Behavior of Radioactive Iodine and Technetium in the Spray Calcination of High-Level Waste

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August 1981

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INTRODUCTION

The Remote Laboratory-Scale Waste Treatment Facility (RLSWTF) was designed and built as a part of the High-Level Waste Immobilization Program (now the High-Level Waste Process Development Program) at the Pacific Northwest Laboratory, which is operated by Battelle Memorial Institute for the Department of Energy. In this facility, which is installed in a radiochemical cell, small volumes of radioactive liquid wastes can be solidified, the process off gas can be analyzed, and the methods for decontaminating this off gas can be tested (Hanson, Knox and Berger 1980). Initial operations were completed with non-radioactive, simulated waste solutions (Knox, Siemens and Berger 1981). The first radioactive operations in this facility were performed with a simulated, commercial waste composition containing tracer levels of ^{99}Tc and ^{131}I . This report describes the facility and test operations and presents the results of the behavior of ^{131}I and ^{99}Tc during solidification of radioactive liquid wastes.

DESCRIPTION OF TEST PROGRAM

The RLSWTF (Figure 1) consists of a feed-preparation module, a waste-solidification module and an effluent-treatment module. The waste-solidification equipment used for this operation was a spray calciner. The effluent-control module consists of a number of components that can be operated in different sequences. For this experiment, the process off gas was drawn by vacuum from the spray calciner through stainless steel sintered-metal filters, a venturi scrubber and a packed scrubber. Water was used as the scrubbing solution in the venturi and packed scrubbers.

A nonradioactive, simulated waste solution (Table 1) was prepared and transferred to the feed-preparation module where 13 L of the solution were spiked with ^{99}Tc and ^{131}I . Technetium is a weak beta emitter that is difficult to detect in the presence of other radionuclides. Therefore, it was decided to study its behavior in the high-temperature waste-solidification process before the equipment became contaminated with other radionuclides. Iodine was included in the test as ^{131}I , which was readily available and would not interfere with technetium analyses due to its short half life (8.3 days)^(a).

Due to the small quantity of technetium available, the RLSWTF was started up with the unspiked, simulated waste composition. This unspiked waste was calcined for approximately two hours until all temperatures, pressures, flow rates, etc., had stabilized and the off-gas sampling apparatus had been set up. At this time, the spiked waste was added to the feed, and calcination was continued until the spiked feed was exhausted (6-1/2 h). A sample of this spiked feed was taken for analysis. The "actual" feed composition differed from the nonradioactive, simulated composition due to dilutions with water that occurred when the spiked waste was added and when the feed line was flushed. The results of the feed analysis are given in Table 2.

(a) The iodine was allowed to decay ten half lives before the technetium analyses were started.

FIGURE 1. Remote Laboratory-Scale Waste Treatment Facility

TABLE 1. Nonradioactive, Simulated Waste Composition^(a)

<u>Component</u>	<u>Quantity, g/L</u>
Fe(NO ₃) 9H ₂ O	41.30
NaNO ₃	10.80
Rare earth mix	07.30
ZrO(NO ₃) ₂ 2H ₂ O	03.00
CsNO ₃	02.40
Ba(NO ₃) ₂	02.40
Ni(NO ₃) 6H ₂ O	01.60
75% H ₃ PO ₄	00.70
Cr(NO ₃) ₃ 9H ₂ O	01.65
Sr(NO ₃)	00.60
Cs(NO ₃) ₂ 6H ₂ O	00.30
TeO ₂	00.20
KNO ₃	00.10
Cd(NO ₃) ₃ 4H ₂ O	00.06
AgNO ₃	00.04

(a) Final HNO₃ concentration of 2.06M.

TABLE 2. Spiked Waste Composition^(a)

<u>Component</u>	<u>Quantity, g/L</u>
Fe	6.2
Na	1.6
⁹⁹ Tc	.08 (Ci/L)
¹³¹ I	.0004 (Ci/L)

(a) Specific gravity =
1.1 g/cm³; nitric acid
concentration = 1.38M.

