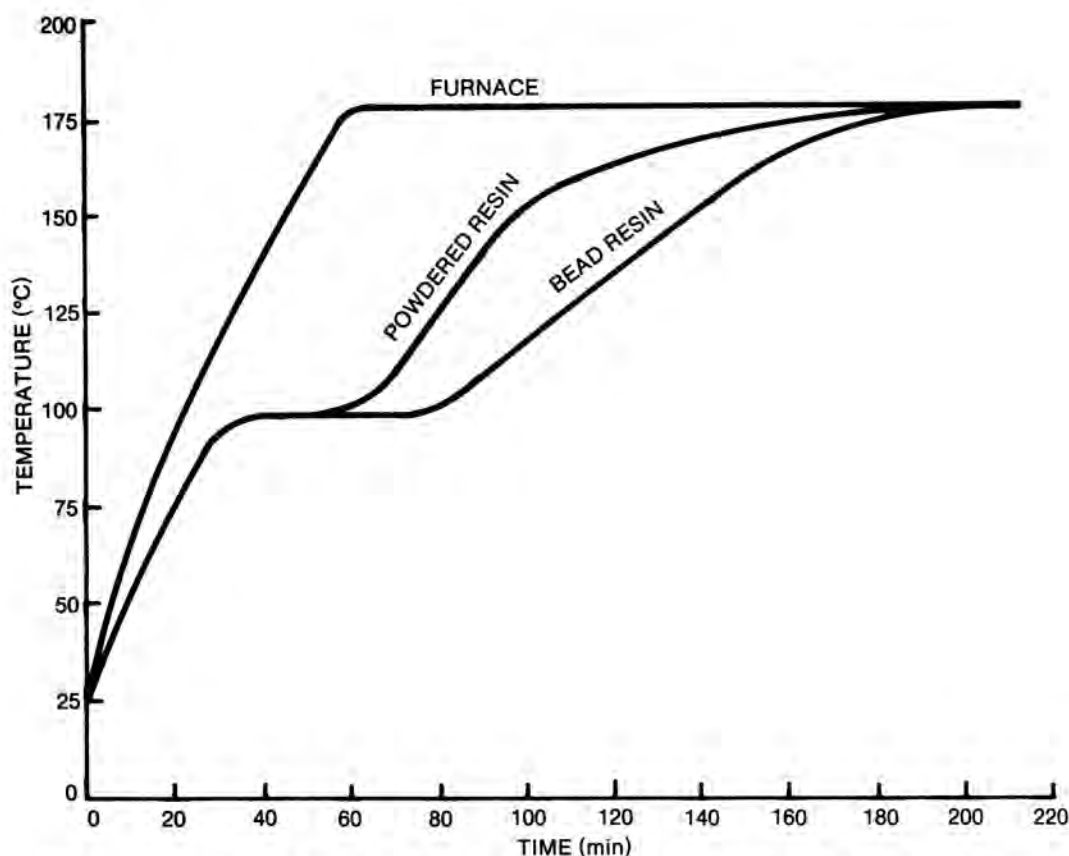


Fig. 3. Temperature history of the furnace, powdered resin bed, and bead resin bed during the cesium and iodine volatility test at 180°C.

TABLE III

Cesium and Iodine Volatilization As a Function of Temperature

Sample Identification	Temperature (°C)		
	140*	180	265
Epicor powdered resins			
Cesium loaded on resins, mg Cs	4770.	5070.	8920.
Cesium volatilized, mg Cs	<20.	<10.	<10.
Cesium volatilized, %	<0.2	<0.2	<0.2
Iodine loaded on resins, mg I	4150.	4260.	8210.
Iodine volatilized, mg I	<12.	12.	99.
Iodine volatilized, %	<0.3	0.3	1.2
Amberlite bead resins			
Cesium loaded on resins, mg Cs	5390.	5920.	8770.
Cesium volatilized, mg Cs	<20.	<10.	<10.
Cesium volatilized, %	<0.2	<0.2	<0.2
Iodine loaded on resins, mg I	4830.	4730.	8080.
Iodine volatilized, mg I	<10.	12.	62.
Iodine volatilized, %	<0.2	0.3	0.8

*Nitrogen was the drying/carrier gas at 140°C.

TABLE IV

Distribution of Iodine in Loaded Resins, Resin Condensate, and Carrier Gas Scrubber Solutions

Sample Identification	Temperature (°C)		
	140	180	265
Epicor powdered resins			
Loaded resins, mg I	4150.	4260.	8210.
Resin condensate, mg I	<2.	7.	16.
H ₂ O scrubber, mg I	6.	5.	31.
NaOH scrubber, mg I	<4.	<2.	52.
Total volatile, mg I	<12.	12.	99.
Amberlite bead resins			
Loaded resins, mg I	4830.	4730.	8080.
Resin condensate, mg I	<2.	12.	12.
H ₂ O scrubber, mg I	<4.	<2.	40.
NaOH scrubber, mg I	<4.	<2.	10.
Total volatile, mg I	<10.	12.	62.

waste 7 is normally equipped with an off-gas treatment system consisting of fabric filter, HEPA filters, and standard charcoal filters (when iodine is expected in the feed material). Charcoal filters typically have a decontamination factor of greater than 200.

The maximum permissible release limit for Iodine-131 is 1.0×10^{-10} $\mu\text{Ci}/\text{m}^3$ of air. Assuming 1.2% evolution, a spray dryer system for ion exchange resins with an air flow rate of $28.3 \text{ m}^3/\text{min}$ (1000 scfm) will be below the iodine release limit with an iodine loading of $0.13 \mu\text{Ci}$ of I-131 per cc of resin. When iodine is present in spent resins, its activity is typically about 1% of total resin activity.⁸ Thus, a total resin activity of $13 \mu\text{Ci}/\text{cc}$ is an approximate upper limit for waste activity in this example. Low-level waste ion exchange resins are usually much lower than this activity,⁹ but charcoal filters are recommended for enhanced safety.

CONCLUSIONS

Volatilization of cesium from ion exchange resins treated at drying temperatures was found to be less than 0.2% of the absorbed cesium. Iodine was found to volatilize significantly if dried in an oxidizing atmosphere in an acidic medium. Iodine evolution could be minimized by neutralizing the surrounding solution or converting the solution to a pH greater than 7. Iodine does show a small tendency to volatilize at drying temperatures, with about 1% volatilization at 265°C . In our tests, iodine volatilization from powdered resins is slightly greater than from bead resins which may be due to the larger exposed surface area of powdered resins. Design of off-gas treatment systems should include charcoal filters to reduce the iodine concentration to permissible levels.

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