The feed was fed to the calciner at a constant feed rate of 2 L/h. During this operation, the venturi scrubber solution was sampled every 30 minutes, and the packed-scrubber solution was sampled every hour. These samples were then analyzed for the ^{99}Tc and the ^{131}I . Particulate carryover from the calciner was also determined by analyzing these samples for iron. Three samples of the off-gas stream were taken by drawing the off-gas stream through a scrubber solution of .2M NaOH for one hour, as shown in Figure 2. The scrubber solution was then analyzed for ^{99}Tc and ^{131}I . Two of these samples were taken from the sample port located downstream of the sintered-metal filters. The other sample was taken downstream of the venturi scrubber.

FIGURE 2. Off-Gas Sample Apparatus

RESULTS

The venturi scrubber samples were analyzed for iron to determine particulate carryover through the spray calciner's sintered-metal filters. These samples indicated particulate losses of 0.3 wt%, which corresponds to a decontamination factor (DF) of 318, a lower than expected value. However, sintered-metal filters become more efficient after they have been coated with calcine. Since the filters in this run had not been in service for very long, they may not have accumulated a sufficient coating of calcine. In addition, during this run these filters were routinely blown back with air (although the pressure drop across them had not increased significantly), and this frequent use of filter blowback may have partially removed the calcine coating. In subsequent runs, these filters were blown back only when the pressure drop increased, which indicates excessive calcine buildup. This action should increase the filter operating efficiency so that the expected DFs of 1000 to 3000 are obtained.

The venturi scrubber and packed-scrubber samples were analyzed for ^{99}Tc . These analyses indicated ^{99}Tc losses of 0.15 wt% from the calciner at 800°C , which is equivalent to a DF of 500 across the sintered-metal filters. The off-gas samples indicated a slightly lower loss (0.1 wt%); however, the small difference is probably due to inleakage into the off-gas sampling system. Figures 3 and 4 are the plots of the ^{99}Tc sample results as a function of time for the venturi scrubber and the packed scrubber. Of the volatilized ^{99}Tc that entered the off-gas system, 83% was removed in the venturi scrubber (DF = 6 for ^{99}Tc).

As was expected, the ^{131}I volatilized extensively. Thirty-one percent of the ^{131}I escaped from the calciner to the off-gas system. Of the volatilized ^{131}I , 52% was found in the venturi scrubber, 23% was found in the packed scrubber and 25% escaped to the building off-gas system where it was removed by the building iodine adsorber. Figures 5 and 6 present plots of the total ^{131}I present as a function of time for the venturi scrubber and for the packed scrubber. These results represent DFs for ^{131}I of 3, 2, and 2 for the sintered-metal filters, the venturi scrubber and the packed scrubber, respectively. Liquid scrubbers were not effective in removing ^{131}I from the off-gas stream. Adsorbents must be used to remove iodine from the off-gas stream.

FIGURE 3. Technetium-99 Concentrations in the Venturi Scrubber

FIGURE 4. Technitium-99 Concentrations in the Packed-Scrubber Solution

FIGURE 5. Iodine-131 Concentrations in the Venturi-Scrubber Solution

FIGURE 6. Iodine-131 Concentrations in the Packed-Scrubber Solution

CONCLUSIONS AND RECOMMENDATIONS

During the spray calcination of commercial high-level liquid waste spiked with ^{99}Tc and ^{131}I , there was a 0.3 wt% loss of particulates, a 0.15 wt% loss of ^{99}Tc and a 31 wt% loss of ^{131}I past the sintered-metal filters. These filters and a venturi scrubber were very efficient in removing particulates and ^{99}Tc from the off-gas stream. Liquid scrubbers were not efficient in removing ^{131}I , as 25% of the total lost went to the building off-gas system. Therefore, solid adsorbents will be needed to remove iodine. For all future RLSWTF operations where iodine is present, a silver zeolite adsorber will be used.

The volatility weight percents from this operation on particulate, technetium and iodine losses would be greater for higher-temperature processes and/or for processes that do not use filters. If the wastes had been vitrified instead of just calcined, the results would have been different. We recommend that these tests be performed for any high-temperature process being considered for high-level-waste immobilization. Similar tests are also needed on other potentially volatile fission products, in particular ruthenium, cesium, and cerium.

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